POLYTHENE ASSISTED ENHANCEMENT IN BINDER PROPERTY OF BITUMEN

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DECLARATION

I hereby declare that the thesis entitled, **"Polythene Assisted Enhancement in Binder Property of Bitumen"** submitted for Ph.D. Chemistry Degree, to Department of Chemistry, Lovely Professional University is entirely original work and all ideas and references have been duly acknowledged. The research work has not been formed the basis for the award of any other degree or fellowship previously at any university.

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ABSTRACT

Bitumen is used as a binder in construction of flexible pavements since long. With the increase in number of vehicles and increase in population, load on roads have been increased day by day and roads are being deteriorated due to increase in temperature (global warming) as well as water logging (accumulation of water) during rains. Thus roads which consist of unmodified bitumen suffer from serious drawbacks in the due course of time like rutting, thermal cracking, fatigue cracking, pothole formation etc. Hence, it is necessary to add a modifier in bitumen to enhance the binding property of later. Polyethene waste, responsible for pollution is generated, owing to its high consumption. This polyethene waste needs to be removed from our surroundings otherwise it could become unsolvable problem of future. Polyethene (melted at melting point 120-180 °C; thermal degradation above 400 °C) becomes sticky in nature so can act as a binder. Also, major parts of both polyethene and bitumen are hydrocarbon, hence polyethene wastes (PE) can be used to modify the bitumen and enhance the binder property of it. Like polyethenes, degradation of other polymeric wastes is also challenging and can be utilized for other purposes for minimizing the wastes and improvement in quality of available products.

Present research work is divided into six chapters: Chapter 1 involves introduction of the topic followed by the survey of literature. The chapter discusses about the plastic being used in daily life, the problems associated with it, its management and probable role of polyethene (a type of plastic) in enhancing binder property of bitumen. This is based on the hypothesis that modification of bitumen leads to the improvement in properties of bitumen. The literature part explains about the various polymers used as modifiers in the bitumen. The main objectives discussed below, are also given in this chapter.

- To study the effect of temperature and pH variation on the physical properties of bitumen
- To determine the optimal ratio of polyethene: bitumen that may provide highest thermal as well as pH variation resistance
- To study the mechanical properties of bitumen after addition of different proportions of polyethene / waste plastics

- Comparative studies regarding thermal strength, mechanical strength, resistivity towards environmental changes, using various types of plastics

Research methodology is given in the form of flowchart followed by the expected outcome in this chapter.

Chapter 2 is named as Methods and Experimental Procedures. This chapter deals with the grade of bitumen and types of polymers used for its modification. Fabrication of apparatus (by me) on some base requirements for synthesis of polymer modified bitumen is discussed. This apparatus comprises of high shear mixer with thermostatic control and polymer modified bitumen (PMB). Synthesis conditions optimized in terms of the type of mixer, number of rpm of mixer, temperature of mixing and time of mixing, used in the research work are discussed. Samples of modified bitumen were synthesized using Low Density Polyethene (LDPE) and High Density Polyethene (HDPE) pellets as modifier in VG-30 bitumen. Also modified bitumen samples were kept at different pH for a fixed time interval. The PMB samples were characterized according to conventional tests (penetration point, softening point, ductility test) and analyzed by Morphological analysis (SEM), Spectroscopic analysis (FTIR), Thermal analysis (TGA) techniques, the detailed methods of which were included in Chapter 2.

Chapter 3 deals with the output of modification of bitumen using low density polyethene. The results of penetration point, softening point, ductility, SEM, FTIR, TGA of LDPMB (low density polyethene modified bitumen) are compared with the bitumen. Penetration point of LDPMB is found lower than that of bitumen indicating that bitumen becomes hard after modification. Softening point of LDPMB is higher than that of bitumen thus pointing towards decrease in temperature susceptibility after modification. Ductility of PMB is lower than bitumen but above 5.0% concentration of LDPE, it decreases below the minimum acceptable value. Hence 5.0% was the optimum concentration of LDPE for modification of bitumen. Morphological analysis of bitumen and LDPMB was conducted using SEM technique. The results clearly prove the homogeneous dispersion of LDPE in bitumen at low concentrations of polymer but at high concentrations heterogeneous samples are formed which is not suitable. LDPE modified bitumen exposed to acidic and basic medium exhibit cracks and holes on the surface respectively thus proves that LDPE modified bitumen is not resistant to pH variations in environment. IR spectra of LDPMB and bitumen clearly show small change in frequency of peaks in case of non-polar polymer like LDPE. There is only physical modification of bitumen with LDPE and no new chemical compound is formed. Thermo-gravimetric analysis using TGA also points out that 5LDPMB and 5LDPMB exposed to different pH (5.0, 7.0, 9.0)is thermodynamically more stable than unmodified bitumen.

Chapter 4 deals with the modification of bitumen using high density polyethene. The results of penetration point, softening point, ductility, SEM, FTIR, TGA of HDPMB (high density polyethene modified bitumen) are compared with the bitumen. Penetration point of HDPMB is found lower than that of bitumen, indicating that bitumen becomes hard after modification. Softening point of HDPMB is higher than that of bitumen thus pointing towards decrease in temperature susceptibility after modification. Ductility of PMB is lower than bitumen but above 3.0% concentration of HDPE, it decreases below the minimum acceptable value. Hence 3.0% was optimum concentration of HDPE for modification of bitumen. Morphological analysis of bitumen and HDPMB was conducted using SEM technique. The results clearly prove the homogeneous dispersion of HDPE in bitumen at low concentrations of polymer, but at high concentrations heterogeneous samples are formed which is not suitable. HDPE modified bitumen exposed to acidic and basic medium exhibit cracks and holes on the surface respectively thus proves that HDPE modified bitumen is not resistant to logged water of different pH.IR spectra of HDPMB and bitumen clearly show small change in frequency of peaks. There is only physical modification of bitumen with HDPE and no new chemical interaction is formed. Thermo-gravimetric study using TGA also points out that 3HDPMBexposed to different pH (5.0, 7.0, 9.0) is thermodynamically more stable than unmodified bitumen.

Chapter 5 deals with the modification of bitumen using a polar polymer that is polyethylene-vinyl acetate polymer (EVA). The results of penetration point, softening point, ductility, SEM, FTIR, TGA of EVAMB (ethylene-vinyl acetate modified bitumen) are compared with the bitumen. In case of EVA modified bitumen (EVAMB) penetration point decreases, softening point increases and ductility decreases (above 5.0%) after the modification. Thus 5.0% was the optimum concentration in case of EVAMB.SEM images of EVAMB exposed to water of different pH show no cracks or holes, thus proves that EVA modified bitumen is resistant to the logged water of different pH. The IR spectrum of polar polymer like EVA modified bitumen shows decrease in intensity of major peaks thus proves

intermolecular interaction between polar components of bitumen and the polar polymer. Thermo-gravimetric study using TGA also points out that 5EVAMB and 5EVAMB exposed to different pH (5.0, 7.0, and 9.0) is thermodynamically more stable than unmodified bitumen.

Chapter 6 includes comparison of all the data of three polymers used, gives important conclusions and future recommendations of the research work.

Entire work suggested that the polymer modified bitumen has better properties than unmodified bitumen and thus help in enhancement in binding property of bitumen. LDPMB and HDPMB are not resistant to pH variations in the environment but they are thermodynamically more stable than bitumen. EVAMB is resistant to pH variations as well as thermodynamically more stable than bitumen. The damage caused to roads due to water logging can be solved by the use of EVAMB. The research work will help in modifying bitumen for improving the quality of roads.

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(Sonu Sharma)

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GLOSSARY OF ABBREVIATIONS

HDPE	High Density Polyethene
LDPE	Low Density polyethene
PE	Polyethene
PVC	Polyvinyl Chloride
PS	Polystyrene
PP	Polypropylene
EVA	Ethylene- Vinyl Acetate
PMMA	Polymethyl methacrylate
BDP	Biodegradable plastic
PHA	Polyhydroxy Alkanoate
EBA	Ethyl butyl acrylate
EMA	Ethyl methyl polyacrylate
SBR	Styrene butadiene rubber
SBS	Styrene butadiene styrene
GTR	Ground tire rubber
FTIR	Fourier Transform Infra Red
PMB	Polymer modified bitumen
SARA	Saturates aromatics resins asphaltenes
RPE	Recycled polyethene
DSC	Differential Scanning Calorimetry
LLDPE	Linear low density polyethene
ISTM	Indirect tensile stiffness modulus
RLA	Repeated load axial
ITFT	Indirect tensile fatigue test
PPA	Polyphosphoric acid
PET	Polyethyleneterephthalate
SMA	Stone mastic asphalt
TLPP	Thin liquid polyol PET
VPP	Viscous polyol PET
SEM	Scanning electron microscope

EDS	Energy dispersive X-ray spectroscopy
DSR	Dynamic shear rheometer
BBR	Bending beam rheometer
CR	Crumb rubber
MDSC	Modulated differential scanning calorimetry
HMA	Hot mix asphalt
ITS	Indirect tensile strength
WPM	Waste polymer modifier
WPPM	Waste polymeric packaging material
RTFOT	Rolling thin film oven test
PAV	Pressure ageing vessel
SHRP	Strategic highway research program
EPDM	Ethylene-propylene-diene-monomer
STR	Scrap tire rubber
ENR	Epoxidized natural rubber

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Origin of the Problem

Plastics are the macromolecules which are formed by the polymerization of small monomers like ethylene, propylene, styrene and many more. Their remarkable properties such as thermal insulation (low thermal conductivity), insolubility in the common organic and inorganic solvents, versatile, recyclable, UV resistant, corrosion resistant etc. make them the materials of choice for various applications ranging from common domestic articles to sophisticated scientific and medical instruments [1]. Due to their low cost of manufacturing and processing the consumption of plastics has been increased around the world. In India the usage of plastics has increased from 5 metric ton/year in 2005 to 8 million ton/year in 2008 and expected to rise 24 million ton/year by 2020 [2]. Around 1.3 million ton plastic wastes is generated annually in India but due to lack of proper waste management strategies, only 42% plastic waste is recycled whose quality decreases after each recycling in comparison to pure plastic [3]. Among different types of plastics, polyethene is the most commonly used plastic. Polyolefin alone accounts for 60% of the total plastic consumption in India [4]. Demand of high density polyethene (HDPE) is increasing day by day due to its use in the construction sector followed by low density polyethene (LDPE) which is used in packaging industry because of its moisture susceptibility and transparent nature. Due to their more use their waste is also increasing day by day. Their non-biodegradable nature makes them one of the major soil and water pollutant which poses greater risk to land fertility as well as health of different living organisms [5]. Therefore, there is an urgent need to find some alternative ways for their safe disposal.

For over a century, in order to bind aggregate, bitumen is employed as an adhesive material during the road construction because of its properties like excellent binding properties, water proofing behavior and low cost [6]. However, due to increased traffic load and extreme climatic variations, various problems such as rutting, pothole formation, thermal cracking, and fatigue cracking [6] are appeared on the surface of the bituminous road. Therefore, in order to enhance the performance of road, an additional substance is required which is cheap, can be homogenously mixed along with bitumen (in a molten form) to form composite materials which show high thermal stability, weight bearing, water resistant properties etc. as compared to bitumen. The polymers are the materials of choice and these days have gain lot of interest, the polyethene is one of them**.** the polyethene is one of them**.** the polyethene is one of them**.** the polyethene is one of them**.** the polyethene is one of them**.** the polyethene is one of them**.** the polyethene is one of them**.** [7]. Thus an innovative use of polyethene waste is in the road construction. Waste polyethene as a modifier tends to enhance the properties of bitumen thus increasing the strength of roads. Its addition to bitumen represents an environmental friendly alternative approach for the future of waste polyethene. By the use of this waste polyethene durable roads can be constructed as well as this is one of the best methods for easy disposal of waste polyethene.

1.2 Two problems: Polyethene Waste and Need of Modified Bitumen, Single line solution

There are two major problems existing in the society: (a) Non- biodegradable polyethene waste which persists in the environment over longer periods of time (a big health hazard for living beings and associated environmental problems) and (b) Need of modification of bitumen in order to enhance life of roads. Now both bitumen and polyethene are non-polar in nature and melting point of polyethene is in a range that it can be mixed with the bitumen. Hence single line solution for these two problems is utilization of polyethene (and likewise polymeric) waste in modification of bitumen.

1.3 General Introduction

1.3.1 Road Materials – A Comparison

Pavements are classified in two categories: Flexible pavement (bitumen roads) and rigid pavement (concrete roads). Bitumen is used as a binder with aggregates of different sizes along with sand. The name flexible is derived from the flexible nature of bitumen; hence the road is named as flexible pavement. As bitumen is flexible such pavement can bear heavy loads and can perform well for longer periods of time. Rigid pavement uses cement as binder along with aggregates of different sizes, water and sand. Table 1.1 highlights the main differences between concrete roads and bitumen roads.

Table 1.1: Difference between concrete roads and bitumen roads

Sr. No.	Concrete Roads	Bitumen Roads
1.	Costly	Cheaper
2.	More durable	Less durable
3.	More eco friendly	Less eco friendly
4.	Low skid resistance	Better skid resistance
5.	No flexibility at all	Flexible enough to accommodate imperfections in underlying surfaces
6.	Maintenance is slower and costlier	Maintenance is faster and cheaper
7.	Cost and time consuming	Cost and time saving
8.	Lot of polluting gases are emitted during production of cement	No such gases are emitted during production of bitumen
9.	Higher paving cost	Lower paving cost
10.	More time to lay road	Less time to lay a road
11.	More resistant to extreme climatic variations	Less resistant to extreme climatic variations
12.	More wear and tear of tyres of vehicles	Less wear and tear of tyres of vehicles

1.3.2 Bitumen in India: Uses and Challenges

There are some basic requirements for a substance so that it can act as a binder in road construction. A good binder should have adequate viscosity, optimum adhesion between binder and aggregates and not highly temperature susceptible. Bitumen meets all these basic requirements. Moreover it has excellent binding properties as well as water proofing behavior. In addition, it is quite cheap, viscoelastic, highly impermeable, flexible hence it is used as a binder in roadway construction and in making waterproofing and protective coverings for roofs [6,8- 11]. But there are some inherent drawbacks in usage of bitumen also. It is brittle and hard in cold environments. The winter fragility leads to low temperature cracking. It becomes soft in hot environments which cause rutting on roads [12]. Sometimes at quite high temperatures bitumen start melting or bleeding which decrease the performance of road [13-15]. If bitumen is exposed to oxygen for longer periods of time then this will result in cracking of bitumen. Moreover, when comes in contact with water bitumen get separated from the aggregate due to which potholes are formed on the road.

Bitumen is derived from petroleum hence it is quite costly. With the tremendous rise in population need of transportation is increased, which leads to increase of volume and load, speed of traffic over the last decades. Moreover, in India there are extreme weathers prevailing. There are geographical areas where temperature rises up to 50 degrees and also where temperature falls up to -5 degrees. Now, due to combined effect of heavy traffic and adverse climatic conditions, life span of road pavements laid with bitumen gets decreased with the passage of time and pavement shows serious defects. The most common pavement defects are rutting or permanent deformation due to thermal susceptibility [16], thermal cracking [17], and fatigue cracking due to ageing of bitumen. These are the challenges which India is facing in regard to bitumen.

1.3.3 Plastic: Uses and limitations

Today every important area of the economy may it be packaging, automobile, building construction, agriculture; communication has been virtually transformed by the usage of plastics. These are used to manufacture everyday products like toys, furniture, beverage containers etc. Major two types of plastics are given ahead.

1. Thermoplastics – These are hard at room temperature but become soft on heating and again hard on cooling. These can be remolded in different shapes multiple times. Basically in a thermoplastic material the weak van der Waal forces are responsible for holding the molecules together. Examples of thermoplastics are polyethene (PE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), nylon, polyethylene vinyl acetate (EVA), polymethyl methacrylate (PMMA). Thermoplastics used as a modifier in bitumen at ambient temperature tend to enhance the viscosity and stiffness but have no role in elastic behavior [18].
2. Thermosetting Plastics- These plastics contain long molecular chains interlinked by strong chemical bonds. Such plastics cannot become soft on heating and hence cannot be remolded multiple times. Examples are Phenol formaldehyde, melamine formaldehyde, bakelite, urea formaldehyde, polyesters etc. [19].

Plastics are highly resistant to water and chemicals and do not allow heat and electricity to pass through them so can be used in electrical wires. These are cheap and lighter in weight so used for packaging of industrial products and food products; do not undergo corrosion hence used in manufacture of different types of pipes that can be used for laying water pipes and laying sewers. Items which are used on daily basis are partially or completely made up of plastic and this waste plastic ultimately ends up in the landfills.

Polyethene bags are the most famous commodity plastic, hence widely available as a waste material. These bags are mainly used for food packaging and sachet water bags. These are convenient, cheap and easy to use; hence they are extensively used for shopping and carrying things. Polyethene is used in manufacturing variety of subjects, ranging from small gift items and finishing building for boats. In addition polyethene is not decomposed in contact with oil and other petroleum products. So, polyethene is often used for the manufacture of various storage tanks for petroleum products. The biggest harm of use of polyethene bags is their non-biodegradable nature, take more time for decomposition thus remains in the environment for a very long duration; hence their proper disposal is a great concern of today. Improper disposal of polyethene bags, cause land, water and air pollution. Polyethene bags restrict supply of mineral salts (increase the soil fertility) and oxygen to the soil thus decreases the soil fertility. Polyethene bags can block the sewerage and water pipes and as a result water resources, road sides are filled with waste polyethene. These bags along the shore of rivers, ponds, and springs are also posing threat to aquatic life, may trap small pool of water which acts as breeding places for the vectors like female anopheles mosquito and lead to spread of diseases like malaria. Domestic animals like cows and goats swallow the waste polyethene bags that can block their digestive system causing death. Polyethene is also a cancer causing agent and contains at least 54 carcinogens. Highly toxic gases like phosgene, chlorine, carbon mono oxide, nitrogen oxide, sulphur dioxide and dioxin are released after burning of polyethene bags [20]. Food stored or packed in polyethene bags; render it unfit for consumption because chemicals within the polyethene bag can seep out into the food. Unnecessary littering of the polyethene waste on the roadsides destroys the beautiful scenery which makes the surroundings untidy thus result in visual pollution. So mismanaged polyethene wastes are a serious threat to the environment. Majority of polyethene are prepared from crude oil which is a non-renewable resource hence production of polyethene is also leading to depletion of natural resources. So polyethene is the biggest reason of environmental pollution.

1.3.4 Plastic Waste Management

The main plastic waste disposal methods include land filling, incineration, and littering. Such disposal methods have an adverse effect on human health and environment. Plastic pollution can be handled by using strategy of 6R's refuse, reduce, repair, reuse, recycle and recover. There should be total refusal to use of one time plastic. Plastic pollution can be minimized by using less plastic products and exploring better options. The use of disposable plastics in our lives can be reduced. Refillable water bottles can be used instead of disposable plastic bottles. Similarly use of cloth, paper and jute bags must be encouraged in order to reduce polyethene pollution like a handmade paper making unit and a plastic weaving loom in Coorg, Bangalore (India) is functional [21]. Repair of damaged plastic articles should be there in order to enhance lifetime of these products. Reuse is the action of using something again and again. So if plastic bottles are used again and again that will ultimately reduce the demand of plastic and hence decreasing the generation of plastic waste. Plastic recycling is the process of collecting the plastic waste and reprocessing it to convert into some useful product. The use of recycled polymers will have multifold benefits. It will lead to environmental protection, lower energy consumption and these will be comparatively cheap. So it is urgent to have a sector for recycled polymers so that they can be converted into a profit generating material [22-24]. Soft drink bottles can be melted down and new plastics chairs and tables can be made from them. All plastics are not recyclable although LDPE, HDPE, PP, PS, PVC are recyclable. Rate of recycling of plastic waste is higher in India (60%) as compare to other countries like South Africa (16%), Japan (12%), USA (10%), and Europe (7%) (19). Different types of plastics which are recycled in India are PVC (45%), LDPE (25%), HDPE (20%), PP (7.6%) and PS (2.4%) [25]. The energy contained in plastic can be utilized to produce electricity, synthetic gas, fuels and recycled raw materials for new plastics. This energy recover can lead to decrease in waste sent to landfills and supplements plastics recycling. Biodegradable plastics (BDP) can be used; of which polyhydroxy alkanoate (PHA) is the major component. BDP can decompose naturally and break into natural and safe products [26]. Natural renewable resources have been used to prepare plastic that is biodegradable under certain conditions of temperature and humidity. BDP is an important alternative, because it decreases dependence on petroleum and reduces the amount of waste products, while still giving a product that provides similar benefits of conventional plastics. BDP can retain all the benefits of conventional plastics without the negative environmental impacts. The cost of production of BDP is very high. So there is need to develop some cheaper and energy saving methods for synthesis of BDP. An alternative way to minimize plastic pollution is to convert plastics waste into liquid fuel. Waste plastics have high heat of combustion, used as a raw material for fuel production. Pyrolysis of waste plastics into fuel leads to conservation of valuable petroleum resources as well as protection of environment. Waste plastic is degraded catalytically into fuel range hydrocarbon like petrol, diesel, kerosene etc. Waste plastic were heated and resulting gases were condensed to recover liquid fuels [27].

1.3.5 Bitumen and its chemical composition

Bitumen is a black or dark colored solid consisting of high molecular weight hydrocarbons obtained as a byproduct from fractional distillation of petroleum. Bitumen is the heaviest fraction of crude oil and its boiling point is 525 °C. It is viscoelastic in nature. Sometimes it behaves like a viscous liquid and sometimes it behaves like an elastic solid. There are some essential parameters which decide the rheological properties of bitumen like source of crude oil, the method used for the refining of oil and addition of different modifiers [28]. It contains highly condensed polycyclic aromatic hydrocarbons having 95% carbon and hydrogen (87% carbon and 8% hydrogen), sulphur, nitrogen, oxygen and few metals. The heteroatoms tend to impart polarity and functionality to the molecules [29]. Heavy metals Vanadium and Nickel sometimes exist in the form of inorganic salts and oxides [30, 51]. Basically bitumen is a colloidal mixture which contain around 300-2000 chemical components and an average of about 500-700. Bitumen consists of asphaltenes dispersed into an oily matrix of maltenes. Maltenes are further divided into saturates, aromatic hydrocarbons and resins [31]. Actually bitumen is a mixture of polar and non-polar components where polar components impart elasticity while non-polar components provide viscosity to bitumen. Asphlatenes are the highly polar, complex aromatic materials with the largest average molecular mass among crude oils [32]. Colloidal structure of bitumen is responsible for rheological properties of asphalt which varies from a fluid Newtonian zone to a solid non- Newtonian zone [13]. The thermo mechanical properties of bitumen actually depends on complex colloidal structure of bitumen and this is an interesting field for researchers because bitumen is being used in road paving applications [33]. Table 1.2 gives detailed description about different components of bitumen.

Table 1.2: Chemical Components of Bitumen

Property	Asphaltene	Saturates	Aromatics	Resins
State	Amorphous black or brown solid	Straw or white viscous oils	Dark brown viscous liquids	Dark brown solid or semi solid
% in Bitumen	5-25%	5-20%	40-65%	10-20%
Solubility in n-Heptane	Insoluble	Soluble	Soluble	Soluble
Molecular Weight	High 1000-100,000	300-600	Lowest 300-2000	500 - 50,000
Constituents	Complex aromatic materials	Straight, branched chain aliphatic hydrocarbons with alkyl naphthenes and alkyl aromatics	Naphthenic and aromatic compounds	
Polarity	Highly Polar	Non Polar	Non Polar	Polar
Role	Dispersed Phase	Dispersed Phase	Dispersion medium	Dispersing agents or peptizers

1.3.6 Formulation of Research Problem

The present research problem is based on the hypothesis that modification of bitumen leads to the improvement in properties of bitumen. In the literature, polyethene waste, its management, its innovative use as a modifier in bitumen is already discussed, but the effect of medium on such modified bitumen is unanswered till now. The pH of river water is alkaline and during rains this water overflows on the roads, decreasing their strength, resulting in eroding of the roads. In addition due to environmental pollution acid rain takes place at places resulting in deterioration of roads. Thus there must be effect of medium on condition of roads. Whether the medium is acidic or alkaline, it must be affecting the state of bitumen. This is a societal problem and to solve this problem the topic was selected which involves the present research work.

1.3.7 Polymers as modifiers in bitumen

The most commonly used modifiers in flexible pavements are polymers [34]. The researches have been performed on various types of polymers as modifier in bitumen such as Polyethene terephthalate (PET), Low density polyethene (LDPE), High density polyethene (HDPE), Polystyrene (PS) etc. [35-38]. Hence, use of bitumen with various types of modifiers has been reported in literature [39-42]. The modifiers were used such as rubber, fibres, polymers and nanoparticles [43-46]. Addition of reactive polymers to the bitumen can be advantageous because the functional groups present in them can react with components of the bitumen [47]. Modification of the bitumen with modifiers can enhance the performance of roads and blending is the most suitable method of modifying it [33]. There are two methods of modification of bitumen. Indirect modification involves dry process which includes incorporation of waste plastic that is blended with aggregate before adding in bitumen and the direct modification involves wet process in which bitumen and waste plastic is simultaneously blended together [48].

The differences in molecular weight and polarity of base bitumen and polymer has significant effect on affinity between the two irrespective of the type of method of mixing used, whether it is mechanical or chemical method [18]. The polymers interact with the bitumen either by swelling in bitumen or by absorbing or dissolving in it. The polymers reduce the thermal susceptibility and permanent deformation and enhance the resistance to cracking of bitumen thus it becomes more durable and workable at wide temperature range [49]. The polymer modified bitumen has enhanced ductility, viscosity, softening point, better elastic response and cohesion than unmodified bitumen [50-51]. Polymers used as modifier can be classified into two types - plastomers and elastomers. Plastomers form tough, rigid, three dimensional network within the bitumen and provide high initial strength to the bitumen to resist heavy loads, but have less resistance towards strain and can crack at high strains. Plastomers used to modify bitumen are polyethylene-vinyl acetate (EVA), polyethylene butyl acrylate (EBA), ethylene methyl polyacrylate (EMA) and polyethene (PE). Elastomers are rubber like elastic materials, stretched like a rubber band, can regain their shape on release of stretching force. Hence the elastomers can resist permanent deformation (rutting), have enhance elasticity, durability, adhesion and toughness. The elastomers used to modify bitumen are natural rubber, styrene butadiene rubber (SBR), styrene butadiene styrene rubber (SBS) and neoprene. Globally the polymer usage consists of 75% elastomeric modified bitumen, 15% plastomeric and rest 10% consists of either rubber or other modifiers [52]. Polymer modified bitumen also shows a dual phase morphology depending on nature of polymer and its concentration. Either the system consists of asphalt rich phase with uniform dispersion of polymer spheres (low concentration of polymer) or polymer rich phase with asphaltene globules dispersed in it (high concentration of polymer) [53]. A polymer is mixed with the bitumen, fraction of oil content of bitumen get absorbed by it and it swells [54]. On increase in concentration of swollen polymer, it becomes polymer rich continuous phase and the swollen strands join together at nodes to form a three dimensional network. This network has significant impact on the mechanical properties of bituminous binder [54]. Polymers being costly and cannot be used at large scale; hence should be substituted for cheaper plastic waste.

1.3.8 Modifiers in bitumen and performances:

According to literature it has-been proved that plastomeric polymers are good in improving the rut resistance, but elastomers are better than them as later exhibit high percentage of elastic recovery, becomes insoluble in solvents, infusible when melted, more resistant to harm caused by ageing factors [55-56]. Moreover, plastomers do not enhance low-temperature performance of asphalt but elastomers can increase fatigue resistance and cracking resistance, but it is not good in improving the heat resistance. Thus, it is wise to combine the benefits of plastomeric polymer and elastomers and using these composite materials into asphalt as a modifier. This would be another way of recycling waste polymer to enhance the properties of asphalt pavement [57–61]. As per literature it has been observed that properties of bitumen can be enhanced by use of polymers as modifiers. Each polymer tends to improve one or other property of bitumen. It is found that life of pavement can be enhanced by using even small amount of polymers [62]. Figure 1.1 gives the structural formula of various polymers used as modifiers in bitumen.

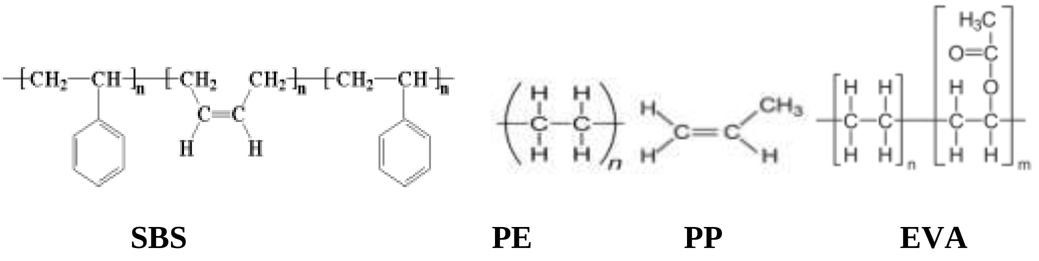

Figure 1.1: Structural formula of different polymers used as modifiers in bitumen

1.3.8.1 Low density polyethene as a modifier

Panda *et al.* examined the effect of reclaimed polyethene derived from low density polyethene (LDPE) and synthesized four modified asphalts by mixing reclaimed polyethene (2.5%, 5.0%, 7.5%, 10.0% content by weight of asphalt) with base asphalt 80/100. It was found that different percentages of polyethene require different temperatures of mixing. The results indicated that the reclaimed polyethene as a modifier tends to enhance moisture susceptibility, marshal stability, fatigue life and resilient modulus of mixes. Asphalt modified with the 2.5% reclaimed polyethene was the optimally modified asphalt [63]. Fuentes-Auden *et al.* studied the role of polymer concentration on the physical and thermal properties of recycled polyethene (RPE) modified bitumen. Blends of bitumen were synthesized at 180 °C in an open reactor on the different weight percentage of recycled polymer taken (2.0%, 5.0%, 15.0%, 25.0%, 50.0% wt. %). It was concluded that recycled polyethene tends to enhance the rheological and mechanical properties of bitumen and leads to have greater resistance against rutting, thermal and fatigue cracking. Moreover, low recycled polyethene concentration (up to 5.0 wt.%) was found suitable for binders in road applications and high concentration (up to 15.0 wt.%) for binders in roofing applications [64]. Use of pyrolysis polyethene as a modifier was studied by Al- Hadidy *et al.* Pyrolysis LDPE was produced by means of thermal degradation and converted to powder by mechanical grinding and mixed pyrolysis LDPE in different percentages (2.0%, 4.0%, 6.0%, and 8.0% by weight of asphalt) at 160 °C with high speed stirrer at 1750 rpm for 3-5 minutes. LDPE modified asphalt mixtures can perform well at low temperature, high temperature and much rain zone. Inclusion of 6.0% pyrolysis LDPE result in durable, economic and high performing flexible pavement [65]. According to literature, ternary blends of LDPE/ ground tire rubber (GTR)/elastomer were used as modifier in bitumen. LDPE/GTR ratio was varied while the elastomer content was kept constant. Results of dynamic mechanical analysis showed that addition of these ternary blends to bitumen improves the flexibility and enhances stiffness at low temperature. Ground tire rubber has cross linked structure and minimum flow ability thus the interfacial interactions between bitumen and ternary blends are decreased with the rise in content of GTR [66]. Ahmedzade used gamma irradiated recycled low density polyethene as a modifier in bitumen. The effects of modifier on bitumen and aged bitumen were studied by means of conventional tests, rotational viscosity, Fourier Transform Infra-Red (FTIR) spectroscopy, morphological analysis, dynamic shear rheometer and bending beam rheometer tests. The results indicated that γ-$LDPE_R$ has stiffening effect on bitumen due to which its temperature susceptibility is increased and performance grade is improved [67]. According to literature, bituminous binders containing 2.0-5.0 wt.% $LDPE_R$ dispersed as oil in water emulsions by in line emulsification process at a particular pressure and temperature were used. The basic method was to prevent separation of polymer and improving the tools for energy saving. Calorimetric and Optical studies performed on bituminous residues proved that shear parameters during emulsification increased the dispersion of the swollen polymer phase resulting in enhanced properties than the parent polymer modified bitumen (PMBs) at high in service temperatures [68]. Kishchynskyi *et al.* used recycled polyethene obtained from processing of waste plastic products as modifier in bitumen. Modified bitumen becomes less susceptible to temperature changes and moisture damage. There was decrease in rate of thermal ageing [69]. Saroufim *et al.* used LDPE, HDPE and EVA as modifier in bitumen. Base bitumen was analysed using SARA analysis while the polymers were studied using FTIR spectroscopy. Fluorescent light optic microscopy was performed to examine the morphology of the mixtures and dynamic mechanical analysis was performed to study the mechanical properties. The research proved that simple tests can be helpful finding the internal structure of the polymer modified binders and hence the appropriate polymer/bitumen blend can be selected [70]. Murphy *et al.* conducted experiments using recycled polymers like polyethenes, polypropylenes, polyurethane, truck tire rubber and ground rubber. Tests like penetration, softening point, rheology, viscosity, ageing were performed. The blend with 3.0% LDPE substituted for 1.0% SBS exhibited same properties like that of polyflex75 but had less stiffness. The best modifier was a combination of bitumen, LDPE and EVA [71]. Yousefi *et al.* used recycled polyethylene modified with different co-polymers as a modifier in asphalt. It was found that RPE particles get swollen by asphalt because of physical interactions. Moreover, copolymers alter the RPE affinity towards asphalt [72]. Optical measurements performed on polyethene modified bitumen confirmed that there were two different phases present one is bitumen rich and other is polymer rich [73]. Singh *et al.* used maleated bitumen instead of pure bitumen with recycled LDPE to form polymer modified bitumen. The findings proved that maleated bitumen-recycled LDPE mixtures have enhanced softening point and elastic recovery with better performance during storage and implementation in practical field [74]. Ho *et al.* highlighted that the molecular weight and its distribution is an important factor in case of LDPE to act as a good modifier of asphalt [75]. Costa *et al.* used waste plastics containing polyethene to modify the bitumen and worked on the storage stability of modified bitumen. Penetration tests, softening point, dynamic viscosity and storage stability of unmodified and modified bitumen were noted. The findings confirmed that SBS, EVA or HDPE had better storage stability [34]. Zoorab *et al.* proved that used waste can be used as apart in stone materials during modification of asphalt. There was replacement of 30.0% such material with waste plastics containing LDPE. The results revealed rise of 250.0% in Marshall Stability and enhancement in tensile strength of asphalt [76].

1.3.8.2 High density polyethene as a modifier

HDPE is a polymer, strongly affects the mechanical properties of bitumen. Perez-Lepe *et al.* investigated the effect of concentration of HDPE on microstructure and rheological properties of modified bitumen using morphological analysis, differential scanning calorimetry (DSC) and linear viscoelastic measurement tests etc. and concluded that HDPE enhances the mechanical properties of bitumen with 3.0% HDPE binder structure changes to gel like, thus giving more elastic properties [77]. Hinislioglu *et al.* investigated the use of plastic wastes having HDPE as modifier in asphalt concrete. Mixing time, mixing temperature and content of HDPE was varied and effect of these parameters on Marshal Stability, flow and marshal quotient was studied. The research revealed that the HDPE modified asphalt enhanced Marshal Stability and Marshal Quotient value and provide better resistance against permanent deformations. Mixtures containing 4.0% HDPE at 165 °C within 30 minutes was the most stable [78]. Casey *et al.* tested various thermoplastic polymers and optimized the mixing procedure in terms of mixing parameters and binder additives and reported that the usage of 4.0% recycled HDPE as a modifier gave convincing results [79]. Waste HDPE was used as a stabilizer in the synthesis of recycled asphalt mixtures to enhance their performance in terms of mechanical, economic and environmental parameters. According to literature, 7.5% of used motor oil and 4.0% of HDPE can be utilized in a new modified binder for asphalt having improved properties [80]. HDPE was used in pellet form as a modifier (of 80/100 grade asphalt), decrease moisture susceptibility and temperature susceptibility of asphalt. 5.0% HDPE content was recommended for improvement of asphalt performance [81]. A comparative study was carried out by Habib *et al.* on the rheological properties of 80/100 bitumen modified by linear LDPE, HDPE and polypropylene (PP). The outcomes showed that PP blends better as compare to LDPE and HDPE and polymer tends to enhance viscosity of bitumen. Modified bitumen performs better in case polymer concentration was below 3.0% [82]. Awwad *et al.* used LDPE and HDPE to coat the aggregates and reported that grinded HDPE as modifier tends to have enhanced engineering properties. HDPE tends to enhance the air voids, stability and decrease the density and act as a better modifier than LDPE in terms of enhancement of properties of asphalt. The optimum binder content was 12.0% by weight of bitumen [83]. Kofteci *et al.* used plastic waste containing HDPE as a modifier. Modified bitumen samples were studied for stability, flow values and indirect tensile test. HDPE as a modifier tends to enhance resistance to water damage. The bitumen sample modified with 4.0% of HDPE was the optimum concentration in terms of stability values [84]. Costa *et al.* conducted research on different pen grade asphalt binders modified by recycled EVA and HDPE in which amount of recycled plastics was varied. Research concluded that performance of modified binder containing 70/100 base bitumen and 5.0% HDPE or EVA was similar to that of commercial modified binder [85]. Fernandes *et al.* utilized waste motor oil and polymers (like HDPE, crumb rubber, SBS) as modifier in bitumen. 10.0% waste motor oil and 5.0% polymers were mixed in bitumen and simple basic and rheological tests were performed on modified bitumen. There was enhancement in properties of modified bitumen as compare to unmodified bitumen. Modified bitumen showed good behavior at medium/high temperatures and enhancement of fatigue and rutting resistance [86]. The use of HDPE as modifier enhanced the elasticity, creep and fatigue resistance of asphalt mixtures. The optimum content of HDPE was 10.0% using indirect tensile stiffness modulus (ITSM), repeated load axial (RLA) test, indirect tensile fatigue tests (ITFT) etc. It was concluded that the asphalt mixtures modified by HDPE is good to be used in temperate climate and average temperature areas [87].

1.3.8.3 Polyethylene Terephthalate as a modifier

PET is a linear aromatic themoplastic polymer of polyester family. This is formed by step growth polymerization of ethylene glycol and terephthalic acid [92]. The recycling symbol of PET is number 1 and is one of the most widely recycled polymer. Water and soft drink bottles are mainly consists of PET. This was also found to be a promising modifier in the modification of bitumen. Kalantar *et al.* prepared modified binders using PET in 2.0% to 10.0% by weight of 80/100 grade bitumen at 150°C temperature. It was found that PET modified binders had higher softening point than pure bitumen. Hence these were more resistant against rutting and permanent deformations [88]. Karahrodi *et al.* used combination of waste polyethylene terephthalate (WPET) and ground tire rubber (GTR) with different compositions. Performance of these was tested via morphological, thermal and rheological analysis. FTIR spectroscopy was helpful in concluding physical interaction between bitumen and waste PET/GTR blend and morphological analysis confirmed degradation of interaction on increasing the GTR content because of cross linked structure of GTR. The study proved enhancement in thermal and rheological properties by changing composition of WPET/GTR [89]. In Iran PET waste was used as aggregate replacement (plastiphalt) in asphalt concrete mixes and it was found that corresponding marshal stability and marshal quotient values were same as that of control samples. The recycling of PET solved major environmental problem of Iran [90]. The effect of using waste PET bottles on the properties of stone mastic asphalt (SMA) mixture was also studied. The optimum amount of PET was 6.0% by weight of bitumen and it enhanced the properties of SMA [91]. Modarres *et al.* studied the role of waste plastic bottles as a modifier in the asphalt mixes. The findings revealed that waste PET as a modifier had similar effect on the performance of bitumen as SBS at 20^{o}C [92]. Moghaddam *et al.* concluded that PET modified asphalt mixtures had more flow, fatigue strength, and higher sustainability as compare to pure asphalt mixtures. There was also enhancement in service life of asphalt pavement [93]. Guru *et al.* derived two novel additives from waste PET bottles called TLPP (thin liquid polyol PET) and VPP (viscous polyol PET). These additives were used to modify the asphalt. Modified asphalts were analyzed using physical tests, superpave tests, scanning electron microscopy (SEM), FTIR and energy dispersive X- ray spectroscopy (EDS). The results indicated that these additives enhanced the stripping and fatigue resistance as well as marshall stability and low temperature performance [94].

1.3.8.4 Polypropylene as a modifier

Polypropylene is formed by chain growth polymerization of propylene. It is one of the cheapest and lightest among commodity plastic. Its recycling code is 5. Tapkin *et al.* evaluated the role of polypropylene as a modifier in 50/70 bitumen. The research indicated that polypropylene tends to enhance Marshall Stability and Marshall Quotient values, thus improving physical and mechanical properties of bitumen [95]. Al-Hadidy *et al.* investigated the effect of pyrolysis polypropylene in 50/60 asphalt cement. Polypropylene was grinded to powder followed by thermal degradation (pyrolysis). It was reported that the PP decreases the temperature susceptibility of asphalt [96]. Addition of phosphorus compounds like polyphosphoric acid (PPA) can solve the problem of stability during storage for long durations at high temperatures in case of polypropylene modified bitumen. PPA basically changes the structure of bitumen from sol to gel [97]. Zoorab *et al.* used recycled plastics made up of PP and LDPE in bituminous mixtures and reported that these modifiers enhanced durability and fatigue life [76]. Waste thermoplastic polymers like HDPE and PP were also blended in bitumen in country like Ghana. PP tends to show more effect on homogeneity and compatibility as compare to HDPE. There was enhancement in viscosity due to addition of polymers as well as thixotropic effect was seen for both at 60 ^{o}C. The penetration value decreases and softening point increases on increasing the ratio of polymers. The most homogenous blend for HDPE was at 2.0% and for PP was at 3.0% polymer loading [98].

1.3.8.5 Ethylene- Vinyl Acetate polymer as a modifier

EVA is a polymer which is obtained by the polymerization of ethylene and vinyl acetate. It is highly elastic but still tough polymer. Ameri *et al.* studied relative performance of EVA modified bitumen. Modified bitumen were analyzed according to dynamic shear and bending beam rheometer, creep compliance test, dynamic creep test, indirect tensile strength test, indirect tensile fatigue test. The tests results indicated that EVA enhanced fatigue and rutting resistance of bitumen. EVA modified bitumen (2.0%, 4.0%) have better low temperature cracking resistance as compare to bitumen [99]. Singh *et al.* performed a comparative study on the effect of EVA, SBS and Crumb rubber (CR) as modifiers in 60/70 grade bitumen and analyzed the effect of modifiers on physical and rheological properties of bitumen before and after ageing. The outcome showed that these properties get enhanced with the increasing percentage of modifier. This was stated that EVA is a good modifier at very high temperature and heavy traffic areas, SBS as a modifier can be used in all climates, CR as a modifier is suitable in moderately high temperature areas. EVA proved to be having higher rutting resistance as compare to SBS and CR [100]. Some researchers believe that EVA as a modifier improves rheological properties of bitumen [101]. Luo *et al.* studied some physical, thermal and rheological properties of modified bitumen using EVA and EVA grafted maleic anhydride copolymer and found that there was enhancement in physical and rheological properties with some improvement in thermal stability. This was reported that bitumen having EVA-g-MAH had better performance than the EVA modified bitumen [102]. Melting point of polymer decreases when EVA is mixed with bitumen. This was confirmed by modulated differential scanning calorimetric (MDSC) studies. Basic reason was smaller crystallites of polymer. Recycled EVA tends to improve properties of bitumen at both low and high in-service temperatures, as well as is an eco-friendly way for disposal of waste plastics [103]. Brovelli *et al.* modified bitumen from two different sources with an EVA copolymer. The properties of modified bitumen were studied by small amplitude oscillatory shear and steady shear tests and concluded that the influence of EVA on morphology and viscoelastic properties of bitumen is dependent on the type of bitumen grade used [104]. Waste EVA (WEVA) copolymer was mixed with blown asphalt in 3.0%, 5.0% and 7.0%. The purpose was to enhance the elasticity of blown asphalt. Physicochemical and mechanical analysis of modified asphalts was done. There was enhancement in storage modulus and elastic recovery. 5.0% WEVA was considered as the best concentration in terms of performance of blown asphalt binder [105]. Nikhil *et al.* optimize the conditions of temperature, rate of mixing and time for the synthesis of homogenous mixture of EVA modified bitumen and mixed EVA with VG-10 bitumen at different combinations of these three parameters. Modified bitumen was analyzed by fluorescence microscopy and storage stability test. The research proved that temperature is the most important factor affecting the modification process followed by blending time and blending speed. The optimum conditions of temperature, blending time and blending speed was come out to be 180

^{o}C, 1 hour and 600 rpm respectively. 5.0% EVA was the optimum content for the modification of VG-10 bitumen [42].

1.3.8.6 Styrene butadiene styrene as a modifier

SBS is a block copolymer formed from anionic polymerization of styrene and butadiene. It is a thermoplastic elastomer thus having properties of plastic and rubber at the same time. At room temperature it behaves like an elastomeric rubber but can be processed like plastics when heated. SBS increases stiffness at high temperature and decreases stiffness at low temperature. This results in improvement in temperature susceptibility. Singh *et al.* studied the role of SBS on strength characteristics of hot asphalt mixes (HMA) and concluded that there was enhancement in strength characteristics, rutting resistance and moisture susceptibility of modified mixes [106]. 50/70 grade bitumen was modified with five different percentages of SBS (2.0% to 6.0%).The morphology of samples were characterized using fluorescence microscopy. The use of SBS as a modifier on the long and short term ageing parameters of HMA have been examined by indirect tensile strength (ITS) test. The results of research proved that addition of SBS improved the conventional and mechanical properties of bitumen [107]. It was also reported that SBS as a modifier decreases the long and short term ageing of hot mix asphalt [28]. The effect of ageing on the SBS modified bitumen was also explored [108]. Toraldo *et al.* studied the effect of polymers as modifiers for bituminous mixtures and used three concentrations of LDPE and EVA polymers (3.0%, 6.0%, and 9.0% by weight of bitumen) and concluded that these modifiers decreased mixtures stiffness at low temperatures and fatigue deformations at high temperatures as well as enhance fatigue life at intermediate temperatures. 9.0% of EVA showed maximum improvement in fatigue life [109].

1.3.8.7 Industrial Waste as a modifier

Haddadi *et al.* investigated the effect of industrial waste like polymers on mechanical properties of bitumen. Industrial waste was taken in four different percentages 1.0%, 3.0%, 5.0%, and 7.0% by weight of bitumen and modified bitumen samples were subjected to different conventional tests. The results of tests proved that industrial waste as a modifier tends to enhance mechanical properties as well as resistance to permanent deformation of bitumen. It solved two fold purposes i.e. the problem of solid waste disposal and pavement with greater resistance to rutting were obtained

[110]. Sangita explained the role of waste polymer modifier (WPM) on the mechanical properties of bitumen, by selecting nitrile rubber and waste polyethene in 1:4 ratio. This was proved that bitumen mixtures having 8.0% WPM as modifier were more resistant to water damage and less susceptible to rut deformation [111]. Waste polymeric packaging materials (WPPM) were used to solve problem of rutting in bituminous roads. Used waste milk bags and other HDPE based carry bags used as modifier in bitumen, the outcomes showed that WPPM as a modifier were more useful for preventing rutting and deformation in hot climate areas [112]. Waste motor oil was also a good option as a modifier in bitumen. The motor oil decreased the viscosity of bitumen and mixing / compaction temperatures. The waste motor oil was used as a partial alternative of bitumen, thus added value to paving industry [113]. The effect of waste engine oil on asphalt mixtures having certain percentage of reclaimed asphalt pavement was also studied. The results proved that this combination may oppose or counterbalance the hardness due to ageing of binder in RAP, but there were fewer enhancements in fatigue and rut resistance [114].

Bindu *et al.* used plastic waste as modifier in mastic asphalt and concluded that 10.0% shredded waste plastic by weight of bitumen can be used to enhance performance and durability of flexible pavement [115]. Motlagh *et al.* tried to enhance technical properties of asphalt pavements using waste polystyrene (PS) disposable dishes. Waste PS was utilized in four different ways – mixed to bitumen, bitumen substituted by PS, mixed to aggregates, similar soft aggregates substituted by PS. The problem of drainage and water percolation in asphalt surfaces can be removed using PS as a modifier [116]. Ayar investigated the reuse of reclaimed asphalt, used motor oil and waste HDPE in the creation of recycled asphalt mixtures. HDPE was used to make the mixture stable while used motor oil acted as renewing agent of reclaimed asphalt. 7.5% of used motor oil and 4.0% of HDPE along with 50.0% of reclaimed asphalt were the optimum percentages and can be utilized as a modified additive in asphalt mixtures [80]. Waste pozzolans (Rice husk ash, Coal waste ash, coal waste, fly ash, ground granulated blast furnace slag), lime, cement were used as modifier in bitumen emulsion to enhance the workability of recycled mixture and was found that rutting resistance of recycled mixture bitumen emulsion was enhanced and waste pozzolan can be used as a modifier [117].

1.3.8.8 Rubber as a modifier

According to literature study, rubber can be used as a modifier in bitumen. The performance of crumb rubber (recycled from) waste tires modified bitumen was compared with that of SBS modified bitumen. 8.0% CR content was the optimum content [118]. Yousefi studied the effect of different mixtures of synthetic and natural rubbers and different polyethylenes on the properties of bitumen. Polybutadiene rubber- polyethylene mixtures formed a physical network in bitumen medium but styrene butadiene random copolymer, natural rubber and Styrene- ethylene- butylene-styrene block copolymer did not form such a network. SBR- PE was the best mixtures that enhanced the properties of bitumen [119]. Modifiers like diblock poly (styrene-b-butadiene) rubber (SBR), triblock poly (styrene-b-butadiene–b-styrene) (SBS) and high cure ground tire rubber can decrease oxidative aging rates and thus decrease the stiffening of asphalt which occurs as a result of oxidative aging. This will naturally enhance the life of pavement [120]. The effect of SBS on aging of asphalt also has been studied. Specimens of bitumen and SBS modified bitumen were aged according to rolling thin film oven test (RTFOT) and pressure ageing vessel (PAV) respectively. Then properties of aged specimens were examined using different tests. FTIR studies confirmed that after ageing, SBS modified bitumen undergo less oxidation than bitumen. Thus SBS as a modifier result in less ageing of bitumen [121]. Nejad *et al.* modified 60/70 bitumen and vacuum bottom bitumen with crumb rubber using classic and SHRP methods and proved that the crumb rubber tends to enhance the elasticity of bitumen. Crumb rubber modified bitumen cannot be used for longer periods of time because bitumen mixtures which contain high amount of CR (26%) had proper storage stability [122]. Processed waste crumb rubber of about 5.0-10.0% by weight of bitumen was used, it enhances Marshall Stability, strength, fatigue life which further increases the durability of road [123]. Gonzalez *et al.* examined the role of adding polymeric additives on technological and rheological properties of crumb tire modified bitumen. 10.0 wt.% CR was mixed with bitumen with the help of a rotor stator mixer at 8200 rpm for 30 min at 180 °C in order to synthesize CR modified bitumen. The additives were added to the mixture and blended together. The additives used were polyphosphoric acid, SBS, linker, FT wax, polyoctenamer. The additives improved storage and loss moduli and reduced loss tangent. Polyoctenamer and polyphosphoric acid were the best among all the additives [124]. The performance of bitumen modified with crumb rubber was improved by adding polyphosphoric acid and vestenamer additives. This in turn enhanced the resistance towards cracking and rutting at low and high temperatures respectively [125]. 9.0 wt.% CR was mixed with bitumen at temperatures (between 90 °C and 250 °C) for 90 minutes. At low temperatures, there was no difference in cross linked network of rubber, means interaction between swollen rubber particles and bitumen is responsible for the rheological properties of modified bitumen. There was partial decomposition of cross linked network of rubber at high temperatures; hence the processing temperature during the synthesis of crumb tire modified bitumen directly affects the rheological properties of bitumen [55]. An innovative technique involving crumb rubber obtained from scrap tires using a high pressure water jet method was also investigated. Resulting crumb rubber had smaller particle size than the conventional one and used as a modifier in bitumen. The new crumb rubber was a much better material that can be used in road construction purpose [126]. Junior *et al.* used scrap tire rubber (STR) as a modifier instead of SBS. Four different percentages of STR were used to modify the asphalt. The properties of STR modified asphalt were compared with SBS modified asphalt. Although the properties of SBS modified asphalt were much better than STR modified asphalt but still STR was a good alternative and can be used in place of SBS. Moreover large amount of scrap tires can be disposed of in an environmental friendly way [127]. Liquid rubber had a wide probability to be used as a modifier in bitumen for future use [128]. Senise *et al.* tested the hybrid systems prepared by mixing of polymers like (EVA, EBA, SBS, EPDMs) with model rubber modified bitumen (10.0 wt.% CTR) and cured with sulphur. The modified bitumen was examined by technological and rheological techniques, Fluorescence microscopy and Modulated Scanning Calorimetry. A complicated system was formed which comprises of several phases mainly asphaltene rich phase, polymer rich phase, un-decomposed rubber particles and dissolved rubber chains that finally results in increment of in service properties and storage stability. Hybrid system containing SBS showed sulphur cross linking reactions and formation of a continuous SBS rich network structure hence better results were obtained [129]. Ramez *et al.* investigated the role of epoxidized natural rubber (ENR) as a modifier in bitumen. ENR was mixed with 80/100 bitumen in varying percentages by weight of bitumen (3.0% to 12.0%). Modified bitumen was analyzed for empirical and rheological properties. ENR tends to decrease the temperature susceptibility and enhanced fatigue behavior and rutting resistance at low and high temperatures respectively. Bitumen modified with 6.0% ENR was found to be the optimally modified bitumen [130]. Varied percentages of rubber silicone (1.0%, 2.0%, 3.0%, and 5.0%) were added to asphalt. Six samples were prepared for each percentage and examined according to Marshall Method. Rubber-Silicone as a modifier enhanced the Marshal stability, air voids, and reduced the flow and bulk density of asphalt mixture. It also improved the flexibility properties of the mix and decreased the permanent deformation [131]. It can be stated that crumb rubber as a modifier shows quite promising results in a wide range of temperatures. Being an elastomer, it provides higher flexibility to the pavement so that later can bear heavy traffic loads.

Polymers like EVA and LDPE can be considered as fascinating modifiers of bitumen at high service temperatures as these tend to form a polymer network within the modified bitumen. Polymer modified asphalts are costly, difficult to handle and sometimes immiscible and therefore efforts should be made for utilization of waste or recycled modifiers.

1.4 Objectives

The purpose of present research work was to study the effect of LDPE and HDPE as modifier on the enhancement in binder properties of bitumen. Wet process was used to prepare polyethene modified bitumen. The research plan comprised of four objectives

- To study the effect of temperature and pH variation on the physical properties of bitumen
- To determine the optimal ratio of polyethene: bitumen that may provide highest thermal as well as pH variation resistance.
- To study the mechanical properties of bitumen after addition of different proportions of polyethene/ waste plastics
- Comparative studies regarding thermal strength, mechanical strength, resistivity towards environmental changes, using various types of plastics

Since, both LDPE and HDPE are non-polar polymers, so for the attainment of last objective of comparative studies, one polar polymer that is EVA was used.

1.5 Research Methodology

The research plan began with the formulation of a problem related to the society. It was followed by survey of literature. It incorporated synthesis of polymer modified bitumen (PMB) using wet process. Two non-polar polymers like LDPE, HDPE and a polar polymer like EVA was used for the synthesis of PMB. PMB were kept at different pH for a specific time interval. The PMB were characterized using conventional tests (penetration point, softening point, and ductility test), morphological analysis (SEM), spectroscopic analysis (FTIR) and thermal analysis (TGA). The results of these tests were compared with the bitumen. Figure 1.2 represents the flowchart of the research methodology:

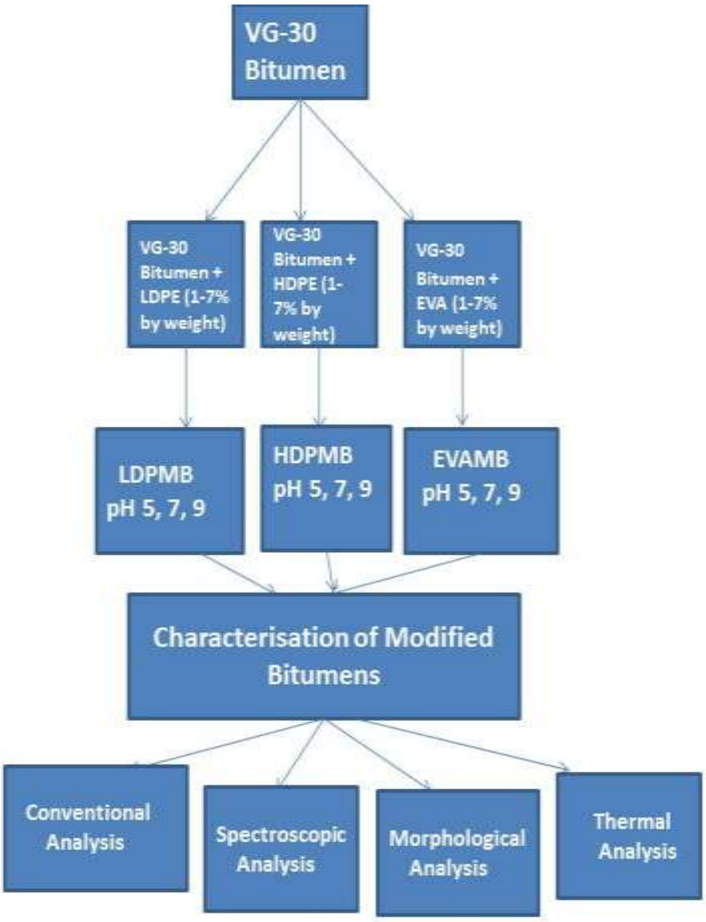

Figure 1.2: Flowchart of Research Methodology

1.6 Expected outcome

The effect of environmental factors like pH and temperature on the properties of bitumen will be understood. As all the polymer wastes are inert to pH, this can be expected that waste polymer added bitumen could be highly stable against pH variation. Hence problem of water logging can be solved. Polymer like polyethene may also act as a good binder which will get less deformed between 0-50 °C, and therefore will provide better strength against thermal variation (which is a very important factor of making roadways in Indian subcontinent). On this basis the optimum binder can be selected according to geographical location of roads.

CHAPTER 2

METHOD DEVELOPMENT AND EXPERIMENTAL PROCEDURES

This chapter discusses about the raw materials i.e. type of bitumen and polymers (non- polar as well as polar) used in the preparation of the polymer modified bitumen (PMB). Experimental methods for the determination of physicochemical properties of bitumen according to Indian Standards (IS) are given. The factors affecting the synthesis process of PMB, fabricated apparatus used in synthesis of PMB and the methods used in the characterization of PMB are also explained.

2.1 Materials

2.1.1 Grade of Bitumen used

VG–30 bitumen was used for the research and it was procured from the S.S. Polymers (Nasrala), Hoshiarpur, India. Table 2.1 gives the physicochemical properties of bitumen used in the present research.

Table 2.1: Properties of VG-30 bitumen

Property	Method	Value
Specific gravity	IS:1202-1978	0.99
Penetration point	IS: 1203-1978	68 dmm
Softening point	IS: 1205-1978	48 °C
Ductility	IS: 1208-1978	76 cm
Flash point	IS:1209-1978	285 °C
Fire point	IS:1209-1978	300 °C
Water content test	IS:1211-1978	0.1%
Loss on heating test	IS:1212-1978	0.7%
Spot test	-	Negative
Solubility in CS_2 (wt. %)	IS:1216-1978	99.7%

2.1.2 Types of Polymers used

There are some basic requirements that a polymer must meet in order to be selected as a modifier of bitumen**.** The modifier should be easy to mix, cheap and must have chemical compatibility with the bitumen. In addition, reaction conditions should be practically optimized like type of mixer, mixing speed, temperature and time of mixing should be feasible and applicable. The modified bitumen should be workable in real conditions as well as homogenously dispersed if stored for longer periods of time. Three different polymers: Low density polyethene (LDPE), High density polyethene (HDPE) and poly (Ethylene-Vinyl Acetate) or EVA were used in the research. First two were non-polar polymers while last one was polar. The purpose to use the polymers which differ in their polarity is to study the effect of exposure of different types of medium (acidic, basic or neutral) on polymer modified bitumen which ultimately is going to affect the binder property of bitumen. All the three polymers were procured from S.K. Industries (Daburji) Amritsar, Punjab, India and were in form of small pellets of 2-3 mm size.

2.1.2.1 Low Density Polyethene (LDPE)

The chemical formula of LDPE is $(C_2H_4)_n$. This is commonly known as polythene with IUPAC name polyethene and its recycling code is 4. It is a type of thermoplastic formed by free radical addition polymerization of ethylene at a temperature of 100 °C to 300 °C under high pressure of 3000 bar. LDPE has branched structure, so intermolecular forces of attraction are weaker, as a result it is loosely packed and hence has low density. It has a density range of 0.910-0.940 g/cm^3 and melting point range is 109-125 °C. It is highly flexible, less strong so has moderate tensile strength and high ductility. It is widely used in electrical insulation and packaging industry due to its moisture susceptibility and transparent nature (83).

2.1.2.2 High Density Polyethene (HDPE)

The chemical formula of HDPE is $(C_2H_4)_n$ and its recycling code is 2. It has a simple linear structure with less or no branching as a result it is closely packed and hence has higher density. HDPE has density greater or equal to 0.941 g/cm^3 with melting point range 130-135 °C. HDPE is used widely in preparation of toys, pipe systems, plastic bottles, household chemical containers because of its UV resistant, non-leaching and chemical properties. These two polyethenes (LDPE and HDPE) are in great demand so their waste is also increasing day by day. Therefore, there is an urgent need to find an alternative way for their safe disposal. Hence the motive of the research was to utilize this polyethene waste in a constructive manner.

2.1.2.3 Poly (Ethylene-Vinyl Acetate) (EVA)

The chemical formula of EVA is $(C_2H_4)_n(C_4H_6O_2)_m$. It is formed by polymerization of ethylene and vinyl acetate. The weight percent of vinyl acetate ranges from 10-40.0% rest being ethene. If content of vinyl acetate is increased then EVA becomes more flexible and transparent and its melting point decreases. EVA has density range of 0.92-0.94 g/cm^3 with melting point range 60-95 °C. EVA is a thermoplastic, polar, highly flexible, tough, and transparent in nature. It is used in adhesives, sealants, coatings and footwear components. Figure 2.1(a) and (b) gives structural formula of polyethene and Ethylene-Vinyl acetate respectively. Figure 2.2 represents all the three polymers used in the present research.

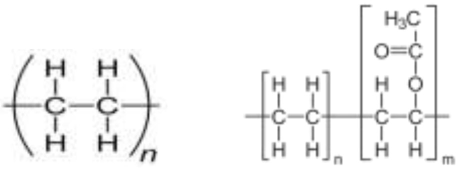

Figure 2.1: (a) Polyethene (b) Ethylene-Vinyl Acetate

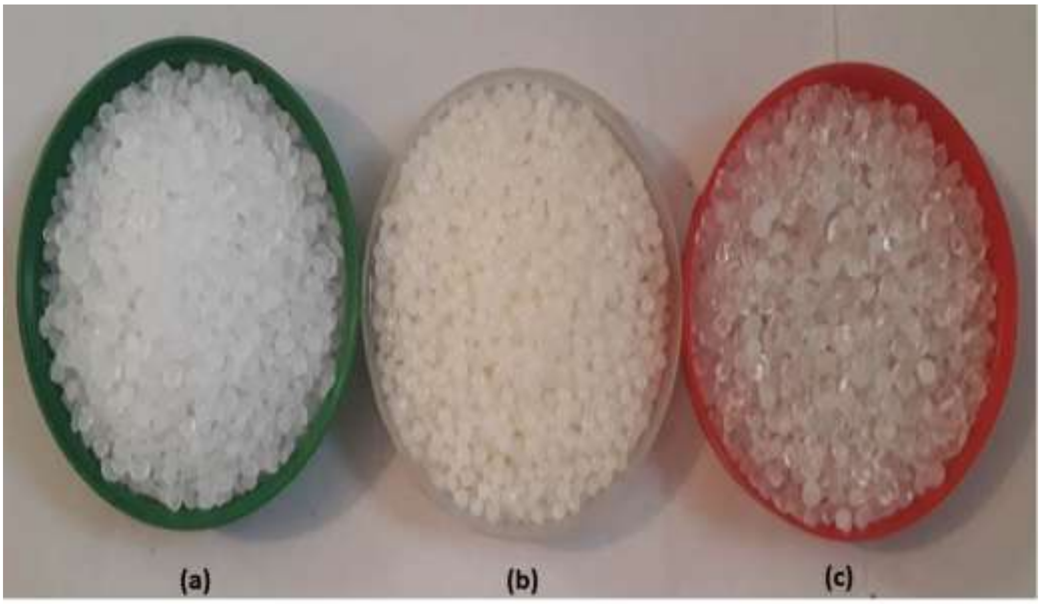

Figure 2.2 : Pellets of (a) LDPE (b) HDPE (c) EVA

The properties of polymers as supplied by the producers are given in the Table 2.2

Table 2.2: Properties of the polymers

Polymer Property	LDPE	HDPE	EVA
Density	0.922 g/cm^3	0.958 g/cm^3	0.95 g/cm^3
Specific gravity	0.918	0.952	0.92
Melting point	115 °C	130 °C	72 °C

2.2 Experimental Procedure

The process of synthesis of PMB involves particular conditions and parameters. These parameters have significant effect on the properties of PMB. The parameters, to be taken care of, while synthesizing PMB, are as follows

1. Type of mixer 2. Number of rpm 3. Temperature of mixing

4. Time of mixing

2.2.1 Type of mixer

There are three types of mixers available, low shear mixture, mid shear mixture and high shear mixture. In low shear mixer, mixing of material particles occur at low speed. This mixer is used in case of free flowing materials. The speed of a mid-shear mixer is slightly higher than that of low shear mixer. As bitumen is a highly viscous and cohesive material so these two types of mixers cannot be used for mixing of polymer with the bitumen. Hence a high shear mixer, whose speed is very high, was used in the research to ensure complete dispersion of polymer in the bitumen and to achieve a homogenous mixture of PMB. This is well known fact that lot of energy is required to drive high shear mixer motors.

2.2.2 Number of Revolutions per Minute (rpm) of the Mixer

Rate of speed of stirring of the mixer is also an important factor which needs to be optimized for the synthesis of PMBs. More the number of rpm of mixer better will be the blending of polymer into the bitumen. Experimentally, it is found that different types of polymers need different numbers of rpm of mixer to ensure homogenous dispersion of polymer into the bitumen. Speed of stirring of the mixer should not be less than 500 rpm in any case.

2.2.3 Temperature of Mixing

One of the important factors on which synthesis of PMB depends is the temperature at which polymer is mixed with the bitumen. The temperature should be higher than the softening point of bitumen but not higher than 180 °C. This is because properties of bitumen changes after 180 °C. The temperature of mixing should be able to melt the polymer so that polymer can be mixed properly in bitumen but the selected temperature should not be so high to cause decomposition of polymer. Keeping these pre requisites in mind, the temperature of mixing of polymer with the bitumen is optimized.

2.2.4 Time of Mixing

Another factor on which synthesis of PMB depends is the time for which polymer should be mixed with the bitumen in the mixing vessel. The motive of present research was that a homogeneous mixture should be formed in which polymer is dispersed uniformly in the bitumen. In case mixing is carried out for lesser time, then the resulting mixture will not be homogenous in nature and the polymer pellets will be clearly visible on the surface of bitumen but if mixing of polymer and bitumen is carried out for longer time then there are chances of loss of volatiles and so mixing time also need to be optimized. It is well known from the literature that the time of mixing should not be less than 1 hr in any case and maximum time varies from polymer to polymer.

2.3 Fabrication of the Apparatus

As bitumen is a highly viscous material and proper mixing of any polymer in it requires lot of energy. Moreover, properties of bitumen are dependent on temperature, so the purpose is homogeneous mixing of polymer in bitumen which requires high shear mixing with temperature control system. Hence an apparatus (Figure 2.3) was fabricated, keeping in mind the conditions of simultaneous heating, stirring and temperature control. Figure 2.3 shows components of fabricated apparatus

Figure 2.3: (a) Six blade mixer (b) Mixing vessel (c) Top view of furnace (d) Mixing vessel in the furnace (e) Front view of furnace (f) Fabricated apparatus

A muffle furnace with digital temperature controller cum indicator was redesigned with a difference that the rectangular thick steel vessel was kept vertical like a top loading box type oven. A high shear mixer with six blades was inserted from the top in the vessel. The vessel was covered with a steel lid having three holes in it, one for inserting the rod of the mixer and other two for escaping of the gases so that high pressure was not built up inside the vessel during simultaneous heating and stirring. This assembly was attached with a digital rpm meter which displayed reading of rpm of the mixer on the screen. The components of fabricated apparatus

(a) Muffle furnace

(b) Rectangular thick steel vessel in which mixing and heating was carried out

(c) Steel lid of the vessel with three holes

(d) Six blade mixer

(e) Digital rpm meter

2.4 Synthesis Methods of Polymer Modified Bitumen (PMB)

There are two methods widely used in the synthesis of PMBs

1. Dry process or indirect modification of bitumen
2. Wet process or direct modification of bitumen

In the research, Wet process or direct modification process was used for the synthesis of polymer modified bitumen. In wet process polymer is added directly into the molten bitumen under fixed conditions of temperature and rpm of mixing and both are simultaneously blended together. In dry process polymer is initially mixed with the aggregate and the resulting mixture is added in the bitumen. Although, wet process is a time consuming and complex process, it is preferred over the dry process here because it results in homogenous dispersion of polymer in the bitumen.

2.4.1 Synthesis of Low Density Polyethene Modified Bitumen (LDPMB)

Using wet process, the VG-30 bitumen was modified with 1.0%, 3.0%, 5.0% and 7.0% by mass of bitumen with the help of fabricated high shear mixer with thermostatic control. Initially, in a steel vessel 1500 g of bitumen was heated until it became a fluid, and as soon as the temperature reached about 160 °C, a pre weighed amount of low density polyethene was slowly added into the molten bitumen in 1.0%, 3.0%, 5.0% and 7.0% by mass of bitumen. The mixture was continuously stirred for 1.5 hr at 1000 rpm under 170 °C in order to get homogenous samples. After, this modified bitumen was poured into small containers and further allowed to cool up to room temperature. In order to protect these samples from environmental oxidation these samples were sealed with aluminum foil and stored for further testing. The obtained low density polyethene modified bitumen samples were labeled as below:

VG-30 Bitumen + 1.0%LDPE = 1LDPMB

VG-30 Bitumen + 3.0% LDPE = 3LDPMB

VG-30 Bitumen + 5.0%LDPE = 5LDPMB

VG-30 Bitumen + 7.0% LDPE = 7LDPMB

2.4.2 Synthesis of High Density Polyethene Modified Bitumen (HDPMB)

Using wet process, the VG-30 bitumen was modified with 1.0%, 3.0%, 5.0% and 7.0% by mass of bitumen with the help of fabricated high shear mixer with thermostatic control. Initially, in a steel vessel 1500 g of bitumen was heated until it became a fluid, and as soon as the temperature reached about 160 °C, a pre-weighed amount of HDPE was slowly added into the molten bitumen in 1.0%, 3.0%, 5.0% and 7.0% by mass of bitumen. The mixture was continuously stirred for 60 minutes at 1200 rpm under 165 °C in order to get homogenous samples. After this, modified bitumen was poured into small containers and further allowed to cool up to room temperature. In order to protect these samples from environmental oxidation these samples were sealed with aluminum foil and stored for further testing. The obtained high density polyethene modified bitumen samples were labeled as below:

VG-30 Bitumen + 1.0%HDPE = 1HDPMB

VG-30 Bitumen + 3.0% HDPE = 3HDPMB

VG-30 Bitumen + 5.0%HDPE = 5HDPMB

VG-30 Bitumen + 7.0% HDPE = 7HDPMB

2.4.3 Synthesis of Ethylene-Vinyl Acetate Modified Bitumen (EVAMB)

Using wet process, the VG-30 bitumen was modified with 1.0%, 3.0%, 5.0% and 7.0% by mass of bitumen with the help of fabricated high shear mixer with thermostatic control. Initially, in a steel vessel 1500 g of bitumen was heated until it became a fluid, and as soon as the temperature reached about 160 °C, a pre weighed amount of EVA was slowly added into the molten bitumen in 1.0%, 3.0%, 5.0% and 7.0% by mass of bitumen in separate containers. The mixture was continuously stirred for 60 minutes at 600 rpm under 175 °C in order to get homogenous samples [42]. After, this modified bitumen was poured into small containers and further allowed to cool up to room temperature. In order to protect these samples from environmental oxidation these samples were sealed with aluminum foil and stored for further testing. The obtained EVA modified bitumen samples were labeled as below:

VG-30 Bitumen + 1.0%EVA = 1EVAMB

VG-30 Bitumen + 3.0% EVA = 3EVAMB

VG-30 Bitumen + 5.0% EVA = 5EVAMB

VG-30 Bitumen + 7.0%EVA = 7EVAMB

Table 2.3 gives the relative masses of bitumen and polymer for the synthesis of required % composition of PMB and Figure 2.4 shows polymer modified bitumen samples.

Table 2.3: Synthesis of polymer modified bitumen

Sr. No.	**Bitumen grade**	**Mass of bitumen in g**	**Type of polymer**	**% of polymer**	**Mass of polymer in g**	**Total mass of mixture in g**
1.	VG-30	1485	LDPE	1	15	1500
2.	VG-30	1455	LDPE	3	45	1500
3.	VG-30	1425	LDPE	5	75	1500
4.	VG-30	1395	LDPE	7	105	1500
5.	VG-30	1485	HDPE	1	15	1500
6.	VG-30	1455	HDPE	3	45	1500
7.	VG-30	1425	HDPE	5	75	1500
8.	VG-30	1395	HDPE	7	105	1500
9.	VG-30	1485	EVA	1	15	1500
10.	VG-30	1455	EVA	3	45	1500
11.	VG-30	1425	EVA	5	75	1500
12.	VG-30	1395	EVA	7	105	1500

Figure 2.4: Polymer modified bitumen samples

2.5 Exposure of modified bitumen to medium of different pH

Modified bitumen samples were immersed in acidic water at pH 5.0 (using 0.01M HCl), pH 7.0 (distilled water maintained by using 0.01M HCl and 0.01 M NaOH if required) and pH 9.0 (maintained by using 0.01M NaOH) for 24 hr, in beakers covered with aluminium foil. These samples were taken out after exposure of medium for 24 hr, dried in air and finally characterized for different properties. Figure 2.5 shows modified bitumen immersed in aqueous solutions of different pH.

Figure 2.5: Polymer Modified bitumen at different pH

2.6 Methods of Characterization of Polymer Modified Bitumen

The properties of polymer modified bitumen were studied and compared with bitumen in order to ascertain if there is some enhancement in binder properties of bitumen after modification with polymers. Following important properties/analysis was studied / conducted.

1. Conventional properties – Penetration point, softening point, and ductility tests were performed to study the physical and mechanical properties of PMB. All these properties depend on intermolecular forces of attraction between molecules of bitumen hence if there is some change in these properties after modification with polymers that will ultimately affect the binding property of bitumen.
2. Scanning Electron Microscopy analysis (SEM) – This test was performed to find the changes in morphology of bitumen after modification with different types of polymers which ultimately give an idea about change in binding property of bitumen.
3. Spectroscopic analysis (FTIR) – Fourier Transform Infrared analysis of bitumen and polymer modified bitumen was performed in order to detect different functional groups and their interactions in PMB.
4. Thermal analysis (TGA) –Thermo-gravimetric analysis was performed to find the thermodynamic stability of polymer modified bitumen at different temperatures.

2.6.1 Penetration point (IS: 1203-1978)

The Bureau of Indian Standards (BIS) categorized bitumen in different categories based on their penetration in 1950. Later on this categorization was revised in 1962 and in 1992. Penetration point gives degree of hardness of bitumen. Penetration point of bitumen is basically how much distance in dmm, a needle can penetrate vertically in the bitumen sample at some particular set of temperature, time and weight. If a bitumen sample is more hard and viscous, the needle will penetrate less in the sample and vice-versa. Therefore hard bitumen will have low value of penetration point while soft bitumen will have higher value of penetration. Soft bitumen is preferred in cold climate and hard bitumen is used in warm climate. Globally, among different penetration grades of bitumen 40-50 grade is hardest of all and used in warmer regions and 200-300 grade is softest of all which is being used in cold climates (132).

Penetrometer was used to find penetration point of bitumen. The apparatus comprised of a flat bottomed, cylindrical metallic container as well as a needle, water bath, thermometer; stop watch. Molten bitumen was poured in the container and kept undisturbed at room temperature for 45 min. Then it was placed in water bath at 25 °C for 45 min. Sample was placed on the apparatus, needle was made to touch surface of the sample and released for 5 sec followed by noting the reading from the dial. Three readings were taken at three different points of sample surface and mean of the readings was the penetration point.

2.6.2 Softening point (IS: 1205-1978)

Bitumen does not have a true melting point. On heating it does not directly change from solid to liquid. Initially it softens then it becomes fluid and finally it is converted to liquid. Hence softening point is defined as the temperature at which bitumen achieves a particular degree of softening under some particular conditions. Softening point is indicative of deformation resistance of bitumen at high temperature. Bitumen with higher softening point is less temperature susceptible and can be used in hotter climates and that with lower softening point is preferred in colder regions (133).

Ring and ball apparatus was used to find the softening point of bitumen. The apparatus consists of two steel balls, two brass rings, supporting rods, thermometer, stirrer and a beaker having boiled distilled water in it. Molten bitumen sample was poured in brass rings and assembly was placed in water having freshly boiled distilled water. The water was heated with continuous stirring at the rate of 5 °C per min. Bitumen in the rings started soften, ball passed through the ring and finally touched the bottom of the beaker. The temperature at which ball touched the bottom was noted. The mean of temperature for the two balls was noted as the softening point.

2.6.3 Ductility Test (IS: 1208-1978)

The ductility value of bitumen is a measure of its ability to stretch**.** The ductility of bitumen is actually how long a bitumen sample can be stretched before breaking at some particular set of conditions. This property is related to elasticity of bitumen and is measure of adhesive nature of it. Bitumen sample should have a specific minimum value of ductility so that it forms thin films and help in binding of the aggregates together. A sample which has low ductility also has poor binding properties and will easily crack under heavy traffic or in extreme climatic variations (134). Ductility testing machine was used to find ductility of modified bitumen at 27 °C. The apparatus comprised of brass moulds, testing machine, water bath and thermometer. Bitumen sample was melted and poured in the moulds that were lubricated with the equal parts of glycerin and dextrin. The moulds were kept at room temperature for 40 min followed by keeping in water bath at 27 °C. The briquette was removed from the plate and clips were pulled horizontally at a uniform speed till the briquette broke. The distance in cm through which the clips were pulled was noted. The average of the three readings was noted as the ductility of the sample.

2.6.4 Scanning Electron Microscopy (SEM) analysis

SEM is a powerful technique to study the surface of polymers, composites, fibrous materials, catalysts, biological materials, metals and ceramics**.** SEM was performed on bitumen samples to examine the morphology of polymer modified bitumen. This analysis explains the nature of dispersion of polymer in bitumen. SEM uses electrons to produce a highly magnified image of surface of a solid sample. An electron beam from an electron gun passes through an evacuated column and focused by condenser and objective lenses on the surface of sample. The electron emitted by the sample is detected, amplified and the resulting signal is used to produce an image. Field Emission Gun Scanning Electron Microscope NOVA NanoSEM 450 was used for SEM analysis of polyethene modified bitumen samples. The SEM analysis of EVAMB was conducted using JEOL IT 500. Gold coating of samples were done in DII-29030 SCTR smart coater for 1 min. For the purpose, a small sample was cut and placed over a conducting carbon tape and coated with gold in a sputtering unit followed by SEM measurement till 10 µm zoom.

2.6.5 Fourier Transform Infra Red (FTIR) analysis

FTIR is one of the important tools to find the structure of a molecule. FTIR spectroscopy was performed on bitumen and modified bitumen samples. This technique is helpful in predicting the functional groups present in the modified bitumen samples and thus helpful in determining the molecular structure. IR spectroscopy is based upon the fact that different molecules vibrate at different frequencies. These frequencies occur in infrared region of electromagnetic spectrum between 200 cm^{-1} to 4000 cm^{-1}. The infrared radiations are passed through a sample; it will radiations are absorbed at frequencies corresponding to molecular vibration frequencies and transmit all other frequencies. These vibrations include stretching and bending modes of various functional groups. The frequencies of radiation absorbed are measured by an infrared spectrometer. A plot is drawn between percent transmittance / %absorbance and wave number / frequency, which are IR spectrum of the sample. Different materials have different vibrational frequencies, hence have different IR spectrum, hence from the vibrational frequencies in the IR spectrum this can be predicted whether a particular functional group is present or absent.

FTIR (Shimadzu-8400S) spectrophotometer was used for monitoring available functional groups in the bitumen and the change in frequency of observed IR peaks in modified bitumen samples. For the purpose, 1.0 mg of bitumen sample was mixed with 3.0 mg dry Potassium bromide (KBr), grounded to a fine powder and compressed to a very high pressure to form pellets which were analyzed in FTIR spectrophotometer. FTIR study of modified bitumen samples was necessary to confirm the interaction of polymer with bitumen. This study throws a light on the type of interaction between bitumen and different polymers. Whether a particular polymer reacts chemically with the bitumen or it is just a physical interaction is confirmed by FTIR studies (135).

2.6.6 Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis can be used for purity determination, evaluation of water content, volatiles and residues, finding thermal and oxidative stability and reaction kinetics. TGA is based on the principle that a bitumen sample loses weight on being heated. There can be weight loss due to evaporation, decomposition, reduction or due to any physical or chemical change occurring in the bitumen sample. This decrease in weight can be used to find the thermal stability and decomposition behavior of the sample. Actually there are different ways to study the thermal properties of a material. TGA/DTA method was used to interpret the behavior of modified bitumen at different temperatures as both TGA and DTA complement each other. STA-449 F1 Jupiter (NETZSCH) was used for the thermal analysis of modified bitumen samples. This instrument measures TG and DTA simultaneously over a wide range of temperature. 2-10 mg of bitumen sample is heated in a Platinum pan and temperature is increased at a rate of 10 °C/min. The heating was started at room temperature and continues up to 1000 °C. The measurement was carried out in an inert atmosphere such as nitrogen atmosphere at a rate of 250 mL/min. The difference in weight of sample was noted during the heating process.

CHAPTER 3

LDPE BASED MODIFICATION OF BITUMEN: FINDING OPTIMUM RATIO AND DETERMINATION OF CHANGE IN PHYSICOCHEMICAL PROPERTIES

Different methods were adopted for preparation of modified bitumen by using LDPE as modifier. Mainly three types of variation were studied: a) operating temperature of mixing b) effect of stirring rate and c) variation in composition of LDPE. Bitumen samples modified by LDPE were exposed to different mediums (of pH 5.0, 7.0 and 9.0) maintained by adding 0.01M HCl or 0.01M NaOH to double distilled water. The samples were characterized for properties like Penetration point, Softening point, Ductility and analyzed by Scanning electron microscopy, Fourier Transform Infra-Red spectroscopy and Thermo-gravimetric analysis techniques**.**

3.1 Penetration Point

Penetration point is one of the basic physical property of bitumen which gives information about the hardness or softness of bitumen. This property depends on intermolecular forces of attraction between molecules of bitumen. With strong intermolecular forces of attraction, harder bitumen use to form. Table 3.1 summarized the result of penetration point for the bitumen and various % compositions of LDPMB.

Table 3.1 - Penetration point test results for bitumen and LDPMB

% of LDPE in bitumen	Penetration point of LDPMB at 25 °C (dmm)	Penetration point of LDPMB at 35 °C (dmm)	Penetration point of LDPMB at 45 °C (dmm)
0	68	69	70
1	55	59	62
3	45	48	50
5	33	33	39
7	30	32	35

First objective of the research is to study the effect of temperature variation on physical properties of bitumen. Hence penetration point of bitumen and LDPE modified bitumen at three different temperatures (25 °C, 35 °C and 45 °C) was determined. Figure 3.1 represents the variation in penetration point of the bitumen and LDPMB at different temperatures versus different percentages of LDPE. Table 3.1 indicates that penetration point of bitumen is 68 dmm which is in the acceptable range of VG-30 bitumen. Results of penetration test shows that the penetration value of bitumen decreases after the addition of LDPE and it further decreases with the increase in the percentage of LDPE (see Figure 3.1). There is sharp decrease in penetration value from 68 dmm for bitumen to 55 dmm for LDPE at 1.0% mixing. Then at 3.0% mixing it falls to 45 dmm. For high mass percentage of LDPE (5.0% and 7.0%) the penetration value for LDPMB falls up to 33 dmm and 30 dmm respectively.

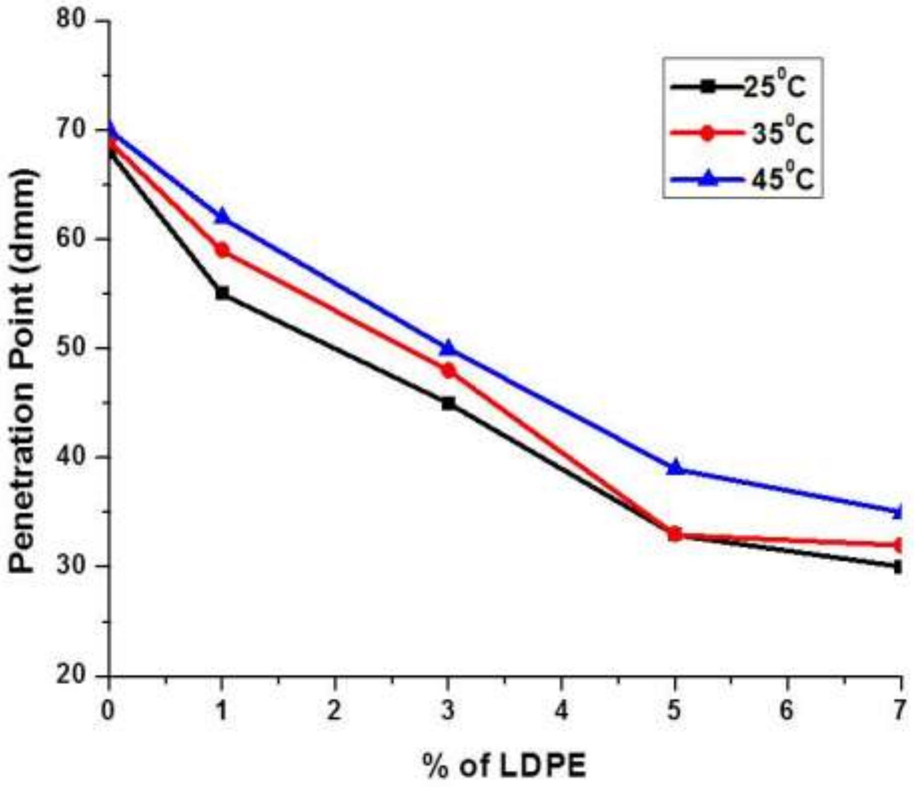

Figure 3.1: Penetration point of LDPMB versus % of LDPE at different temperatures

Overall results of penetration point test show that bitumen becomes harder with the modification of LDPE. The penetration value increases with the increase in temperature for LDPE modified bitumen samples. However, at particular temperature the LDPE modified bitumen samples have low penetration points as compared to bitumen. For example, at 45 ºC, the penetration value is decreased by 50.0% for LDPMB as compare to unmodified bitumen. This can be concluded that that with the incorporation of LDPE, the hardness and stiffness of the bitumen increases, which in turn leads to the enhancement in the resistance of modified bitumen towards permanent deformation, rutting at moderate and high temperatures. Due to this improvement in the hardness, the road constructed using LDPE modified bitumen can resist the penetration in comparison to the road build from unmodified bitumen and therefore, increases the longevity of the road.

3.2 Softening point

Softening point is also basic physical property of bitumen which depends on intermolecular forces of attraction between molecules of bitumen. If the intermolecular forces of attraction are weak, then the bitumen samples will have low softening point and vice versa. Softening point of bitumen and LDPE modified bitumen samples was determined with the help of ring and ball apparatus. Table 3.2 summarized the result of softening point and ductility test for bitumen and LDPE modified bitumen samples.

Table 3.2 – Softening point and ductility test results for bitumen and LDPMB

Sr. No.	% of LDPE in bitumen	Softening point (°C) of LDPMB	Ductility (cm) of LDPMB
1.	0	48	76
2.	1	50	70
3.	3	54	61
4.	5	55	54
5.	7	61	38

Softening point of bitumen is 48 °C. The results of softening point clearly indicate that softening point of bitumen increases after modification with LDPE and it further increases with the increase in its amount. As the softening point increases bitumen becomes less temperature susceptible. This implies that bitumen becomes resistant towards the effect of heat and it will not soften at high temperature. Such modified bitumen can be successfully used in areas with hotter climatic conditions. Figure 3.2 represents the variation in softening point of bitumen and LDPMB versus different percentages of LDPE. At 1.0% composition of LDPE the increase in softening point is very less i.e. 4.2%. When the percentage of LDPE is increased to 3.0%, the rise in softening point becomes 12.5%. At 5.0% composition of LDPE, the rise in softening point is 14.6% for LDPMB. Softening point increases by 27.0% in case of LDPMB at 7.0% composition of LDPE.

3.3 Ductility test

Ductility of bitumen is a mechanical property which is measure of cohesive strength of bitumen and depends on intermolecular forces of attraction. The bitumen sample will be more ductile if the intermolecular forces of attraction are strong and vice versa. Ductility values of bitumen and modified bitumen samples were determined with the help of ductility testing machine.

Table 3.2 summarized the result of ductility test for the bitumen and LDPE modified bitumen samples. It is clear from the table that ductility of bitumen is 76 cm. Ductility of bitumen decreases after the modification with LDPE and with the increase in percentage of LDPE. At 1.0% composition of LDPE modified bitumen, ductility decreases by 7.9%. The decrease is 19.7% for 3.0% composition of LDPE modified bitumen. Decrease in ductility of bitumen is justified because stiffness of bitumen enhances after the modification with LDPE. It decreases by 29.0% at 5.0% composition of LDPE modified bitumen and then it decreases beyond minimum acceptable value of 40 cm. This means bitumen cannot be modified with LDPE beyond 5.0% mass of bitumen. Bitumen which is having very low value of ductility will not act as a good binder because it will not be able to bind the aggregates properly. Hence, bitumen having percent of LDPE greater than 5.0% by mass of bitumen will have poor performance in the pavement, hence should not be used. Therefore, 5.0% LDPE by mass of bitumen is the ideal or optimum concentration for the modification of VG-30 bitumen. Figure 3.3 shows the variation in ductility values for the bitumen and LDPE modified bitumen samples versus different percentages of LDPE.

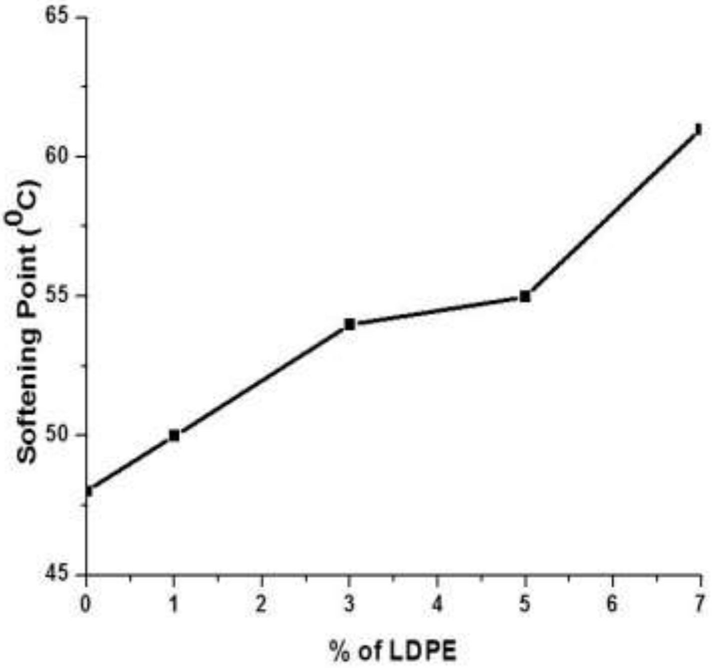

Figure 3.2: Softening point of LDPMB versus % of LDPE

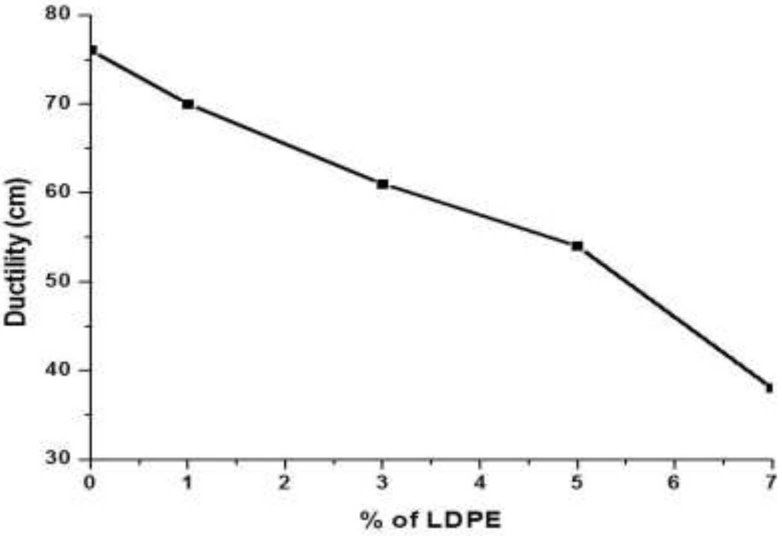

Figure 3.3: Ductility of LDPMB versus % of LDPE

3.4 Scanning Electron microscopy (SEM) analysis of LDPE modified bitumen

SEM analysis was performed on bitumen and LDPE modified bitumen samples to examine the dispersion of LDPE in VG-30 bitumen. SEM images of different compositions of LDPE modified bitumen are shown in the Figure 3.4. Bitumen, itself is black in color, and doped LDPE is obtained in white patches. The images clearly suggest that with the increase in the percentage of LDPE in bitumen, white area is increasing and coming closer. After 5.0% composition of LDPE, the polyethenes are accumulated and ruptured the surface of bitumen that clearly indicates, higher dosage of LDPE are dangerous for road making industry. Lower dosage of LDPE (1.0%) in modified bitumen is although shown to be uniformly distributed, but their amount is very-very less for making any change in the properties of the bitumen.

3.5 SEM analysis of LDPE modified Bitumen at different pH

Once the SEM analysis of bitumen and different compositions of LDPE modified bitumen was performed, similar analysis was performed for LDPE modified bitumen samples exposed to different environmental conditions of pH for a particular time interval. From the ductility test results it was clear that 5.0% LDPE is the optimum composition for bitumen modification. Hence 5.0% LDPMB was selected to study the effect of pH using SEM analysis. There is difference in pH of water at different places worldwide; it may vary from slightly acidic to slightly alkaline. So, this was necessary to find the effect of different type of pH on the surface of LDPE modified bitumen. The effect of acidic water logging was seen on the LDPE modified bitumen surface by dipping the modified bitumen sample into acidic water of pH 5.0 for 24 hr and the morphology of the sample was tested using SEM technique. SEM clearly indicates crack on the surface of the LDPE modified bitumen (Figure 3.5 b). Even after modification with LDPE crack remains there, means modification with LDPE is not enough against the problem of damage caused to roads due to water logging. Similarly, tests were performed for checking effect of neutral water and of basic water by dipping LDPE modified bitumen in distilled water of pH around 7.0 and dipping in alkaline water of pH 9.0 respectively. The surface morphology of these samples indicates the formation of many and large holes (Figure 3.5 d), which itself explain the condition of roads after exposure to alkaline water. Modification with LDPE has given no such solution against the damage caused to roads due to water logging problem. This means LDPE modified bitumen are not resistant to pH variations occurring in the environment.

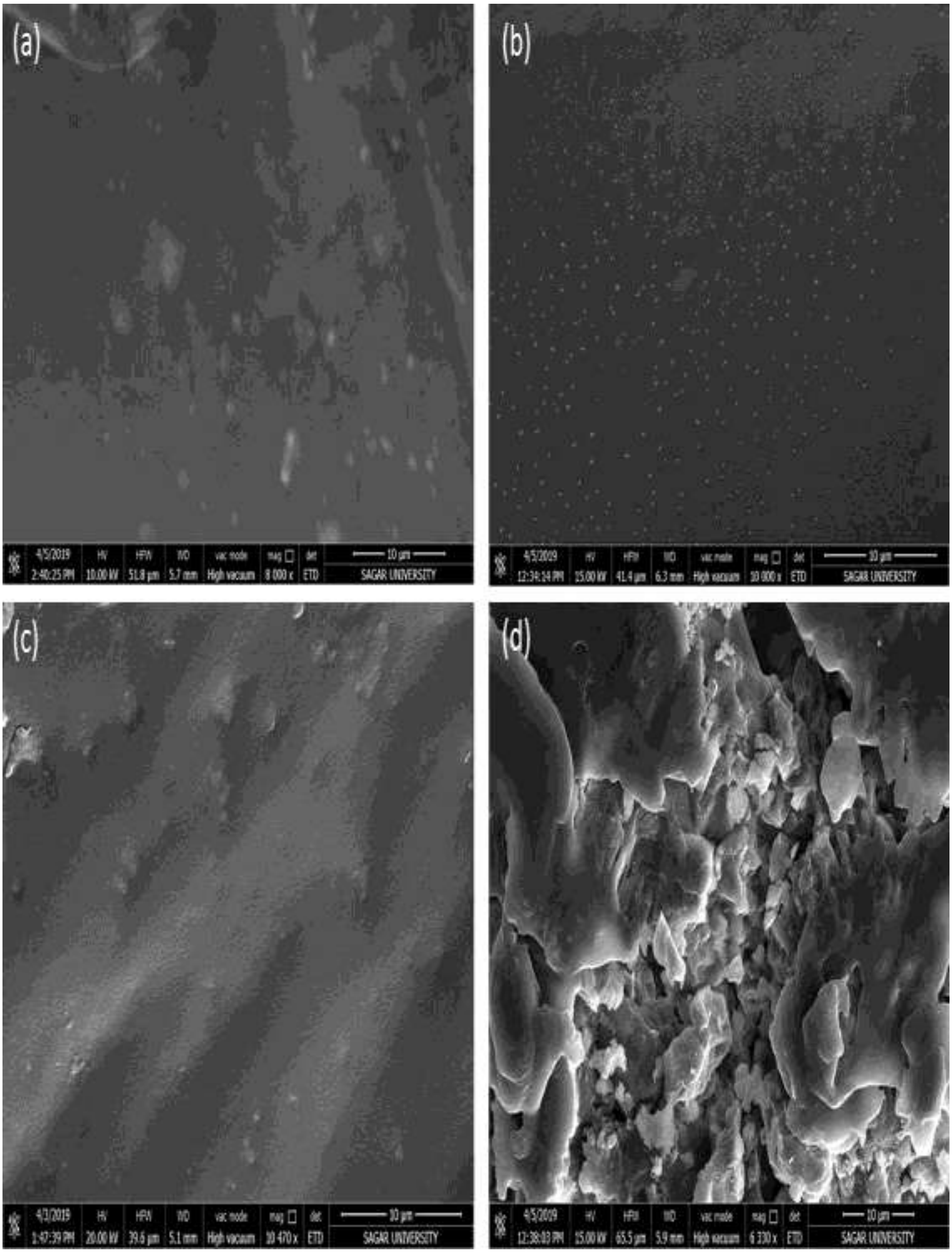

Figure 3.4: SEM images of (a)1LDPMB showing LDPE as small white dots in modified bitumen (b) 3LDPMB having smooth microstructure (c) 5LDPMB showing uniform dispersion of LDPE in modified bitumen (d) 7LDPMB showing coagulation of large swollen particles of LDPE

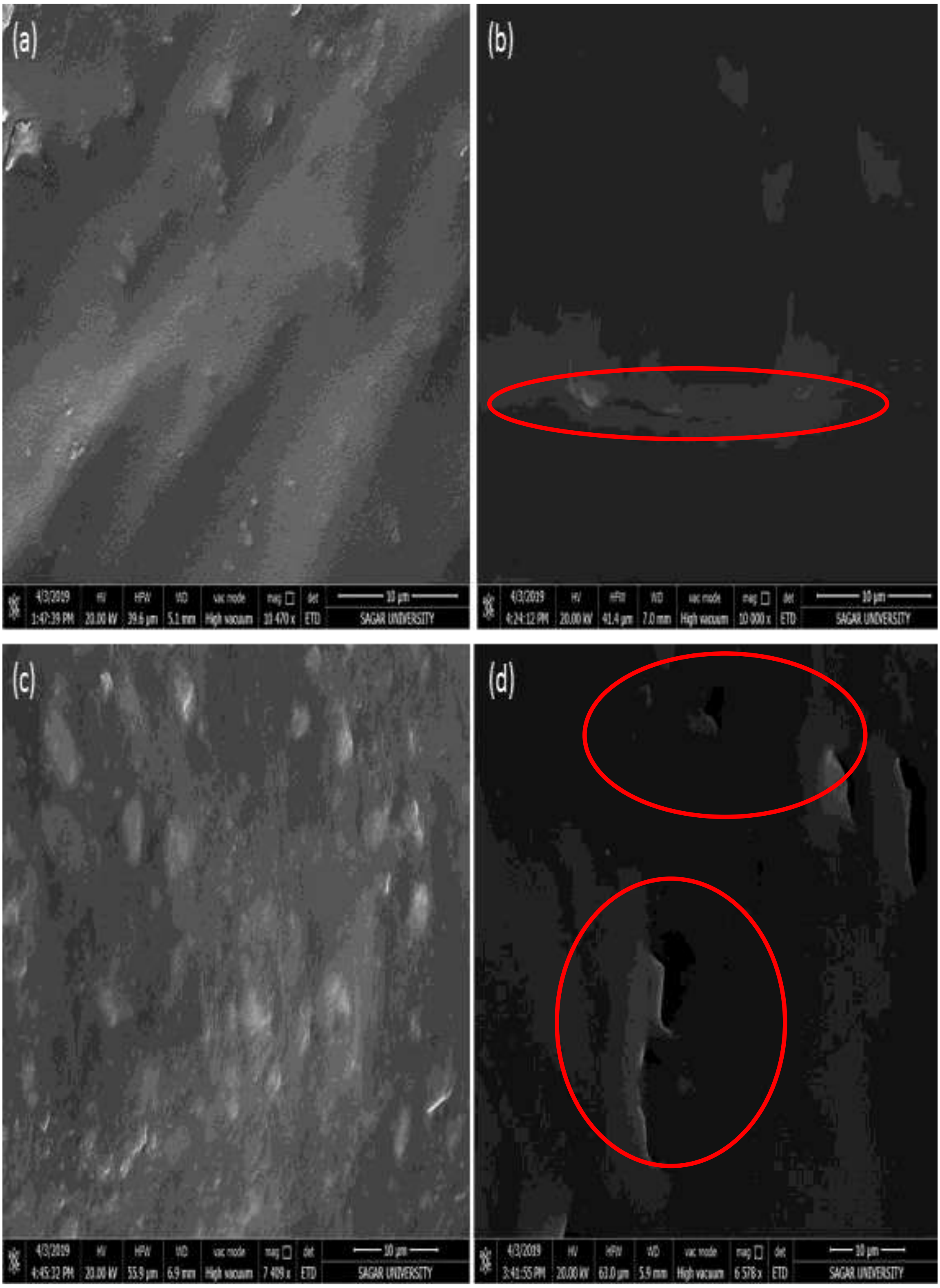

Figure 3.5: SEM images (a) 5LDPMB having uniform dispersion of LDPE (b) 5LDPMB at pH 5.0 showing cracks on the surface of modified bitumen(c) 5LDPMB at pH 7.0 having non uniform dispersion of LDPE(d) 5LDPMB at pH 9.0 showing holes on the surface of modified bitumen

3.6 Fourier Transform Infra-Red analysis (FTIR) of LDPMB

IR analysis of bitumen and LDPE modified bitumen samples was conducted in order to find the changes in functional groups of bitumen, after modification with LDPE. Figure 3.6 (a), (b) shows IR spectra of bitumen and LDPE respectively and Table 3.3 incorporates important IR peak positions of bitumen and LDPE.

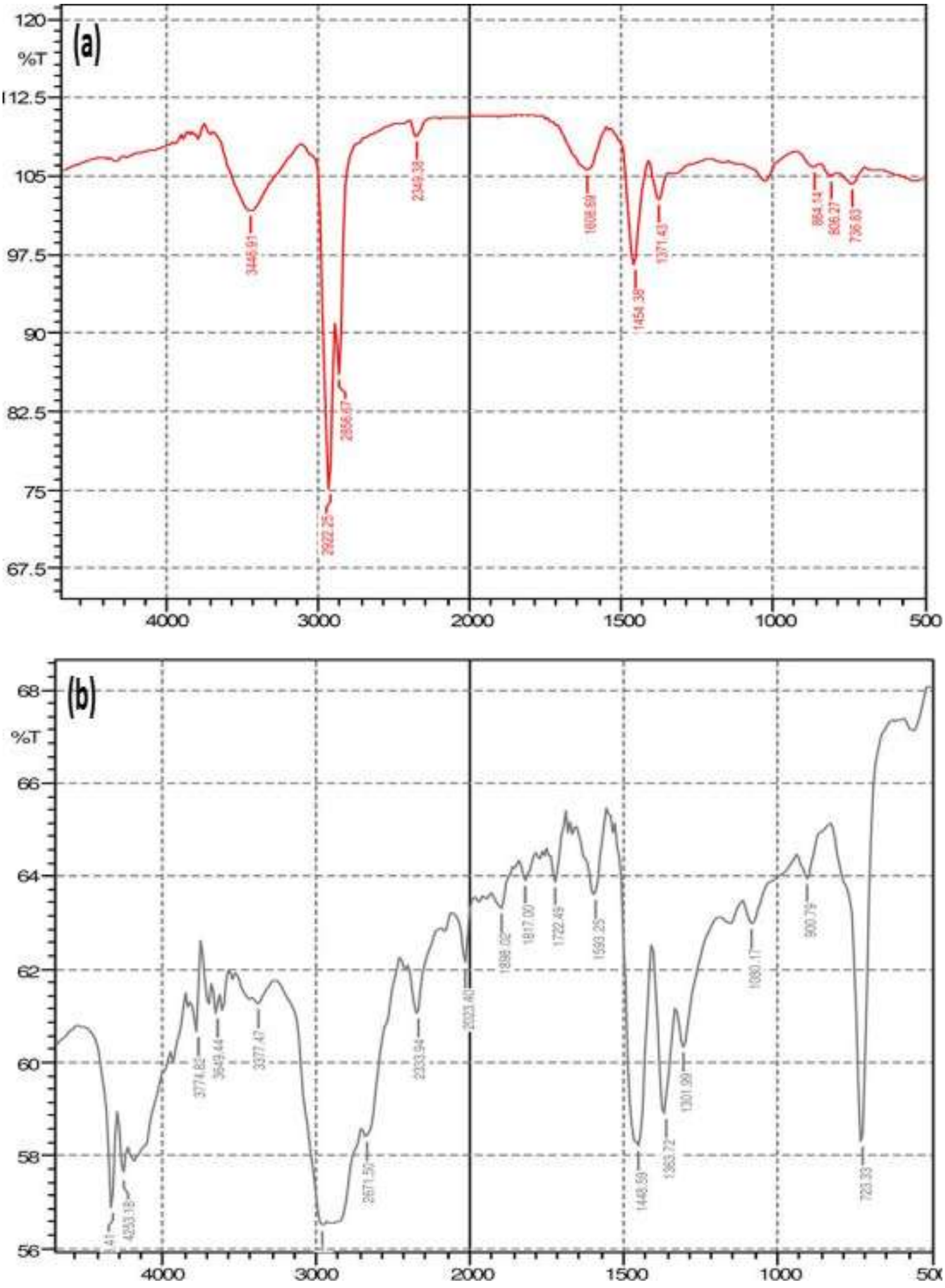

Figure 3.6: IR spectrum of (a) Bitumen (b) LDPE

Table 3.3 - IR peak positions of bitumen and LDPE

Functional group	Wave Number (cm^{-1})	
	Bitumen	LDPE
C-H aromatic / aliphatic stretching	2922, 2856	2956
N-H bending	1608	-
C=C aromatic stretching	1454	-
$-CH_2$ bending	-	1448
C=S / S=O stretching	1371	-
C-H of CH_3 bending	864, 806	1363

IR spectra of VG-30 bitumen shows peaks at 2922 cm^{-1} and 2856 cm^{-1} which correspond to C-H aromatic / aliphatic stretching, peak at 1608 cm^{-1} correspond to N-H bending, peak at 1454 cm^{-1} is due to C=C aromatic stretching, 1371 cm^{-1}correspond to C=S or S=O stretching, peaks at 864 cm^{-1} and 806 cm^{-1} indicates C-H bending mode of $–CH_3$ group respectively. In case of IR spectrum of LDPE peak at 2956 cm^{-1} correspond to C-H aromatic / aliphatic stretching, peak at 1448 cm^{-1} belong to $–CH_2$ bending, peak at 1363 cm^{-1} correspond to C-H of CH_3 bending (Table 3.3). Figure 3.7 (a), (b) shows IR spectrum of 1LDPMB and 3LDPMB respectively and Figure 3.8(a), (b) shows IR spectrum of 5LDPMB and 7LDPMB respectively.

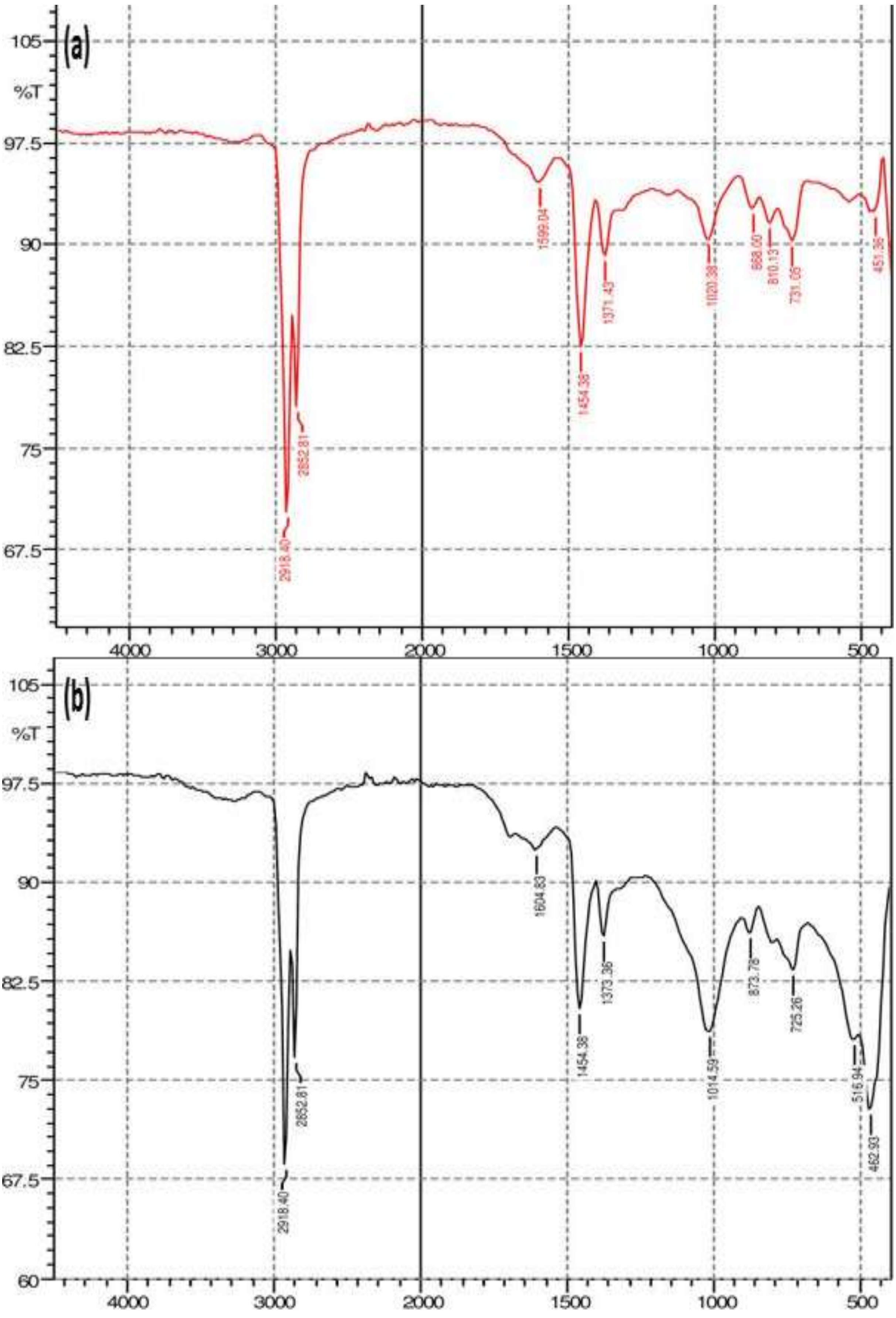

Figure 3.7: IR spectrum of (a) ILDPMB and (b) 3LDPMB

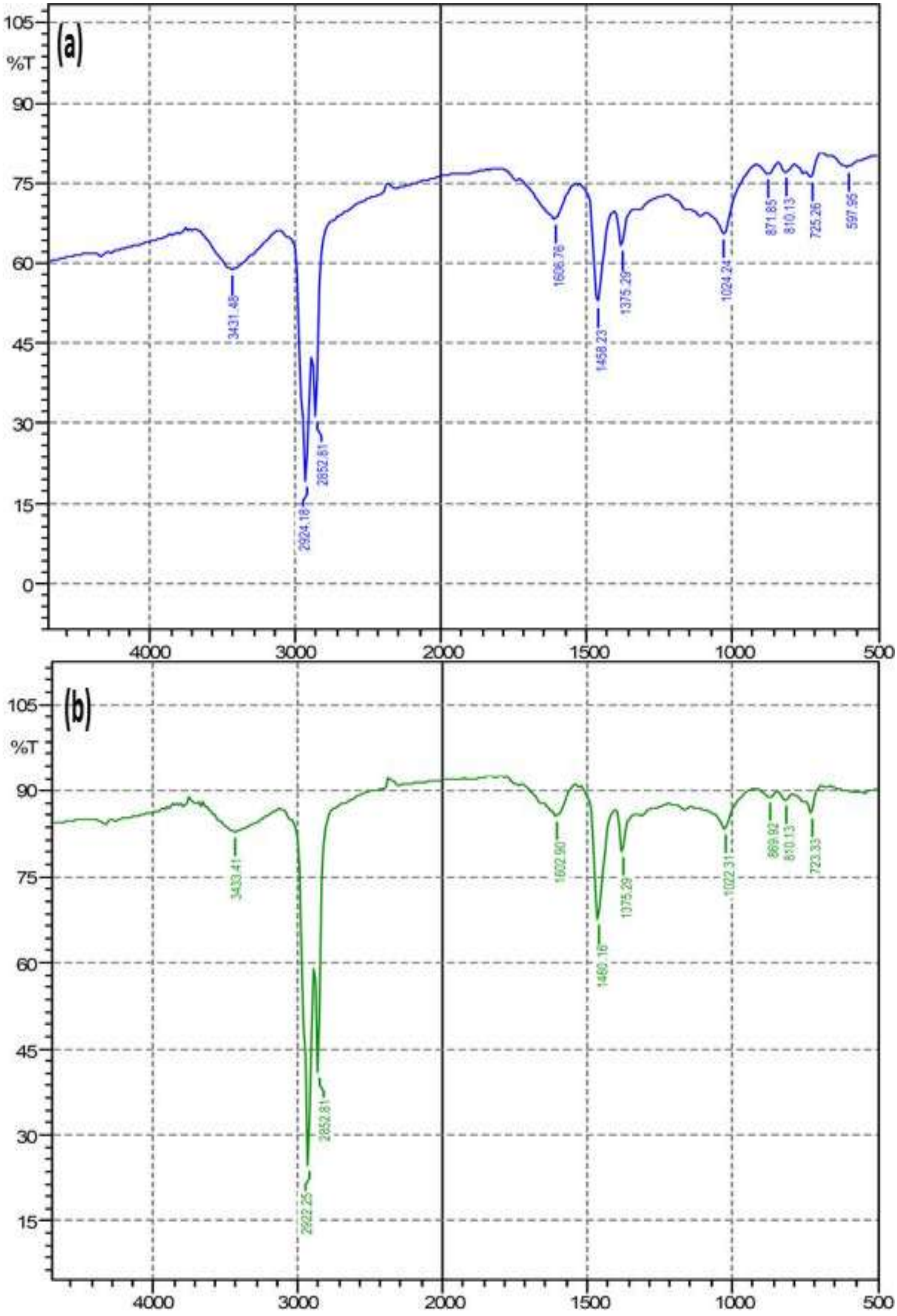

Figure 3.8: IR spectrum of (a) 5LDPMB (b) 7LDPMB

Table 3.4 – IR peak positions of bitumen and different compositions of LDPMB

Functional group	Wave Number (cm^{-1})				
	Bitumen	**1LDPMB**	**3LDPMB**	**5LDPMB**	**7LDPMB**
C-H aliphatic / aromatic stretching	2922, 2856	2918, 2852	2918, 2852	2924, 2852	2922, 2852
N-H bending	1608	1599	1604	1606	1602
C=C aromatic stretching	1454	1454	1454	1458	1460
C=S / S=O stretching	1371	1371	1373	1375	1375
C-H of –(CH_3)- bending	864, 806	868, 810	873	871, 810	869, 810

Table 3.4 incorporates important IR peak positions of bitumen and different compositions of LDPMB. The IR spectrum of bitumen is compared with different compositions of LDPE modified bitumen. A small to no shift in diiferent peaks of IR spectrum was obtained. The peak of 2856 cm^{-1} shifts to 2852 cm^{-1} indicate interaction of C-H bond of bitumen and of LDPE for all compositions of LDPMB. Peak at 2922 cm^{-1} have low to no shifts for all composition of LDPMB. Peak at 1608 cm^{-1} shifts to 1599 cm^{-1}, 1604 cm^{-1} , 1606 cm^{-1} and 1602 cm^{-1} after respective 1.0%, 3.0%, 5.0% and 7.0% mixing of LDPE in bitumen. The peak at 1454 cm^{-1} remain unchanged for 1.0% and 3.0% mixing of LDPE by mass, but shifts to 1458 cm^{-1} and 1460 cm^{-1} after unifom mixing of 5.0% and 7.0% LDPE by mass of bitumen, indicating low to no effect on this peak after mixing. The peak at 1371 cm^{-1} remain unchanged for 1.0%, shifts to 1373 cm^{-1} for 3.0% and to 1375 cm^{-1} for modified bitumen by 5.0% and 7.0% mixing of LDPE in bitumen. The peak at 864 cm^{-1} that corresponds to C-H bending band shifts to 868 cm^{-1}, 873 cm^{-1}, 871 cm^{-1} and 869 cm^{-1} after modification of bitumen by mixing of 1.0%, 3.0%, 5.0% and 7.0% LDPE respectively. Peak of 806

cm^{-1} shifts to 810 cm^{-1} for all the percent composition of LDPE. In FTIR spectrum of 1LDPMB, 3LDPMB, 5LDPMB, 7LDPMB no new peak is observed rather it is seen that the intensity of some of the peaks observed in bitumen enhances and there is broadening of C-H peaks in the spectrum of these LDPE modified bitumen samples (Figure 3.7, 3.8). Moreover there is only slight change in frequency of peaks. No new functional group is observed through IR analysis. These observations give a clear cut interpretation that LDPE does not chemically react with bitumen. As LDPE is a non-polar polymer, its interaction with bitumen is a physical process where there is small physical attraction between LDPE and bitumen. Physical interaction between LDPE and bitumen resulted in enhancement in some of the basic physical and mechanical properties of bitumen.

3.7 Fourier Transform Infra-Red analysis (FTIR) of LDPMB at different pH

Figure 3.9 (a) and (b) shows IR spectrum of 3LDPMB and 3LDPMB at pH 5.0 respectively. Figure 3.10 (a) and (b) shows IR spectrum of 3LDPMB at pH 7.0 and 3LDPMB at pH 9.0 respectively.

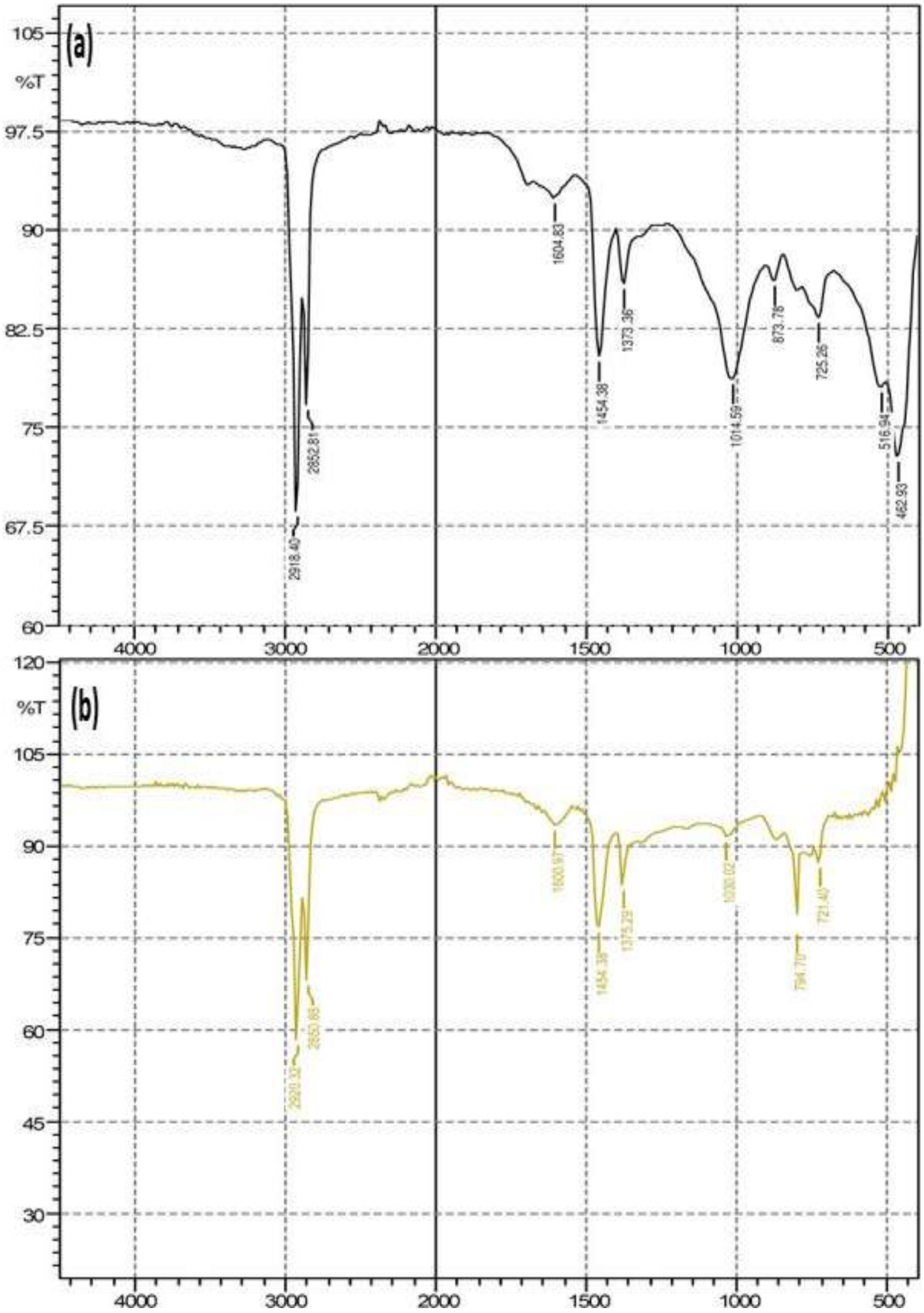

Figure 3.9: IR spectrum of (a) 3LDPMB and (b) 3LDPMB at pH 5.0

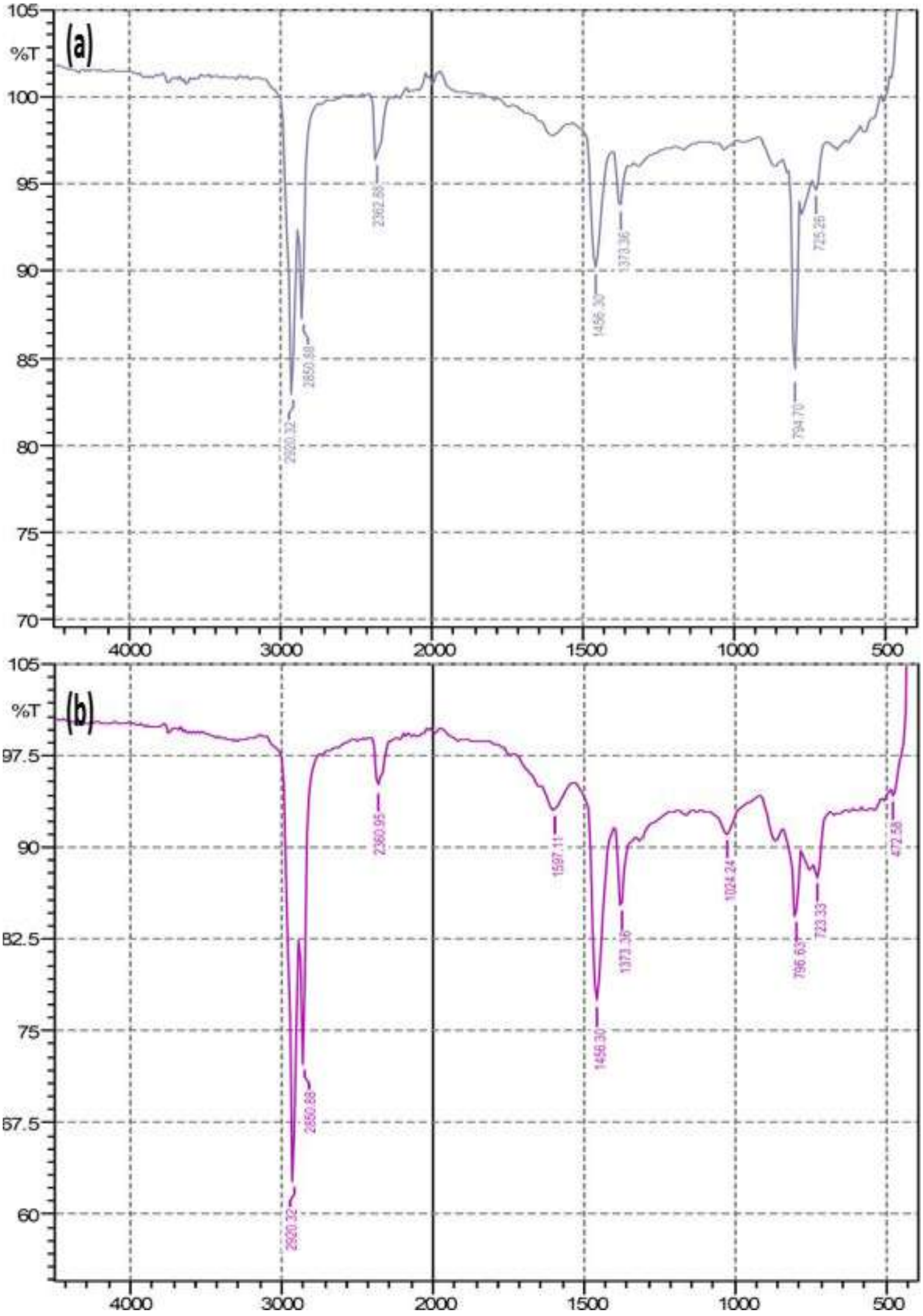

Figure 3.10: IR spectrum of (a) 3LDPMB at pH 7.0 and (b) 3LDPMB at pH 9.0

Table 3.5: IR peak positions of 3LDPMB at different pH

Functional group	**Wave Number (cm^{-1})**				
	Bitumen	**3LDPMB**	**3LDPMB at pH 5.0**	**3LDPMB at pH 7.0**	**3LDPMB at pH 9.0**
C-H aromatic/ aliphatic stretching	2922, 2856	2918, 2852	2920, 2850	2920, 2850	2920, 2850
N-H bending	1608	1604	1600	1606	1597
C=C aromatic stretching	1454	1454	1454	1456	1456
C=S / S=O stretching	1371	1373	1375	1373	1373
C-H of CH_3 bending	864, 806	873	794	794	796

Table 3.5 shows IR peak positions of 3LDPMB and 3LDPMB kept at pH of 5.0, 7.0 and 9.0. The IR spectrum of 3LDPMB at different pH is compared with IR of 3LDPMB. The peak of 2918 cm^{-1} shifts to 2920 cm^{-1} at all the selected pH range. Peak of 2852 cm^{-1} shifts to 2850 cm^{-1} at the selected pH range. Peak of 1604 cm^{-1} shift to 1600 cm^{-1} at pH 5.0, shifts to 1606 cm^{-1} at pH 7.0 and shifts to 1597 cm^{-1} at pH 9.0, shows weakening of N-H (bending band) bond strength in acidic and basic medium. Peak of 1454 cm^{-1} remains unchanged at pH 5.0 and mildly shifts to 1456 cm^{-1} at pH 7.0 and pH 9.0. Peak at 1373 cm^{-1} shift to 1375 cm^{-1} at pH 5.0 and remain unchanged at pH 7.0 and 9.0. Peak of 873 cm^{-1} shift to 794 cm^{-1} at pH 5.0, pH 7.0 and shifts to 796 cm^{-1} at pH 9.0, shows weakening of C-H bond strength. Figure 3.11 (a) and (b) shows IR spectrum of 5LDPMB and 5LDPMB at pH 5.0 respectively. Figure 3.12(a) and (b) shows IR spectrum of 5LDPMB at pH 7.0 and 5LDPMB at pH 9.0 respectively.

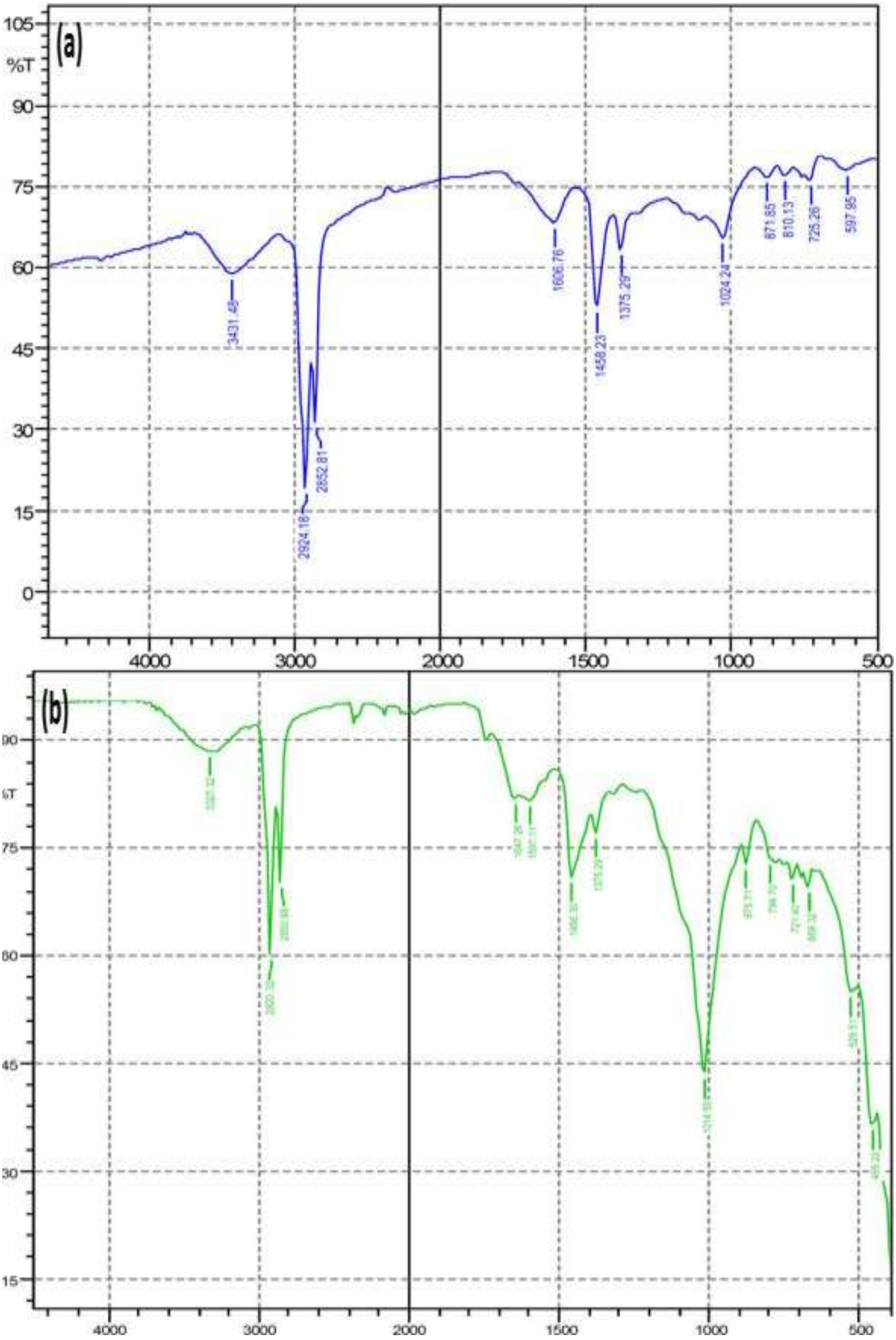

Figure 3.11: IR spectrum of (a) 5LDPMB (b) 5LDPMB at pH 5.0

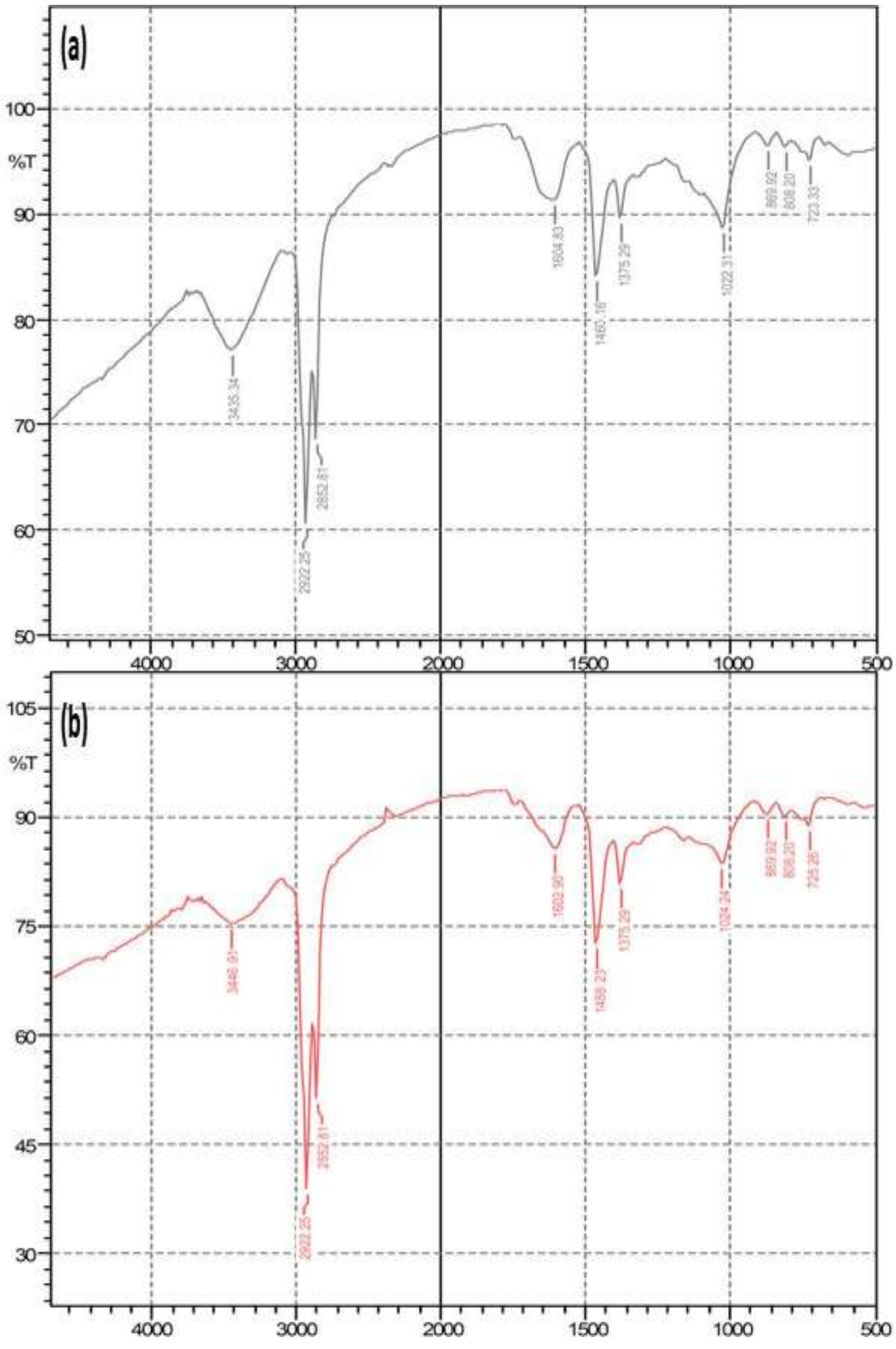

Figure 3.12: IR spectrum of (a) 5LDPMB at pH 7.0(b) 5LDPMB at pH 9.0

Table 3.6: IR peak positions of 5LDPMB at different pH

Functional group	**Wave Number (cm^{-1})**				
	Bitumen	**5LDPMB**	**5LDPMB at pH 5.0**	**5LDPMB at pH 7.0**	**5LDPMB at pH 9.0**
C-H aromatic / aliphatic stretching	2922, 2856	2924, 2852	2920, 2850	2922, 2852	2922, 2852
N-H bending	1608	1606	1597	1604	1602
C=C aromatic stretching	1454	1458	1456	1460	1458
C=S / S=O stretching	1371	1375	1375	1375	1375
C-H of CH_3 bending	864, 806	871, 810	875,794	869, 808	869, 808

Table 3.6 incorporates important IR peak positions of 5LDPMB and 5LDPMB kept at pH of 5.0, 7.0 and 9.0. The IR spectrum of 5LDPMB at different pH is compared with the IR of 5LDPMB. The peak at 2924 cm^{-1} (observed in 5LDPMB) shifts to 2920 cm^{-1} at pH 5.0 and 2922 cm^{-1} at pH 7.0 and 9.0 which shows slight weakening of bond strength in acidic and basic medium. Peak at 2852 cm^{-1} shift to 2850 cm^{-1} at pH 5.0 and remain unchanged at both pH of 7.0 and 9.0. Peak at 1606 cm^{-1} shift to 1597 cm^{-1} at pH 5.0, shifts to 1604 cm^{-1} at pH 7.0 and 1602 cm^{-1} at pH 9.0. Peak at 1458 cm^{-1} remains unchanged at pH 9.0 but shifts to 1456 cm^{-1} at pH 5.0 and 1460 cm^{-1} at pH 7.0. Peak at 1375 cm^{-1} remain unchanged at all the pH. Peak at 871 cm^{-1} shift to 875 cm^{-1} at pH 5.0, shifts to 869 cm^{-1} at pH 7.0 and 9.0. Peak at 810 cm^{-1} shift to 794 cm^{-1} at pH 5.0 and to 808 cm^{-1} at both the pH of 7.0 and 9.0. The changes are small enough to predict any new change by chemical forces. However, new peaks for O-H stretching bands use to be observed at pH 5.0, 7.0 and 9.0 indicating existence of water molecule in modified bitumen exposed to water. Figure 3.13(a) and (b) shows IR spectrum of 7LDPMB and 7LDPMB at pH 5.0 respectively. Figure 3.14(a) and (b) shows IR spectrum of 7LDPMB at pH 7.0 and 7LDPMB at pH 9.0 respectively.

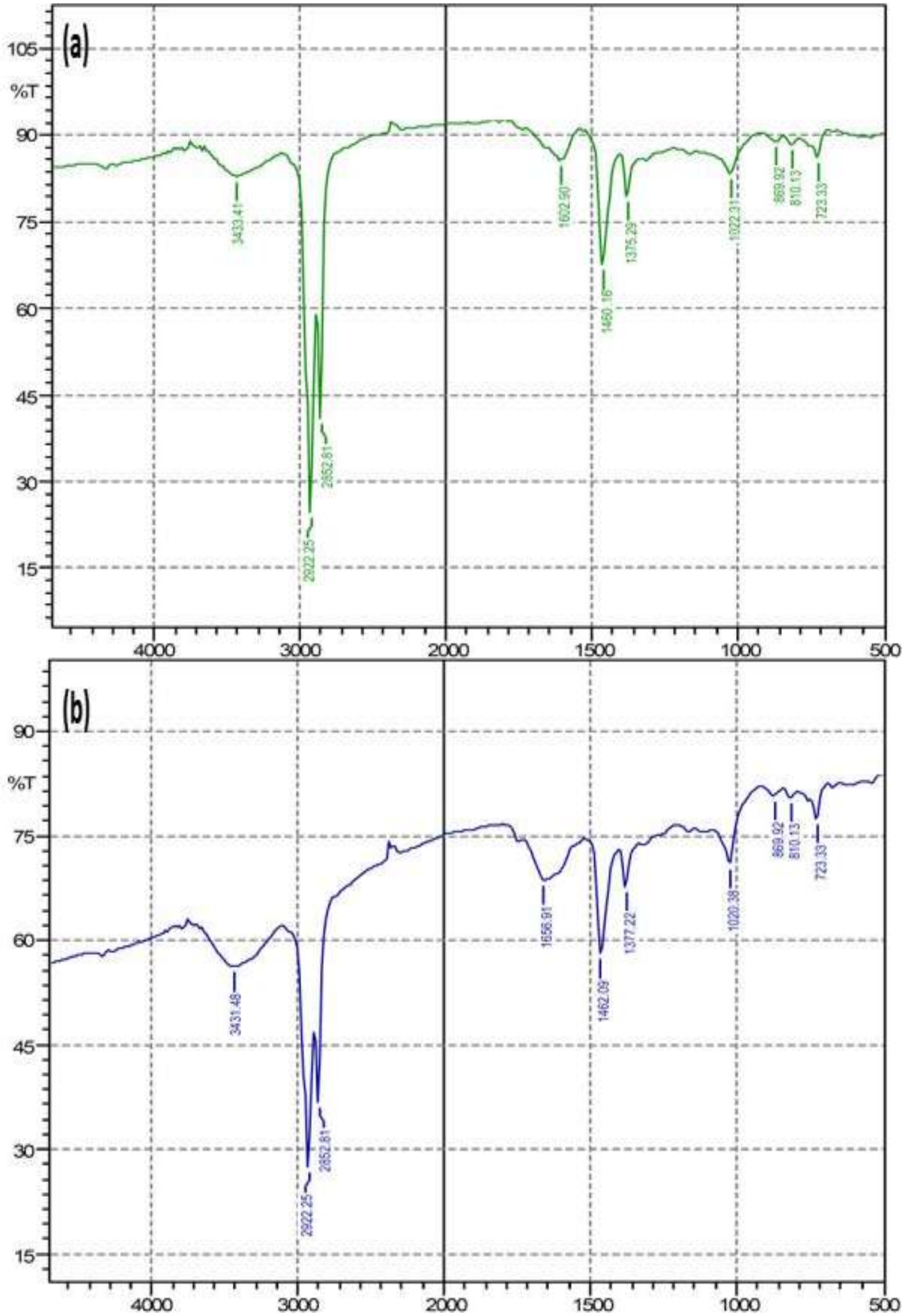

Figure 3.13: IR spectrum of (a) 7LDPMB (b) 7LDPMB at pH 5.0

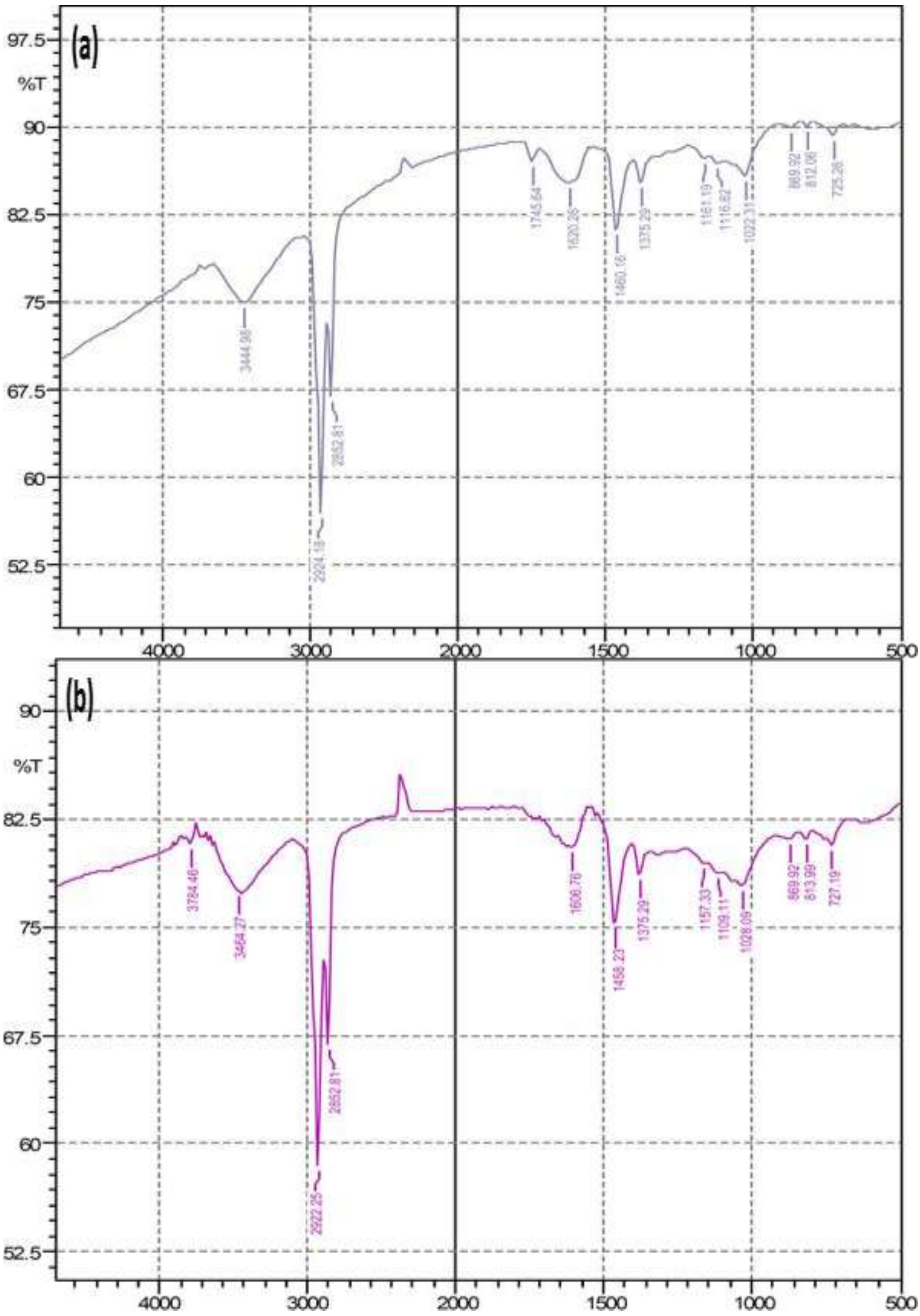

Figure 3.14: IR spectrum of (a) 7LDPMB at pH 7.0(b) 7LDPMB at pH 9.0

Table 3.7: IR peak positions of 7LDPMB at different pH

Functional group	**Wave Number (cm^{-1})**				
	Bitumen	**7LDPMB**	**7LDPMB at pH 5.0**	**7LDPMB at pH 7.0**	**7LDPMB at pH 9.0**
C-H aromatic / aliphatic stretching	2922, 2856	2922, 2852	2922, 2852	2924, 2852	2922, 2852
N-H bending	1608	1602	1656	1620	1606
C=C aromatic stretching	1454	1460	1462	1460	1458
C=S / S=O stretching	1371	1375	1377	1375	1375
C-H of CH_3 bending	864, 806	869, 810	869, 810	869, 812	869, 813

Table 3.7 shows IR peak positions of 7LDPMB and 7LDPMB kept at pH of 5.0, 7.0 and 9.0. The IR spectrum of 7LDPMB at different pH is compared with IR of 7LDPMB. The peak at 2922 cm^{-1} shifts to 2924 cm^{-1} at pH 7.0 and remain unchanged at both the pH of 5.0 and 9.0. Peak at 2852 cm^{-1} remain unchanged at all the selected pH range. Peak at 1602 cm^{-1} shift to 1656 cm^{-1} at pH 5.0, shifts to 1620 cm^{-1} at pH 7.0 and 1606 cm^{-1}at pH 9.0. Peak at 1460 cm^{-1} remain unchanged at pH 7.0 and have minor shift at pH 5.0 and pH 9.0. Peak at 1375 cm^{-1} doesn’t have any observable change at all the three pH. Peak at 869 cm^{-1} remain unchanged at all pH. Peak at 810 cm^{-1} remain unchanged at pH 5.0, shifts to 812 cm^{-1} at pH 7.0 and to 813 cm^{-1}at pH 9.0. Formation of new peak at around 3400 cm^{-1} is an indication of the presence of water in modified bitumen.

3.8 Thermo-gravimetric analysis of bitumen and LDPE modified bitumen

TGA analysis of bitumen and 5LDPMB was conducted. In case of LDPMB, 5.0% composition was chosen because this was the optimum concentration. The thermo-gram of bitumen clearly shows that bitumen decomposes in three steps. As per literature it is found that when the temperature is less than 350 °C there is decomposition of aromatics and saturates due to which bitumen loses its mass. At temperature greater than 350 °C but less than 500 °C asphaltene, resins and aromatics decomposes. When temperature exceeds 500 °C there is major decomposition of asphaltenes and few aromatics as well as resins (136). Figure 3.15 shows TGA plot of bitumen which indicates that major decomposition starts at 200 °C and ends at 500 °C with 79.83% weight loss i.e. from 7.45 mg to 1.20 mg. The residual mass is 10.23% i.e. 0.8 mg may be because of presence of some metal ions.

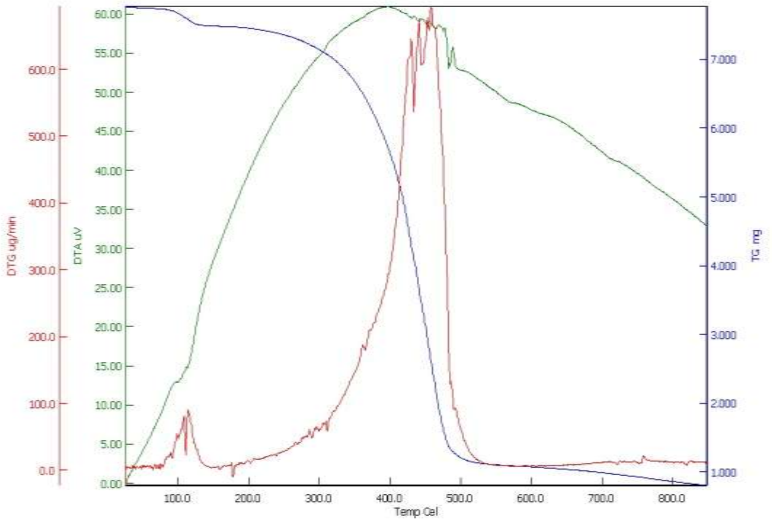

Figure 3.15: TGA plot of Bitumen

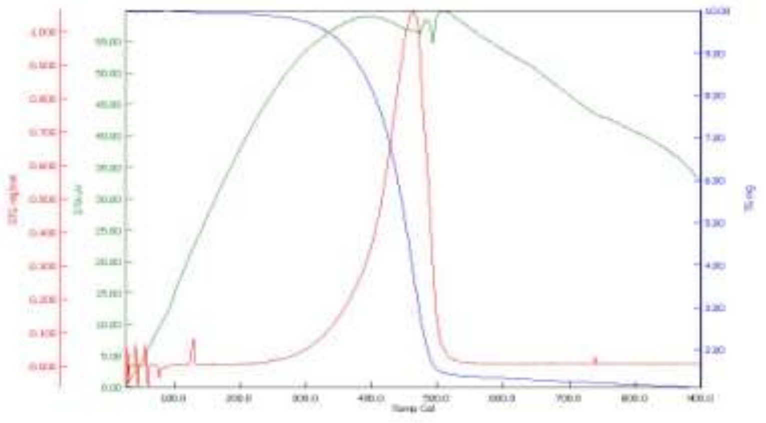

Figure 3.16: TGA plot of 5LDPMB

Figure 3.16 shows TGA plot of 5LDPMB which indicates that major decomposition starts at 265 °C and ends at 500 °C with 83.36%; weight loss from 9.85 mg to 1.52 mg. The residual mass 11.02% (1.1mg) is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 265 °C in case of 5LDPMB. This means thermal stability of bitumen increases after modification by LDPE.

3.9 Thermo-gravimetric analysis of 5LDPMB at different pH

Thermo-gravimetric analysis of 5LDPMB exposed to different environmental conditions i.e. pH 5.0, 7.0 and 9.0 was conducted. The purpose was to check the effect of pH on the thermodynamic stability of 5LDPMB.

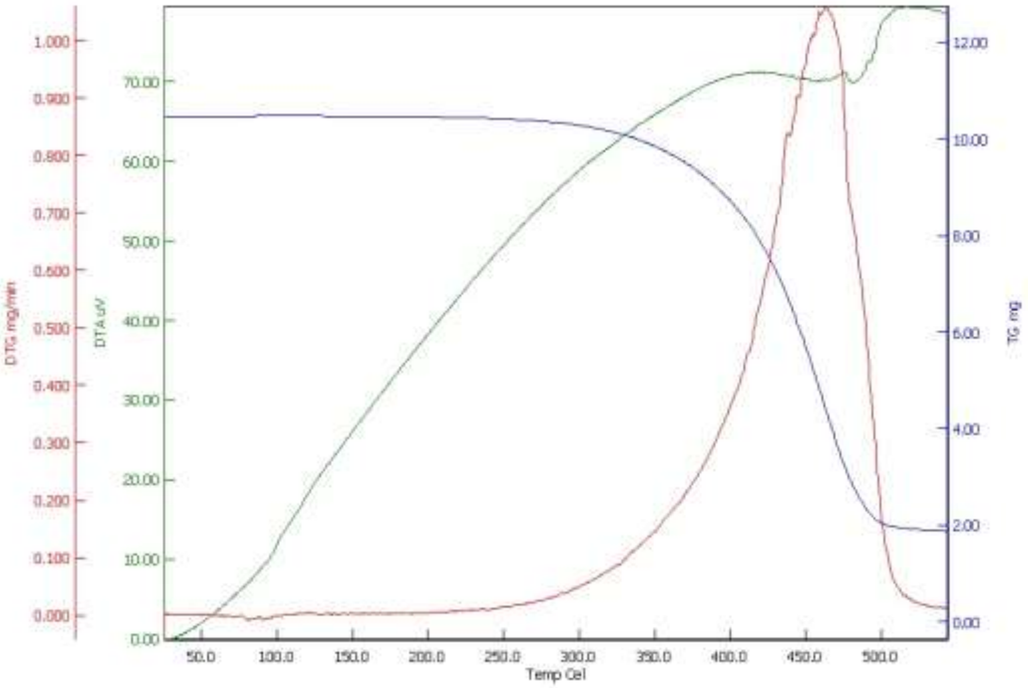

Figure 3.17: TGA plot of 5LDPMB at pH 5.0

Figure 3.17 shows TGA plot of 5LDPMB exposed to pH 5.0, which indicates that major decomposition starts at 338 °C and ends at 500 °C with 75.95% weight loss from 10.0 mg to 2.0 mg. The residual mass is 17.96% that corresponds to 1.88 mg, showing presence of inorganic ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 338 °C in case of LDPE modified bitumen which is kept at pH 5.0. Therefore it can be said that 5LDPMB exposed to pH 5.0 is thermally more stable than bitumen.

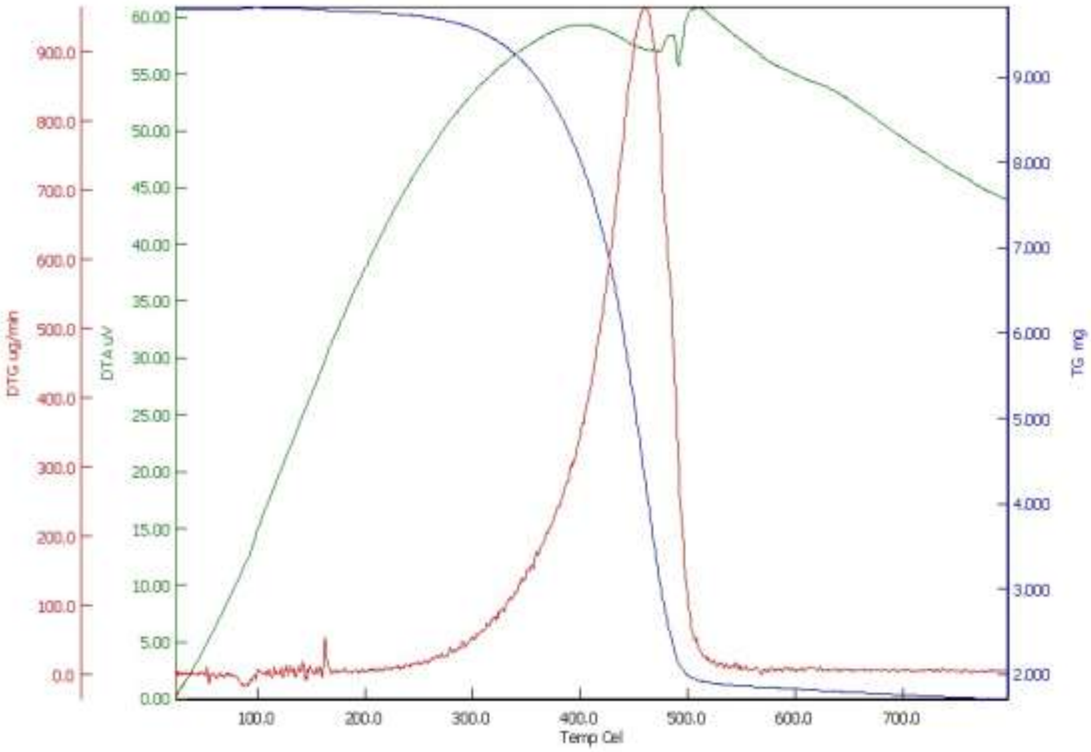

Figure 3.18: TGA plot of 5LDPMB at pH 7.0

Figure 3.18 shows TGA plot of 5LDPMB exposed to pH 7.0 which indicates that major decomposition starts at 265 °C and ends at 500 °C with 78.58% weight loss (from 9.69 mg to 1.99 mg). The residual mass 17.35% (1.7 mg) is due to presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C (in case of bitumen) to 265 °C (in case of 5LDPMB), which is kept at pH 7.0 thus depicting the enhancement in thermodynamic stability of 5LDPMB exposed to pH 7.0 as compare to bitumen.

Figure 3.19 shows TGA plot of 5LDPMB exposed to pH 9.0, which indicates that major decomposition starts at 276 °C and ends at 500 °C with 76.38% weight loss (from 11.50 mg to 2.58 mg). The residual mass 19.56% (2.28 mg) corresponds to presence of inorganic ions. The start of temperature decomposition has been increased from 200 °C (in case of bitumen) to 276 °C (in case of LDPE modified bitumen) when kept under water at pH 9.0 (maintained by 0.01M NaOH) thus showing the increase in thermodynamic stability of 5LDPMB exposed to pH 9.0 as compare to bitumen

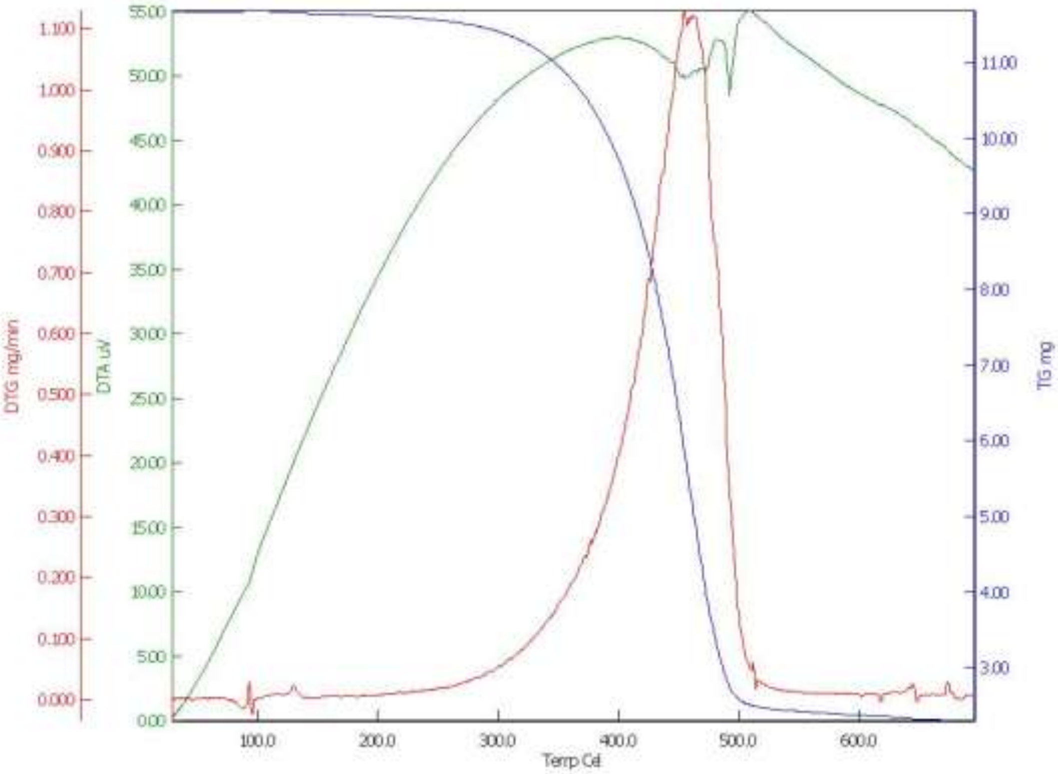

Figure 3.19: TGA plot of 5LDPMB at pH 9.0

Table 3.8 give brief analysis of TGA values of bitumen and LDPE modified bitumen which is exposed to differential environmental conditions of pH.

Table 3.8: TGA values of Bitumen, 5LDPMB and 5LDPMB kept at pH 5.0, 7.0 and 9.0

Step		T_i(^{0}C)	T_f(^{0}C)	Wt. Loss (%)
Bitumen	1.	86	125	2.58
	2.	200	500	79.83
	3.	500	848	5.14
5LDPMB	1.	265	500	83.36
	2.	500	900	4.25
5LDPMB pH 5.0	1.	338	500	75.95
	2.	500	544	1.59
5LDPMB pH 7.0	1.	265	500	78.58
	2.	500	798	2.92
5LDPMB pH 9.0	1.	276	500	76.38
	2.	500	696	2.5

3.10 Conclusion

There is enhancement in physical, mechanical properties of bitumen after modification with LDPE. SEM analyses of the water logged LDPE modified bitumen surface was analyzed, cracks/ holes on the surface of modified bitumen were obtained. To obtain the reason behind these damages on the surface of the LDPE modified bitumen, IR spectra of uniform quantity of bitumen/ LDPE modified bitumen (pellets by mixing 1.0 mg of bitumen / LDPMB with 3.0 mg of KBr) was taken and compared. The important peaks for the expected functional groups are shown in Table (3.3-3.7). The expected functional groups are N-H, C-H, C-C, C=C, C=S etc. The unusual high intensity of the peaks in between 2850-3000 cm^{-1} in the spectrum of bitumen is worth of analyzing. In almost all of the cases this region is known for the sp^2 or sp^3 C-H stretching band, which is very weak in nature. The high intensity of such peaks indicates high polarity in C-H stretching band. This highly polar C-H stretching band has the tendency to interact with electronegative element like oxygen of H_2O/ H_3O^+/ OH^-. There was no remarkable change in the IR spectrum of LDPE modified bitumen as compared to unmodified bitumen. Only decrease in C-H stretching band was observed for the modified bitumen at pH 5.0 and pH 9.0 that indicates interaction of acidic or basic water with the polar C-H band of bitumen. TGA values clearly indicate that on moving from bitumen to LDPE modified bitumen, the temperature of major decomposition shift towards a higher value. This is a positive outcome, because LDPE modified bitumen shows greater thermodynamic stability as compare to unmodified bitumen. When this modified bitumen is exposed to different pH (5.0, 7.0 and 9.0), again the TGA values indicate shifting of major decomposition temperature towards higher side thus confirming that pH has no effect on thermodynamic stability of LDPE modified bitumen. Thus it can be concluded that LDPE modified bitumen is not resistant to pH variations but it is thermodynamically more stable than bitumen.

CHAPTER 4

HDPE BASED MODIFICATION OF BITUMEN: FINDING OPTIMUM RATIO AND DETERMINING CHANGE IN PHYSICOCHEMICAL PROPERTIES

Different methods were adopted for preparation of modified bitumen by using HDPE as modifier. Mainly three types of variation were studied: a) operating temperature of mixing b) effect of stirring rate and c) variation in composition of HDPE. Bitumen samples used in this research were modified by HDPE and exposed to different mediums (of pH 5.0, 7.0 and 9.0), maintained by adding HCl or NaOH to double distilled water. The samples were characterized for properties like Penetration point, Softening point, Ductility and analyzed by Scanning electron microscopy, Fourier Transform Infra-Red spectroscopy and Thermo-gravimetric analysis techniques**.**

4.1 Penetration Point

Penetration point is one of the basic physical property of bitumen which gives information about the hardness or softness of bitumen. This property depends on intermolecular forces of attraction between molecules of bitumen. With strong intermolecular forces of attraction, harder bitumen use to form. Table 4.1 summarized the result of penetration point for the bitumen and different compositions of HDPMB.

Table 4.1 - Penetration point test results for bitumen and HDPMB

% of HDPE in bitumen	Penetration point of HDPMB at 25 °C (dmm)	Penetration point of HDPMB at 35 °C (dmm)	Penetration point of HDPMB at 45 °C (dmm)
0	68	69	70
1	52	57	61
3	43	45	48
5	41	43	46
7	40	43	44

First objective of the research is to study the effect of temperature variation on physical properties of bitumen. So, penetration point of bitumen and HDPE modified bitumen at three different temperatures (25 °C, 35 °C and 45 °C) was determined. Figure 4.1 represents the variation of penetration point test for the bitumen and HDPE modified bitumen samples versus various percentages of HDPE. Table 4.1 indicates that penetration point of bitumen is 68 dmm which is in the acceptable range of VG-30 bitumen. Results of penetration test shows that the penetration value of bitumen decreases after the addition of HDPE and it further decreases with the increase in the percentage of HDPE (see Figure 4.1). This shows that hardness of bitumen enhances after the modification with HDPE. There is sharp decrease in penetration value from 68 dmm for bitumen to 52 dmm and 43 dmm for 1.0% and 3.0% mixing of HDPE by mass of bitumen.

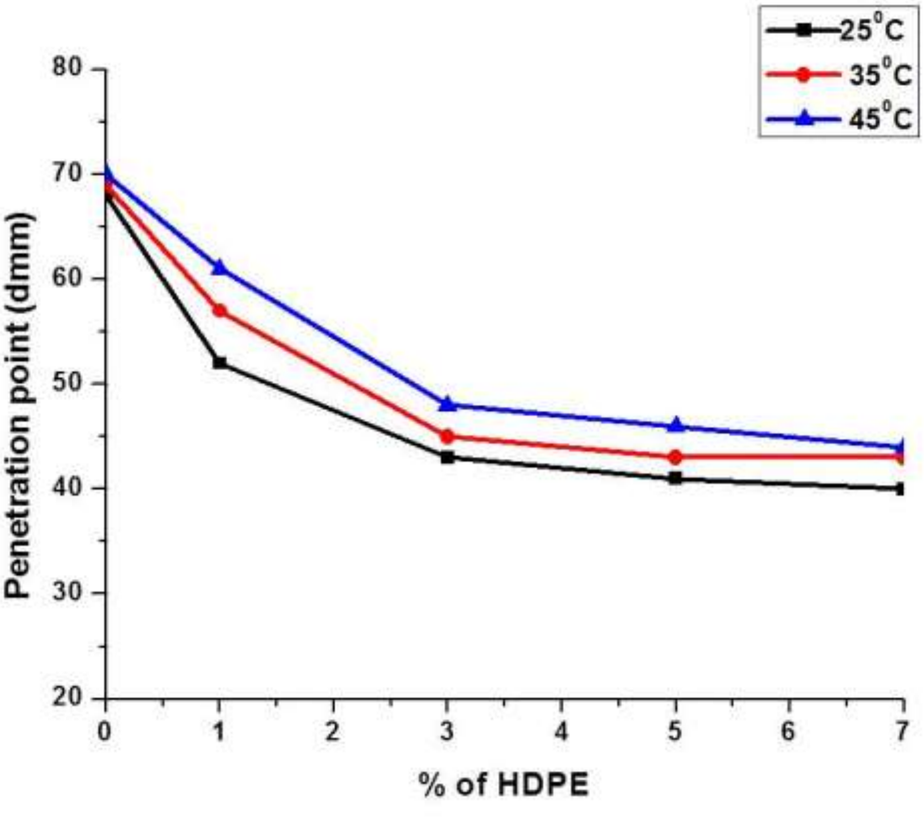

Figure 4.1: Penetration point of HDPMB versus % of HDPE at different temperatures

So bitumen becomes harder with the modification of HDPE. For high mass percentage of HDPE (5.0% and 7.0%) the penetration value for HDPMB falls up to 41 dmm and 40 dmm respectively. Also it is seen that the penetration value increases with the increase in temperature. However, for particular temperature, as compared to unmodified bitumen, the modified bitumen samples have low penetration. For example, at 45 ºC, the penetration value is decreased by 37% for HDPMB as compare to bitumen. Overall, these results show that with the incorporation of HDPE the hardness and stiffness of the bitumen increases, which in turn leads to the enhancement in the resistance of modified bitumen towards permanent deformation, rutting at moderate and high temperatures. Due to this improvement in the hardness, the road constructed using HDPE modified bitumen can resist the penetration in comparison to the road build from bitumen and therefore, increases the longevity of the road.

4.2 Softening point

Softening point is also basic physical property of bitumen which depends on intermolecular forces of attraction between molecules of bitumen. If the intermolecular forces of attraction are weak, then the bitumen samples will have low softening point and vice versa. Softening point of bitumen and HDPE modified bitumen samples was determined with the help of ring and ball apparatus. Table 4.2 summarized the result of softening point and ductility test for the bitumen and different compositions of HDPE modified bitumen samples.

Table 4.2 – Softening point and ductility test results for bitumen and HDPMB

Sr. No.	**% of HDPE in bitumen**	**Softening point (°C) of HDPMB**	**Ductility(cm) of HDPMB**
1.	0	48	76
2.	1	52	68
3.	3	55	58
4.	5	58	39
5.	7	63	37

Softening point of bitumen is 48 °C. The results of softening point clearly indicate that softening point of bitumen increases after modification with HDPE and it further increases with the increase in the percentage of HDPE. As the softening point increases, bitumen becomes less temperature susceptible. This implies that bitumen becomes resistant towards the effect of heat and it will not soften at high temperature. Such modified bitumen can be successfully used in areas with hotter climatic conditions. Figure 4.2 represents the variation in softening point of HDPMB versus different percentages of HDPE. At 1.0% mixing of HDPE, the increase in softening point is very less that is 8.3%. With the increase in percentage of mixing of HDPE to 3.0%, the rise in softening point becomes 14.6% for HDPMB. At 5.0% mixing of HDPE, the rise in softening point is 20.8%. Softening point increases by 31.2% in case of HDPMB at 7.0% mixing of HDPE by mass of bitumen.

4.3 Ductility test

Ductility of bitumen is a mechanical property which is measure of cohesive strength of bitumen and depends on intermolecular forces of attraction. The bitumen sample will be more ductile if the intermolecular forces of attraction are strong and vice versa. Ductility values of bitumen and HDPE modified bitumen samples were determined with the help of ductility testing machine. Table 4.2 summarized the result of ductility test for the bitumen and HDPE modified bitumen samples. It is clear from Table 4.2 that ductility of bitumen is 76 cm. Ductility of bitumen decreases after the modification with HDPE and with the increase in concentration of HDPE. Ductility of HDPMB decreases by 10.5% for 1.0% mixing of HDPE by mass of bitumen. Decrease in ductility of bitumen is justified because stiffness of bitumen enhances after the modification with HDPE. For HDPE, ductility decreases by 23.7% at 3.0% mixing and then it falls below the minimum required value (40cm). This means bitumen cannot be modified with HDPE beyond 3.0% concentration otherwise modified bitumen will have very low value of ductility. Bitumen which is having very low value of ductility will not act as a good binder because it will not be able to bind the aggregates properly. Hence, HDPMB having greater than 3% of HDPE by mass of bitumen will have poor performance in the pavement, hence should not be used. Therefore 3.0% HDPE by mass of bitumen is the ideal or optimum concentration for the modification of VG-30 bitumen. Figure 4.3 shows the variation in ductility values for the bitumen and HDPE modified bitumen samples versus different percentages of HDPE.

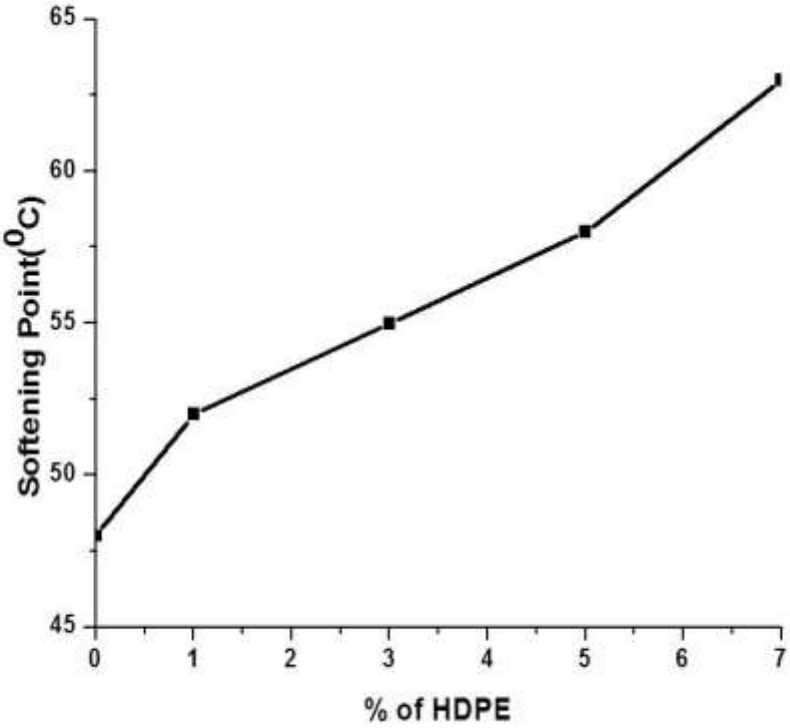

Figure 4.2: Softening point of HDPMB with % of HDPE

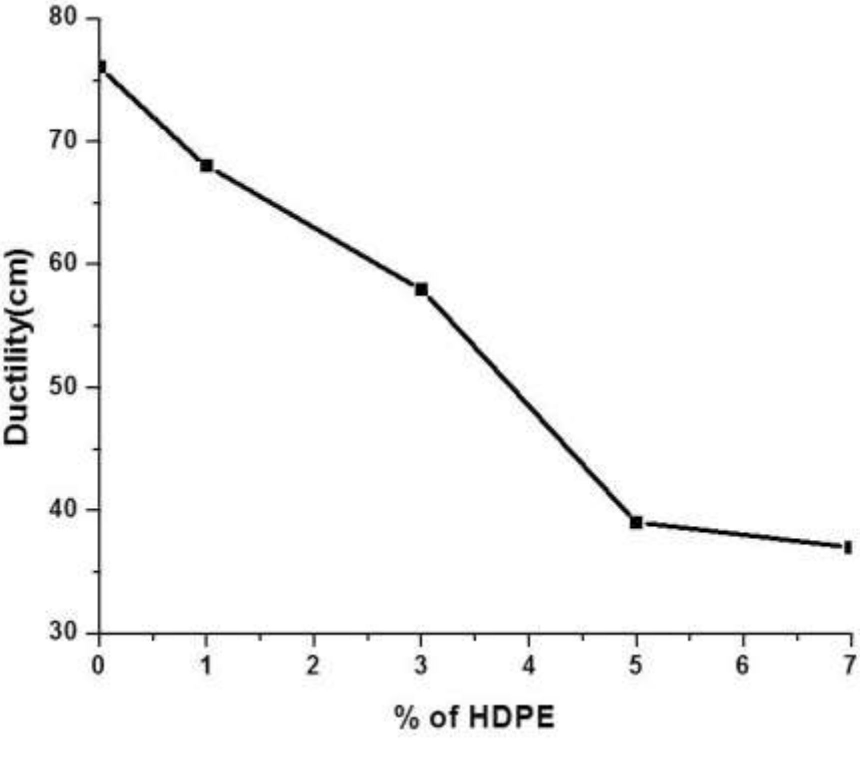

Figure 4.3: Ductility of HDPMB with % of HDPE

4.4 Scanning Electron Microscopy (SEM) analysis of HDPE modified bitumen

SEM images of neat bitumen and different compositions of HDPE modified bitumen are shown in the Figure 4.4. Bitumen, itself is black in color, and doped HDPE is obtained in white patches. The images clearly suggest that with the increase in the percentage of HDPE in bitumen, white area is increasing and coming closure. After 3.0% composition of HDPE, the polyethenes are accumulated and ruptured the surface of bitumen that clearly indicates, higher dosage of HDPE are dangerous for road making industry. Lower dosage of HDPE in modified bitumen is although shown to be uniformly distributed, but their amount is very-very less for making any change in the properties of the bitumen.

4.5 SEM analysis of HDPE modified Bitumen at different pH

Once the SEM analysis of bitumen and different compositions of HDPE modified bitumen was conducted, similar analysis was performed for modified bitumen samples which were exposed to different environmental conditions of pH for a particular time interval. As from the ductility test results, it was clear that 3.0% HDPE was the optimum percentage for bitumen modification. So this was the concentration used to study the effect of pH using SEM analysis. There is difference in pH of water worldwide; it may vary from slightly acidic to slightly alkaline. So this was necessary to find the effect of different type of pH on the surface of HDPE modified bitumen. The effect of acidic water logging was seen on the HDPE modified bitumen surface by dipping the modified bitumen sample into acidic water of pH 5.0 for 24 hr and then the morphology of the sample was tested using SEM technique. SEM clearly indicates crack on the surface of the HDPE modified bitumen (Figure 4.5). Even after modification with HDPE crack remains there, means modification with HDPE is not enough against the problem of damage caused by water logging on roads. Similarly, tests were performed for checking effect of neutral water and of basic water by dipping HDPE modified bitumen in distilled water of pH around 7.0 and dipping in alkaline water of pH 9.0 respectively. The surface morphology of these samples indicates, the formation of many and large holes, which itself explain the condition of roads after exposure of roads to alkaline water. Modification with HDPE has given no such solution against the water logging problem. This means HDPE modified bitumen samples are not resistant to pH variations occurring in the environment. SEM images of different compositions of HDPMB in various pH are shown in the Figure 4.5.

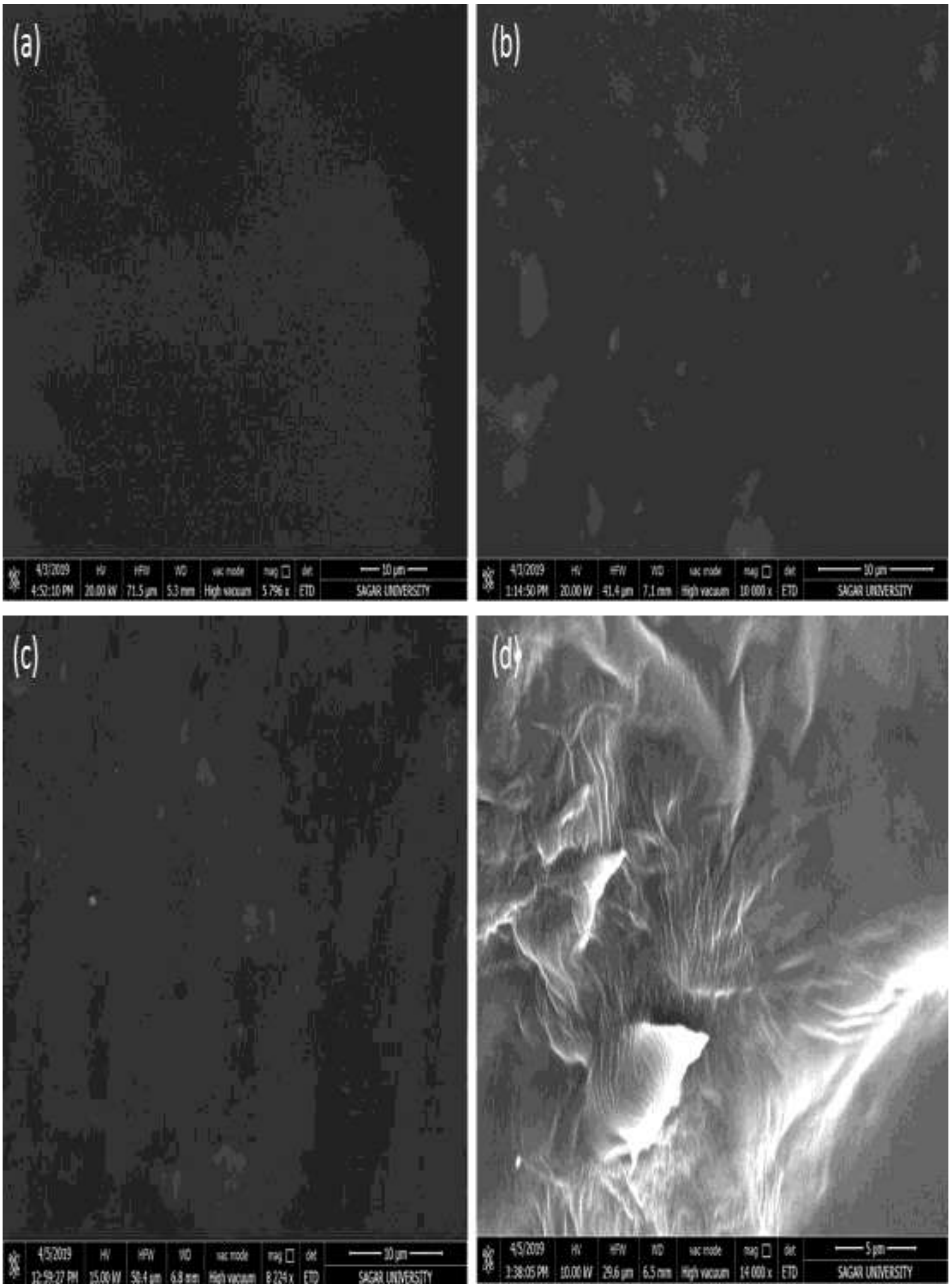

Figure 4.4: SEM images of (a) Bitumen having smooth, uniform black surface
(b) 3HDPMB showing uniform dispersion of HDPE in modified bitumen
(c) 5HDPMB having coagulation of HDPE in modified bitumen
(d) 7HDPMB showing polymer rich phase at high %

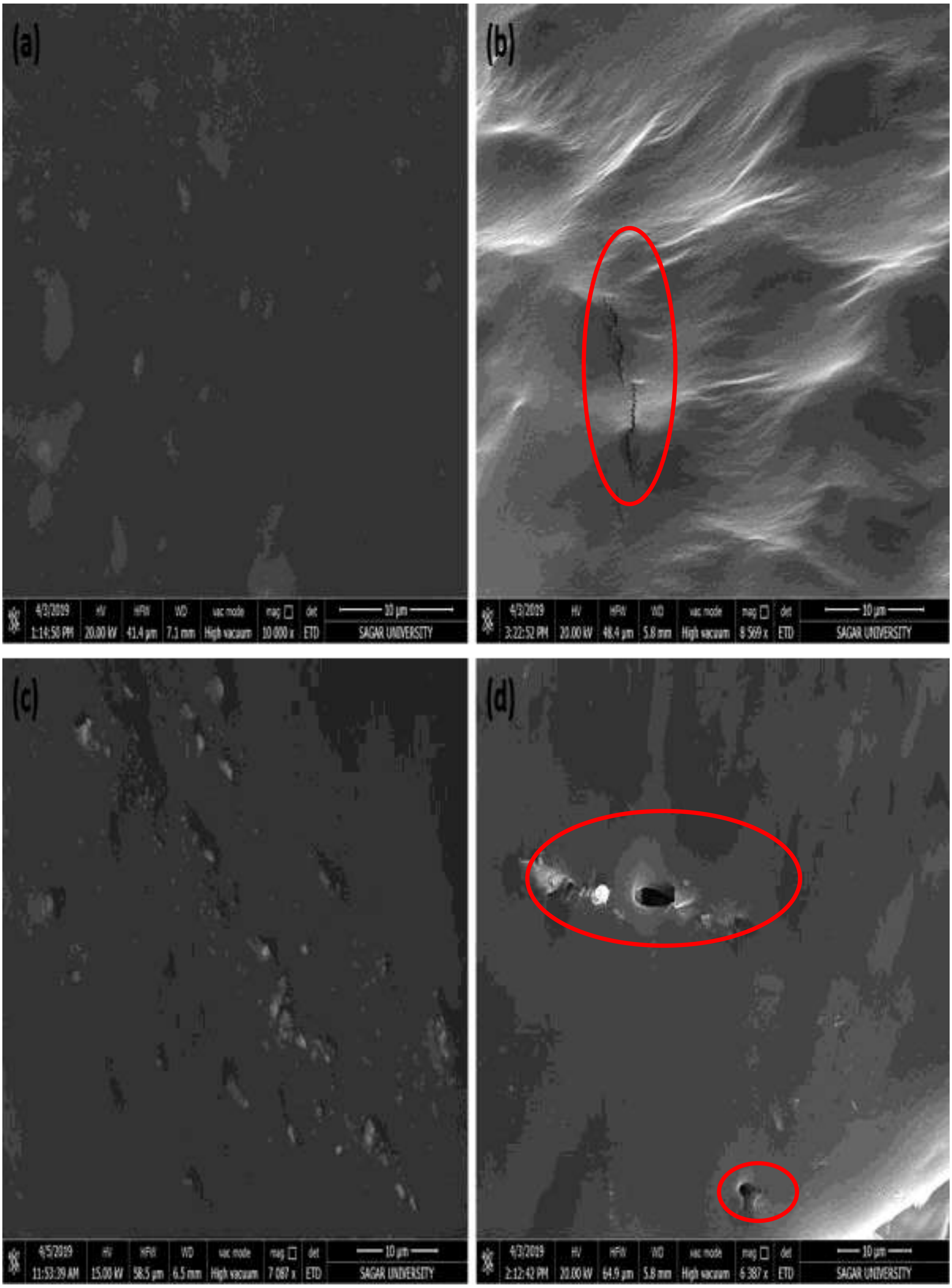

Figure 4.5: SEM images of (a) 3HDPMB having uniform dispersion of HDPE (b) 3HDPMB at pH 5.0 having crack on the surface of modified bitumen (c) 3HDPMB at pH 7.0 showing coagulated HDPE particles on the surface (d) 3HDPMB at pH 9.0 having holes on the surface of modified bitumen

4.6 Fourier Transform Infra Red analysis (FTIR) of HDPMB

IR analysis of bitumen and different compositions of HDPE modified bitumen samples was conducted in order to find the changes in functional groups of bitumen after modification with HDPE. Figure 4.6 (a), (b) shows IR spectra of bitumen and HDPE respectively.

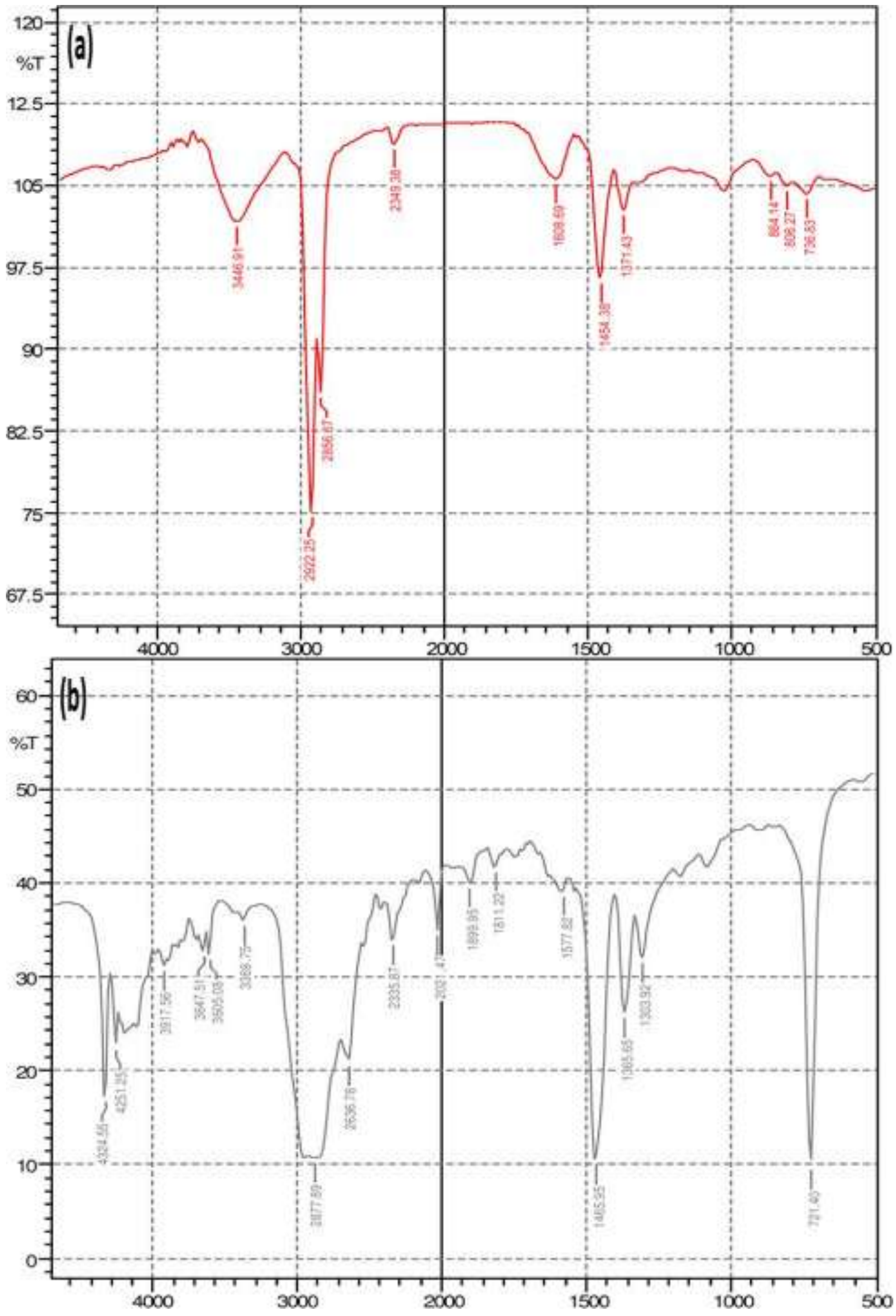

Figure 4.6: IR spectrum of (a) Bitumen (b) HDPE

Table 4.3 - IR peak positions of bitumen and HDPE

Functional group	**Wave Number (cm^{-1})**	
	Bitumen	**HDPE**
C-H aliphatic / aromatic stretching	2922, 2856	2877
N-H bending	1608	-
C=C aromatic stretching	1454	-
$–CH_2$ bending	-	1465
C=S / S=O stretching	1371	-
C-H of CH_3 bending	-	1365
C-H of $–(CH_3)$ bending	864, 806	-

Table 4.3 incorporates important IR peak positions of bitumen and HDPE. IR spectra of VG-30 bitumen shows peaks at 2922 cm^{-1} and 2856 cm^{-1} which correspond to C-H aromatic / aliphatic stretching, peak at 1608 cm^{-1} correspond to N-H bending, peak at 1454 cm^{-1} is due to C=C aromatic stretching, 1371 cm^{-1} correspond to C=S or S=O stretching, peaks at 864 cm^{-1}, 806 cm^{-1} indicates C-H bending mode of $–CH_3$ group. In case of IR spectrum of HDPE peak at 2877 cm^{-1} correspond to C-H aromatic/ aliphatic stretching. Peak at 1465 cm^{-1} belong to $–CH_2$ bending and peak at 1365 cm^{-1} correspond to C-H of CH_3 bending. Figure 4.7 (a), (b) shows important peak positions of IR spectrum of 1HDPMB and 3HDPMB respectively and Figure 4.8 (a), (b) shows important peak positions of IR spectrum of 5HDPMB and 7HDPMB respectively.

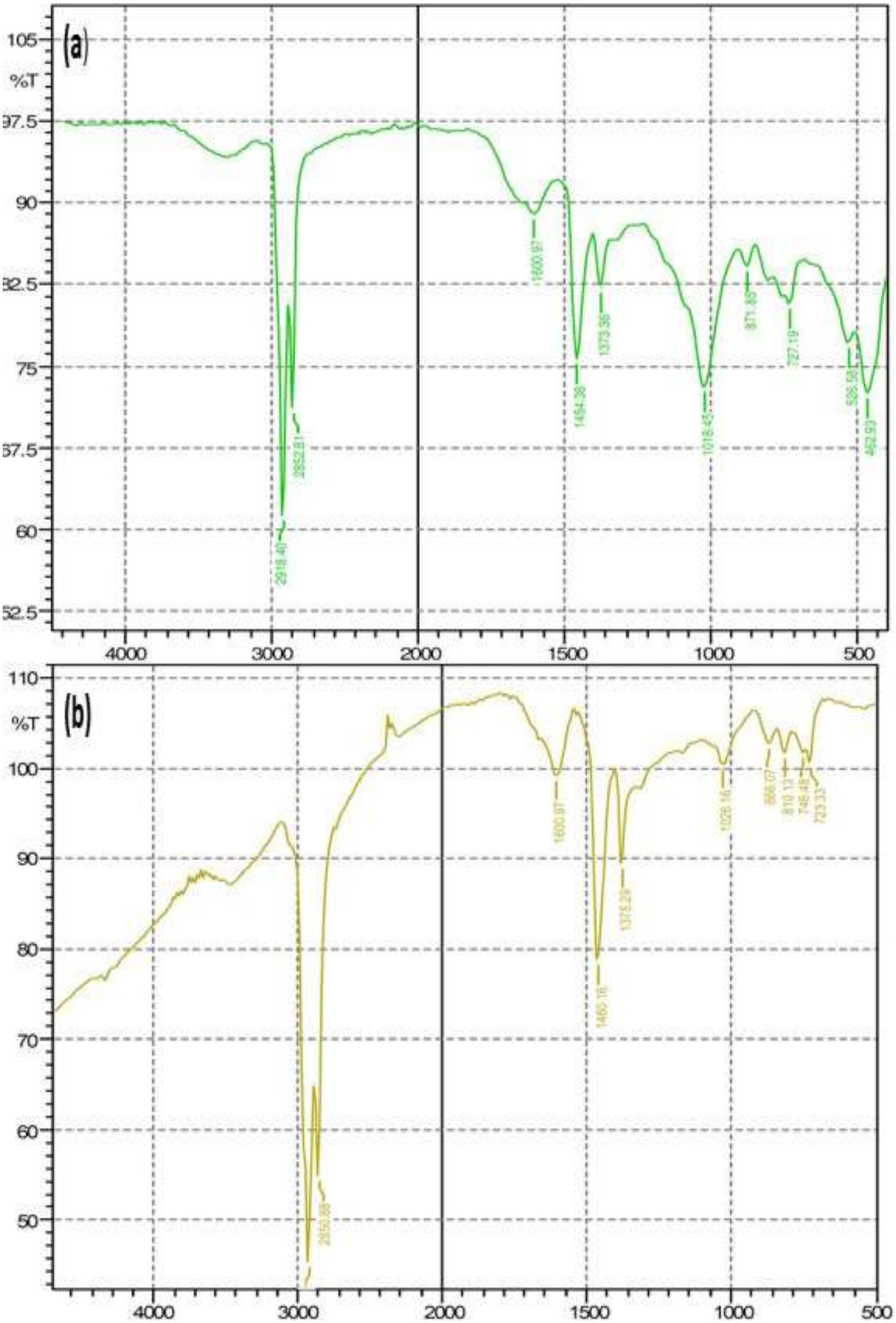

Figure 4.7: IR spectrum of (a) 1HDPMB (b) 3HDPMB

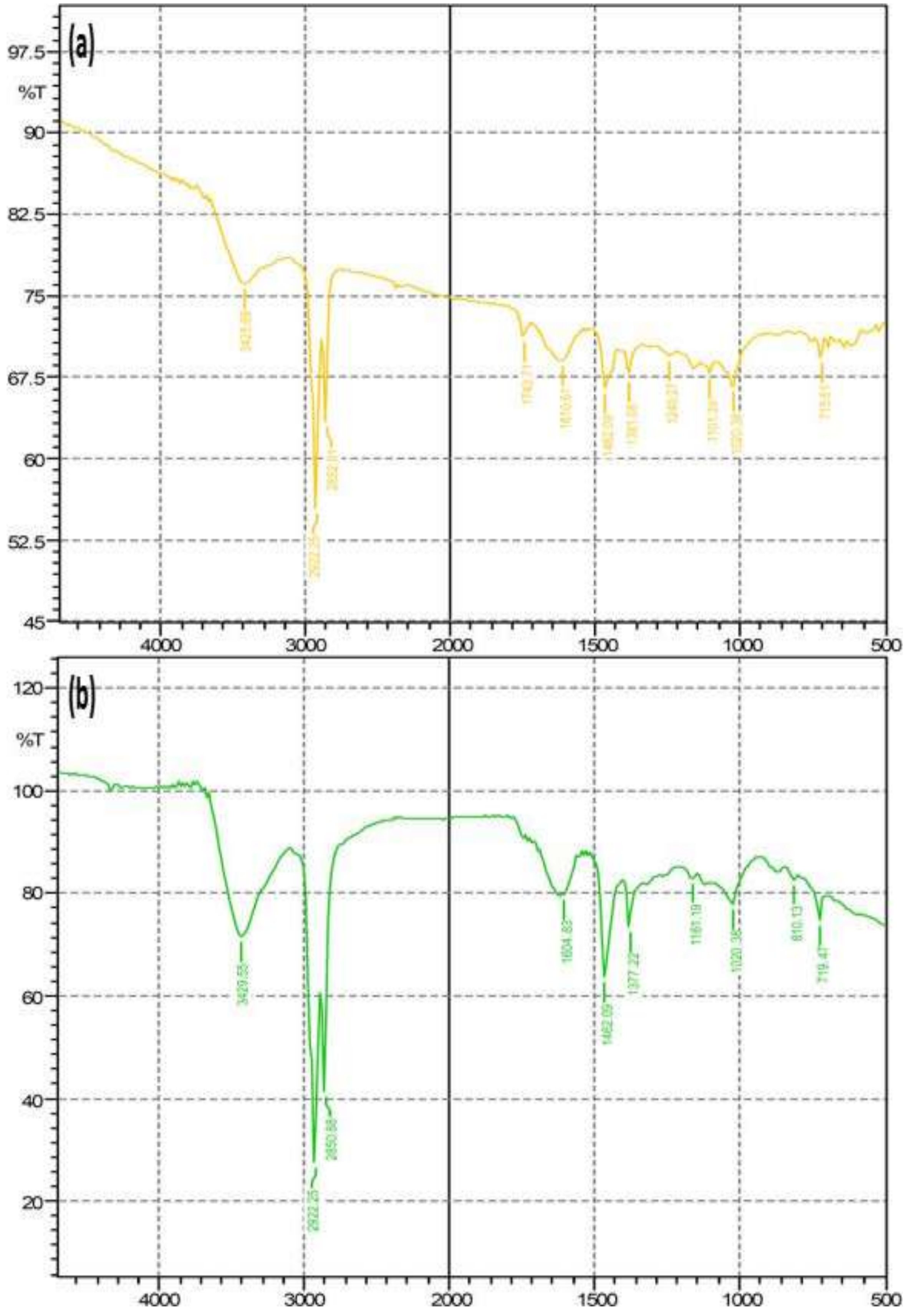

Figure 4.8: IR spectrum of (a) 5 HDPMB (b) 7HDPMB

Table 4.4: IR peak positions of bitumen and different compositions of HDPMB

Functional group	**Wave Number (cm^{-1})**				
	Bitumen	**1HDPMB**	**3HDPMB**	**5HDPMB**	**7HDPMB**
C-H aromatic / aliphatic stretching	2922, 2856	2918, 2852	2922, 2850	2922, 2852	2922, 2850
N-H bending	1608	1600	1600	1610	1604
C=C aromatic stretching	1454	1454	1460	1462	1462
C=S / S=O stretching	1371	1373	1375	1381	1377
C-H of CH_3 bending	864, 806	871	866, 810	-	810

Table 4.4 incorporates important IR peak positions of bitumen and different compositions of HDPMB. The IR spectrum of bitumen is compared with different compositions of HDPE modified bitumen (Table 4.4). A small to no shift in diiferent peaks of IR spectrum was obtained. Peak at 2856cm^{-1} shifts to 2852 cm^{-1} for 1.0% and 5.0%, 2850 cm^{-1} for 3.0% and 7.0% mixing of HDPE, this shift indicates interaction of C-H bond of bitumen and HDPE. Peak at 2922 cm^{-1} have low to no shifts for all composition of bitumen. Peak at 1608 cm^{-1} shifts to 1600 cm^{-1} for both 1.0% and 3.0% mixing and to 1610 cm^{-1} and 1604 cm^{-1} after respective mixing of 5.0% and 7.0% HDPE by mass in bitumen. The peak at 1454 cm^{-1} remain unchanged for 1.0% mixing of HDPE by mass, but shifts to 1460 cm^{-1} for 3.0% and 1462 cm^{-1} by unifom mixing of 5% and 7% HDPE by mass of bitumen indicating low to no effect on this peak after mixing.The peak at 1371 cm^{-1} shifts to 1373 cm^{-1}, 1375 cm^{-1}, 1381 cm^{-1} and 1377 cm^{-1} after modification of bitumen by mixing of 1.0%, 3.0%, 5.0% and 7.0% HDPE respectively.The peak at 864 cm^{-1} that corresponds to C-H bending band shifts to 871 cm^{-1}, 866 cm^{-1}, 871 cm^{-1} and 869 cm^{-1} after modification of bitumen by

mixing of 1.0%, 3.0%, 5.0% and 7.0% HDPE respectively.Peak at 806 cm^{-1} shifts to 810 cm^{-1} for 3.0% and 7.0% concentrations.

In FTIR spectrum of 1HDPMB, 3HDPMB, 5HDPMB and 7HDPMB no new peak is observed rather it is seen that the intensity of some of the peaks observed in bitumen enhances and there is broadening of C-H peaks in the spectrum of the HDPE modified bitumen. Moreover, there is only slight change in frequency of peaks. No new functional group is observed through IR analysis. These observations give a clear cut interpretation that HDPE does not chemically react with bitumen. As HDPE is a non-polar polymer, its interaction with bitumen is a physical process where there is small physical attraction between HDPE and bitumen. Physical interaction between HDPE and bitumen may result in enhancement in some of the basic physical and mechanical properties of bitumen.

4.7 Fourier Transform Infra Red analysis (FTIR) of HDPMB at different pH

Figure 4.9 (a), (b) shows IR spectrum of 3HDPMB and 3HDPMB at pH 5.0 respectively. Figure 4.10 (a), (b) shows IR spectrum of 3HDPMB at pH 7.0 and 3HDPMB at pH 9.0 respectively.

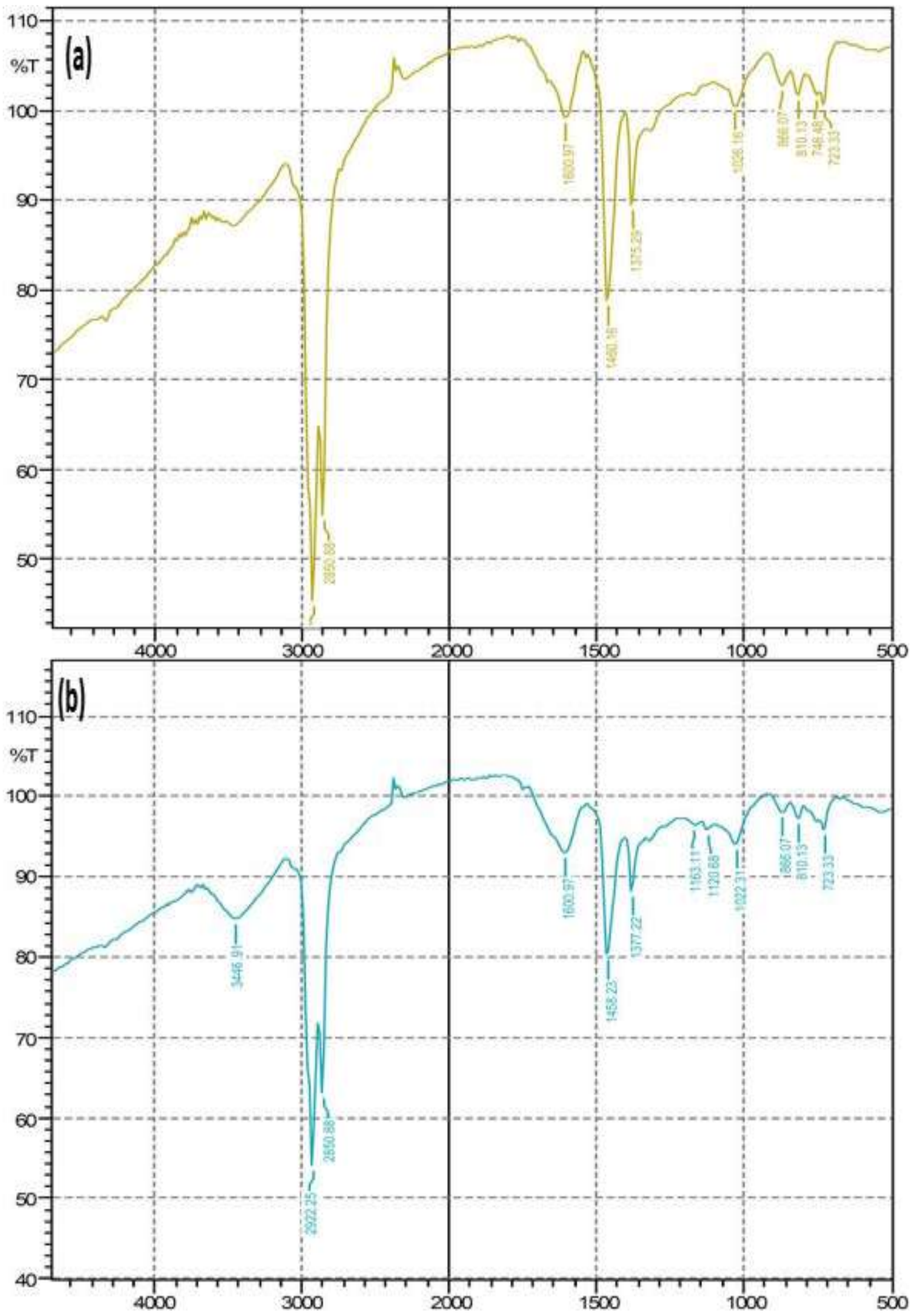

Figure 4.9: IR spectrum of (a) 3HDPMB (b) 3HDPMB at pH 5.0

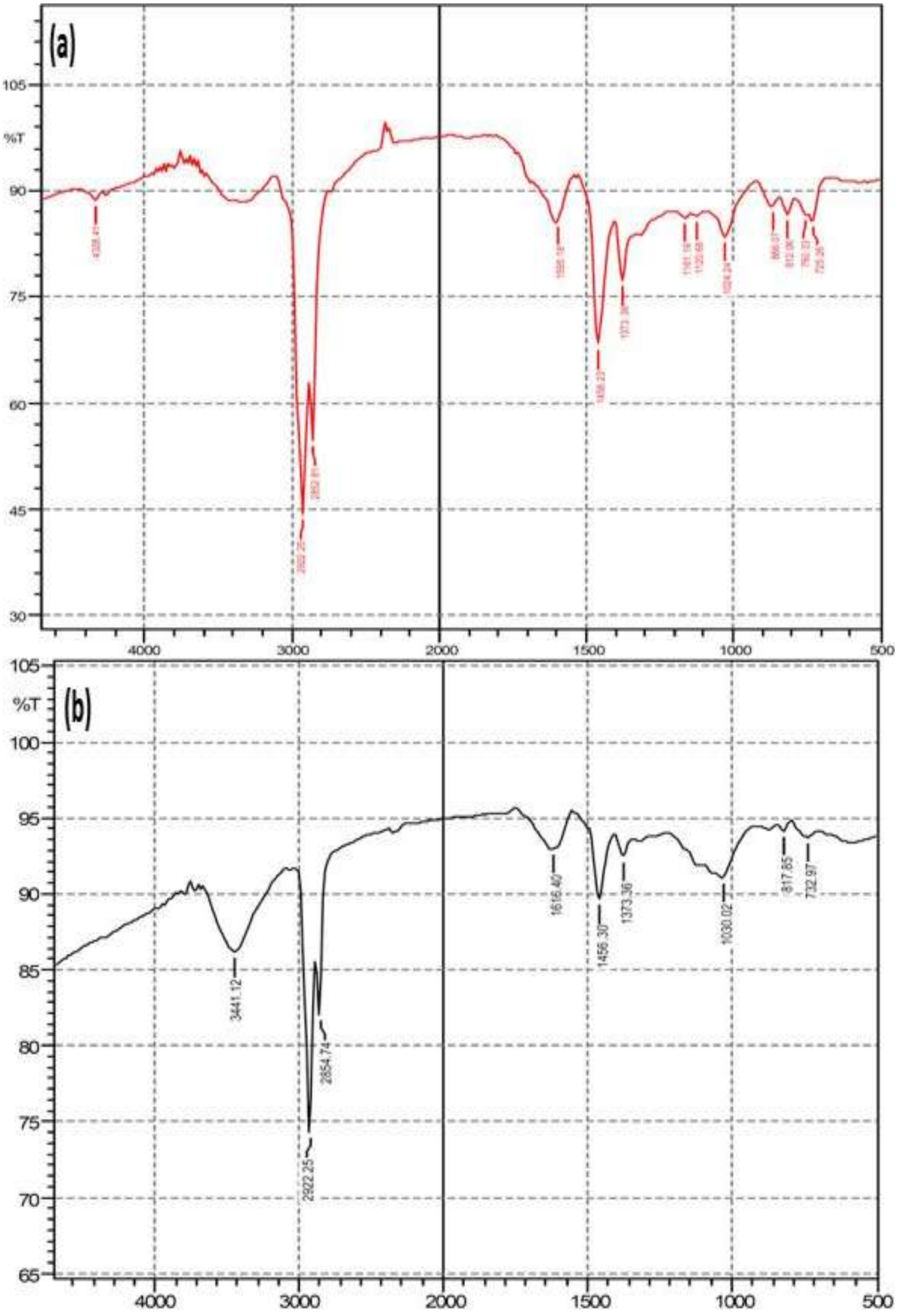

Figure 4.10: IR spectrum of (a) 3HDPMB at pH 7.0(b) 3HDPMB at pH 9.0

Table 4.5: IR peak positions of 3HDPMB at different pH

Functional group	**Wave Number (cm^{-1})**				
	Bitumen	**3HDPMB**	**3HDPMB at pH 5.0**	**3HDPMB at pH 7.0**	**3HDPMB at pH 9.0**
C-H aromatic / aliphatic stretching	2922, 2856	2922, 2850	2922, 2850	2922, 2852	2922, 2854
N-H bending	1608	1600	1600	1595	1616
C=C aromatic stretching	1454	1460	1458	1458	1456
C=S / S=O stretching	1371	1375	1377	1373	1373
C-H of CH_3 bending	864, 806	866, 810	866, 810	866, 812	817

Table 4.5 shows IR peak positions of 3HDPMB and 3HDPMB kept at pH of 5.0, 7.0 and 9.0. The IR spectrum of 3HDPMB at different pH is compared with IR of 3HDPMB. The peak at 2922 cm^{-1} remains unchanged at all the selected pH range. Peak at 2850 cm^{-1} remain unchanged for pH 5.0, shifts to 2852 cm^{-1} at pH 7.0 and shifts to 2854 cm^{-1} at pH 9.0. Peak of 1600 cm^{-1} remain unchanged at pH 5.0, shifts to 1595 cm^{-1} at pH 7.0 and shifts to 1616 cm^{-1} at pH 9.0. Peak of 1460 cm^{-1} mildly shifts to 1458 cm^{-1} at pH 5.0 and 7.0 and shifts to 1456 cm^{-1} at pH 9.0. Peak of 1375 cm^{-1} shifts to 1377 cm^{-1} at pH 5.0 and to 1373 cm^{-1} at both the pH of 7.0 and 9.0. Peak of 866 cm^{-1} remain unchanged at all the pH of study. Peak at 810 cm^{-1} shift to 812cm^{-1}, 817 cm^{-1} at pH 7.0 and 9.0 respectively but remain unchanged at pH 5.0. Figure 4.11 (a), (b) shows IR spectrum of 5HDPMB and 5HDPMB at pH 5.0 respectively. Figure 4.12 (a), (b) shows IR spectrum of 5HDPMB at pH 7.0 and 5HDPMB at pH 9.0 respectively

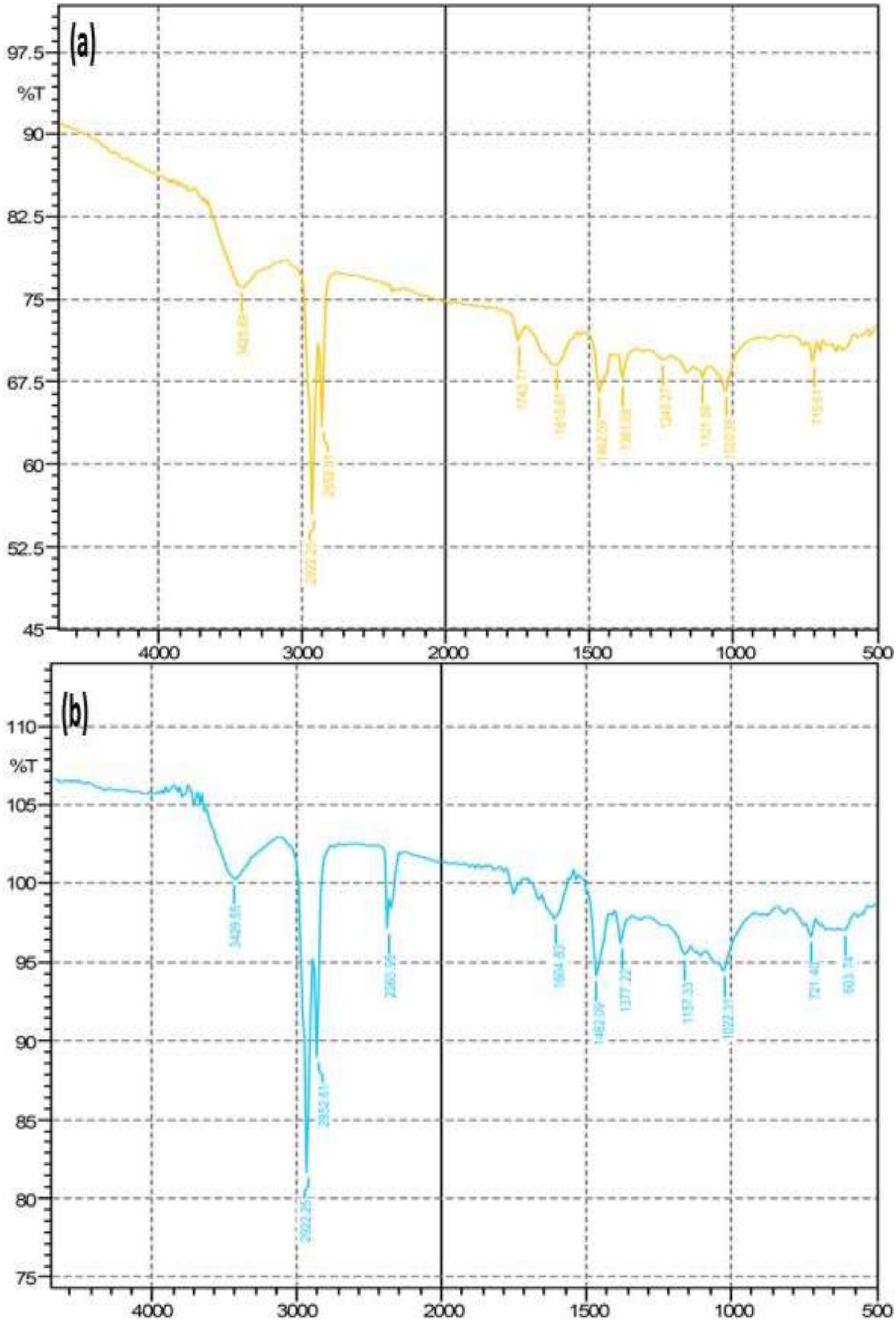

Figure 4.11: IR spectrum of (a) 5HDPMB (b) 5HDPMB at pH 5.0

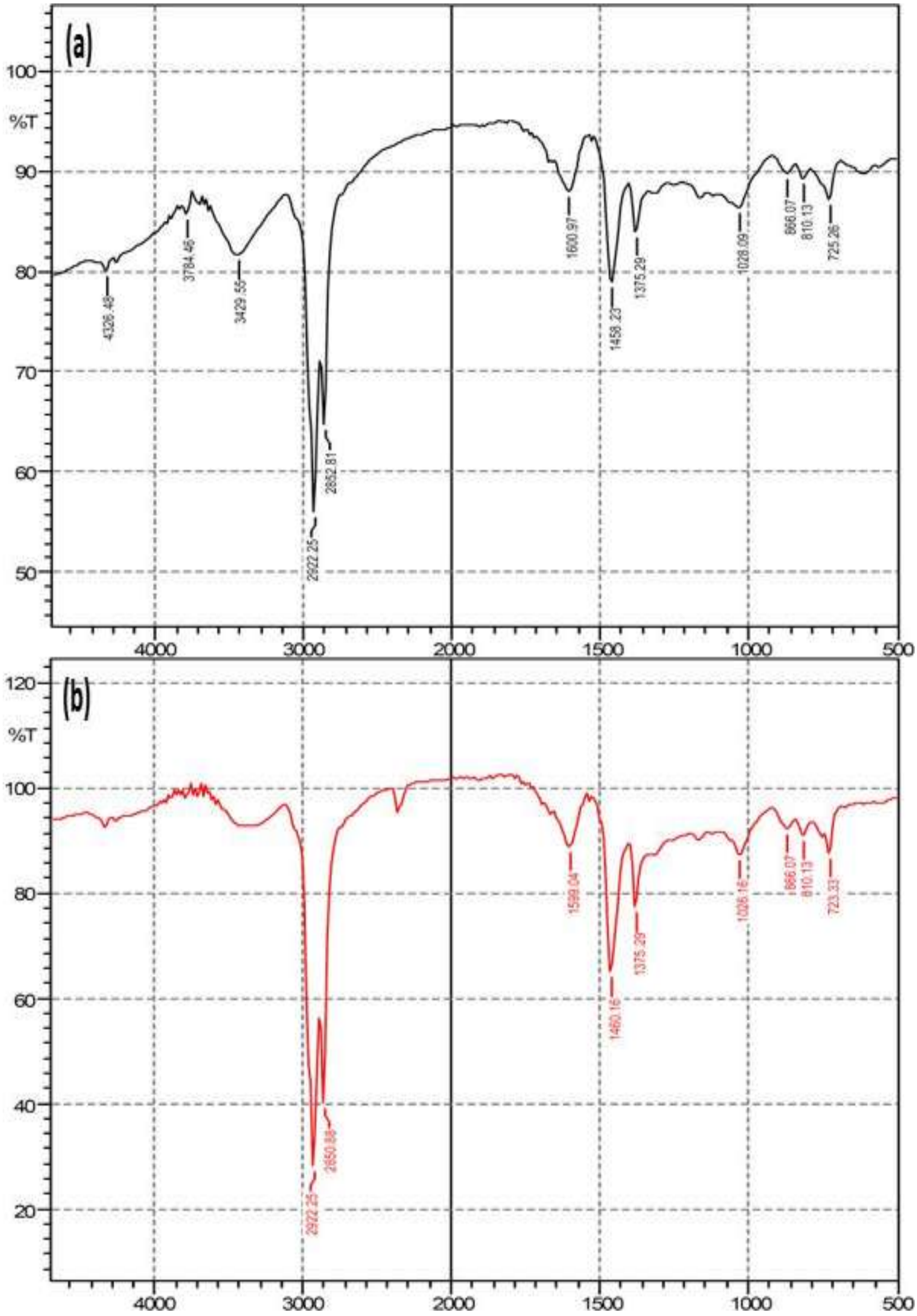

Figure 4.12: IR spectrum of (a) 5HDPMB at pH 7.0(b) 5HDPMB at pH 9.0

Table 4.6: IR peak positions of 5HDPMB at different pH

Functional group	**Wave Number (cm^{-1})**				
	Bitumen	**5HDPMB**	**5HDPMB at pH 5.0**	**5HDPMB at pH 7.0**	**5HDPMB at pH 9.0**
C-H aromatic / aliphatic stretching	2922, 2856	2922, 2852	2922, 2852	2922, 2852	2922, 2850
N-H bending	1608	1610	1604	1600	1599
C=C aromatic stretching	1454	1462	1462	1458	1460
C=S / S=O stretching	1371	1381	1377	1375	1375
C-H of CH_3 bending	864, 806	866, 810	866, 810	866, 810	866, 810

Table 4.6 shows IR peak positions of 5HDPMB and 5HDPMB kept at pH of 5.0, 7.0 and 9.0. The IR spectra of 5HDPMB at different pH are compared with IR of 5HDPMB. The peak of 2922 cm^{-1} remains unchanged at all the selected pH range. Peak of 2852 cm^{-1} shifts to 2850 cm^{-1} at pH 5.0, pH 7.0 and remain unchanged at pH 9.0 which shows slight weakening of bond strength in acidic and basic medium. Peak of 1610 cm^{-1} shift to 1604 cm^{-1} at pH 5.0, to 1600 cm^{-1} at pH 7.0 and to 1599 cm^{-1} at pH 9.0. Peak of 1462 cm^{-1} remains unchanged at pH 5.0 but shifts to 1458 cm^{-1} at pH 7.0 and 1460 cm^{-1} at pH 9.0. Peak of 1381 cm^{-1} shift to 1377 cm^{-1} at pH 5.0 and shift to 1375 cm^{-1} at pH 7.0 and 9.0. Peaks at 866cm^{-1} and 810 cm^{-1} remain unchanged at all the pH of study. The changes are small enough to predict any new change by chemical forces. However, new peaks for O-H stretching bands use to be observed at pH 5.0, 7.0 and 9.0 indicating existence of water molecule in HDPMB at all the pH. Figure 4.13 (a), (b) shows IR spectrum of 7HDPMB and 7HDPMB at pH 5.0 respectively. Figure 4.14 (a), (b) shows IR spectrum of 7LDPMB at pH 7.0 and 7LDPMB at pH 9.0 respectively.

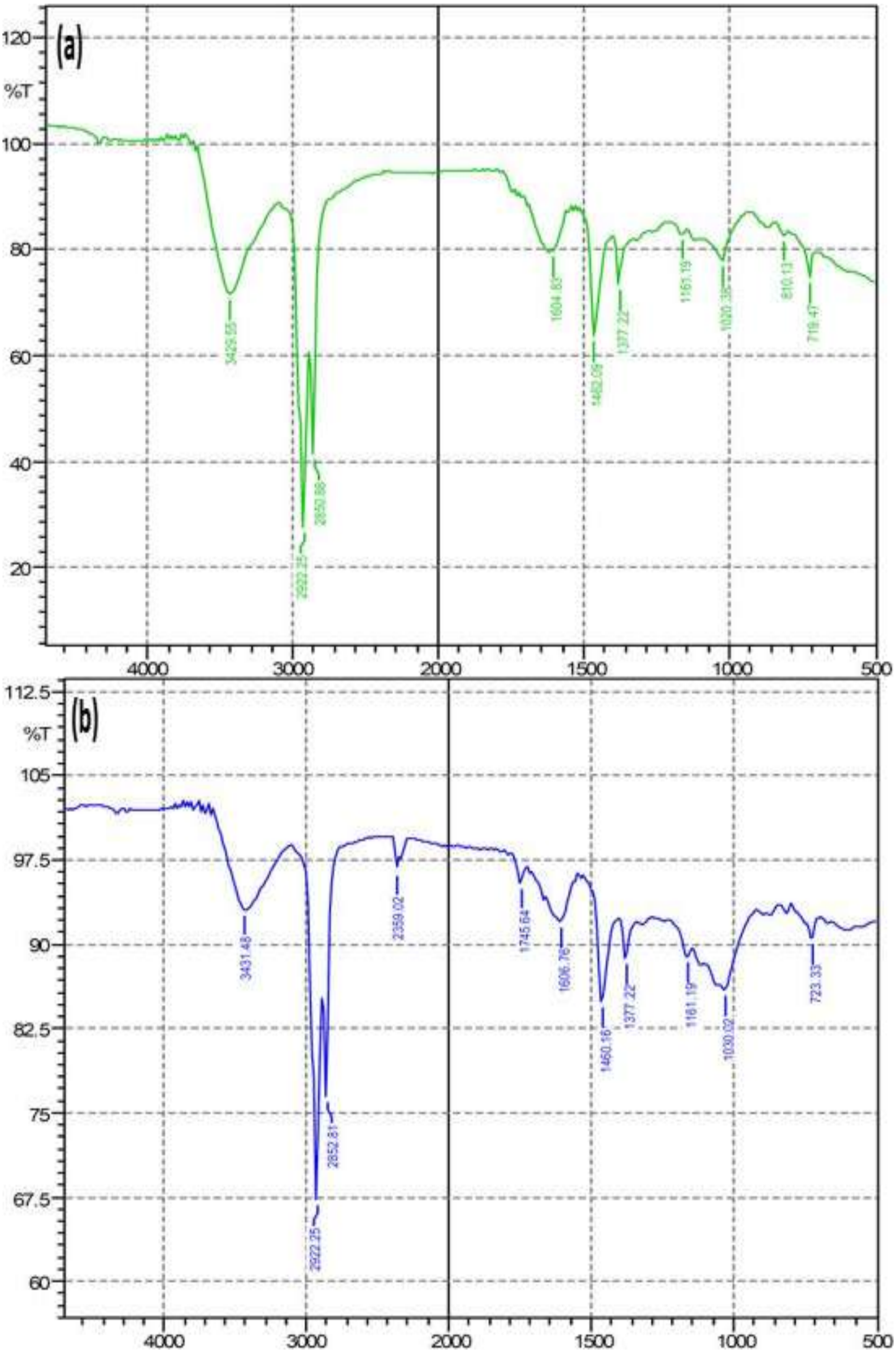

Figure 4.13: IR spectrum of (a) 7HDPMB (b) 7HDPMB at pH 5.0

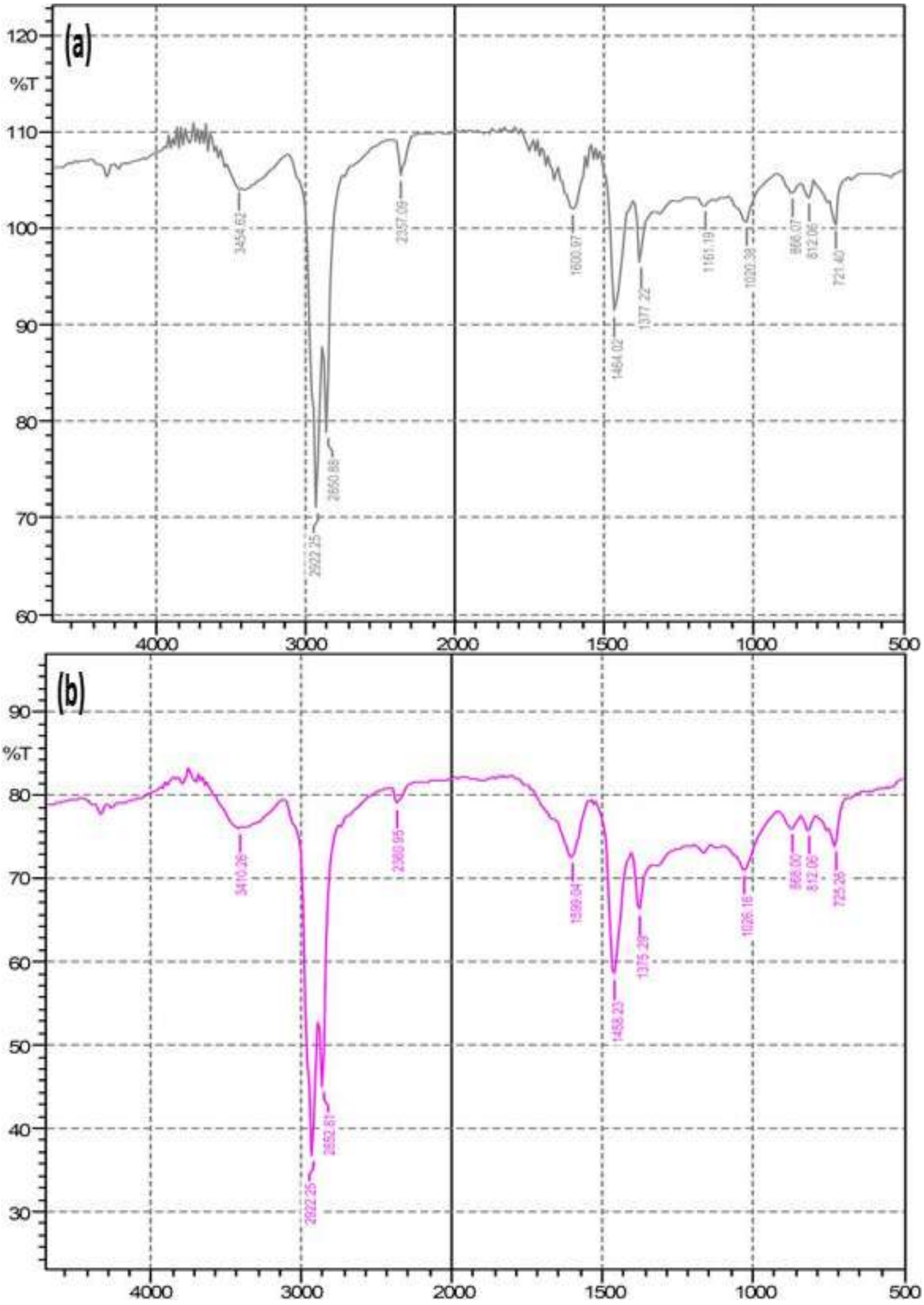

Figure 4.14: IR spectrum of (a) 7HDPMB at pH 7.0(b) 7HDPMB at pH 9.0

Table 4.7: IR peak positions of 7HDPMB at different pH

Functional group	**Wave Number (cm^{-1})**				
	Bitumen	**7HDPMB**	**7HDPMB at pH 5.0**	**7HDPMB at pH 7.0**	**7HDPMB at pH 9.0**
C-H aromatic / aliphatic stretching	2922, 2856	2922, 2850	2922, 2852	2922, 2850	2922, 2852
N-H bending	1608	1604	1606	1600	1599
C=C aromatic stretching	1454	1462	1460	1464	1458
C=S / S=O stretching	1371	1377	1377	1377	1375
C-H of CH_3 bending	864, 806	810	-	866, 812	868, 812

Table 4.7 shows IR peak positions of 7HDPMB and 7HDPMB kept at pH of 5.0, 7.0 and 9.0. The IR spectrum of 7HDPMB at different pH is compared with IR of 7HDPMB. The peak of 2922 cm^{-1} remains unchanged at all the selected pH range. Peak of 2850 cm^{-1} remain unchanged at pH 7.0 and shifts to 2852 cm^{-1} at pH 5.0 and pH 9.0. Peak of 1604 cm^{-1} shift to 1606 cm^{-1} at pH 5.0, shifts to 1600 cm^{-1} at pH 7.0 and to 1599 cm^{-1} at pH 9.0. Peak of 1462 cm^{-1} shift to 1460 cm^{-1} at pH 5.0, 1464 cm^{-1} at pH 7.0 and 1458 cm^{-1} at pH 9.0. Peak of 1377 cm^{-1} doesn’t have any observable change at pH 5.0 and 7.0 and shift to 1375 cm^{-1} at pH 9.0. Peak of 866 cm^{-1} remain unchanged at pH 5.0 and 7.0 and shift to 868 cm^{-1} at pH 9.0. Peak of 810 cm^{-1} shifts to 812 cm^{-1} at pH 7.0 and pH 9.0. Formation of new peak at around 3400 cm^{-1} is indication of the presence of water in modified bitumen.

4.8 Thermo-gravimetric analysis of bitumen and HDPE modified bitumen

TGA analysis of bitumen, 3HDPMB and 3HDPMB exposed to pH 5.0, 7.0 and 9.0 was conducted. In case of HDPMB, 3.0% composition was chosen because this was the optimum concentration. The thermo-gram of bitumen clearly shows that bitumen decomposes in three steps. As per literature it is found that when the temperature is less than 350 °C there is decomposition of aromatics and saturates due to which bitumen loses its mass. At temperature greater than 350 °C but less than 500 asphaltene, resins and aromatics decomposes. When temperature exceeds 500 °C there is major decomposition of asphaltenes and few aromatics as well as resins (136). Fig 4.15 shows TGA plot of bitumen which indicates that major decomposition starts at 200 °C and ends at 499.5 °C with 76.89% weight loss. The residual mass is 18.25% which is because of presence of some metal ions. Figure 4.16 shows TGA plot of 3HDPMB which indicates that major decomposition starts at 275 °C and ends at 499.5 °C with 71.32% weight loss. The residual mass is 22.26% which is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 275 °C in case of HDPE modified bitumen (3HDPMB). This means thermal stability of bitumen increases after modification with HDPE.

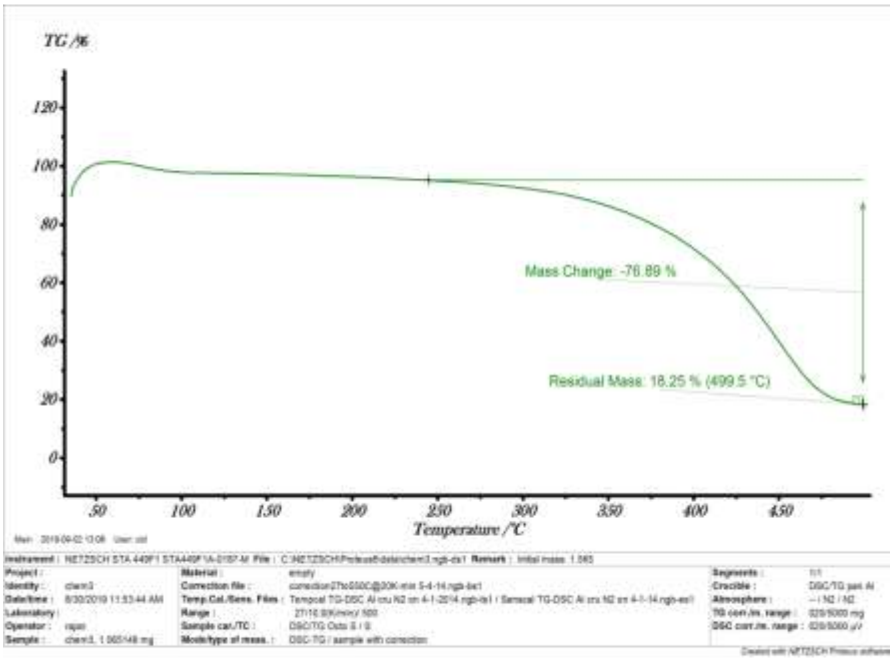

Figure 4.15: TGA plot of Bitumen

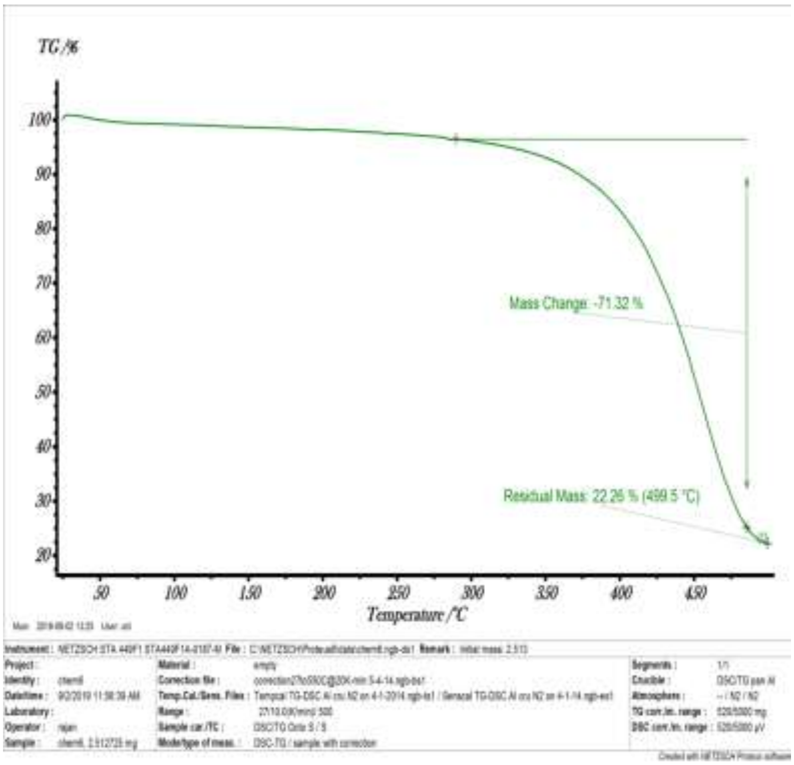

Figure 4.16: TGA plot of 3HDPMB

4.9 Thermo-gravimetric analysis of 3HDPMB at different pH

Thermo-gravimetric analysis of 3HDPMB exposed to different environmental conditions i.e. pH 5.0, 7.0 and 9.0 were conducted**.** The purpose was to check the effect of pH on thermodynamic stability of 3HDPMB. Figure 4.17 shows TGA plot of 3HDPMB exposed to pH 5.0 which indicates that major decomposition starts at 275 °C and ends at 499.5 °C with 70.77% weight loss. The residual mass is 24.20% which is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 275 °C in case of HDPE modified bitumen which is kept at pH 5.0. Figure 4.18 shows TGA plot of 3HDPMB exposed to pH 7.0 which indicates that major decomposition starts at 375 °C and ends at 499.5 °C with 69.98% weight loss. The residual mass is 25.83% which is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 350 °C in case of HDPE modified bitumen which is kept at pH 7.0. Figure 4.19 shows TGA plot of 3HDPMB exposed to pH 9.0 which indicates that major decomposition starts at 350 °C and ends at 499.5 °C with 70.92% weight loss. The residual mass is 25.34% which is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 350 °C in case of HDPE modified bitumen which is kept at pH 9.0.

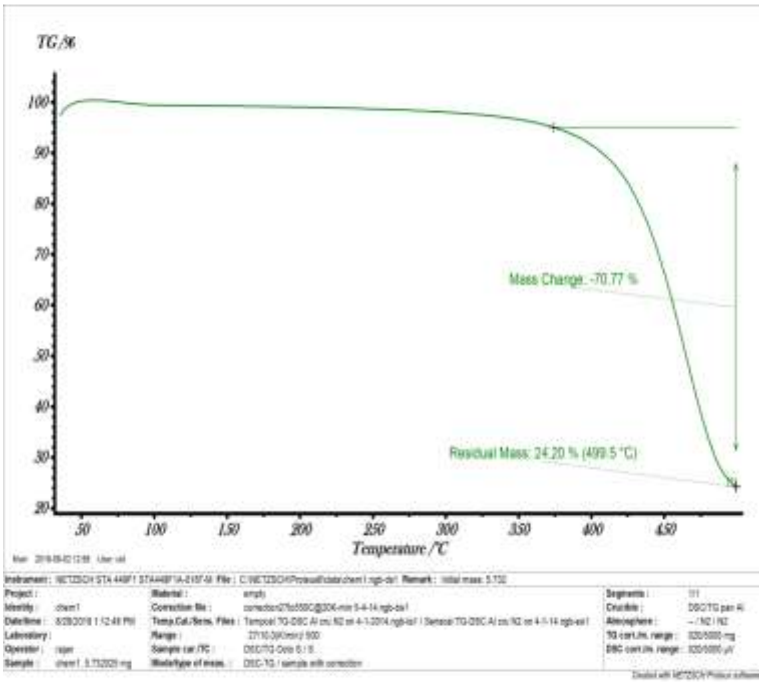

Figure 4.17: TGA plot of 3HDPMB at pH 5.0

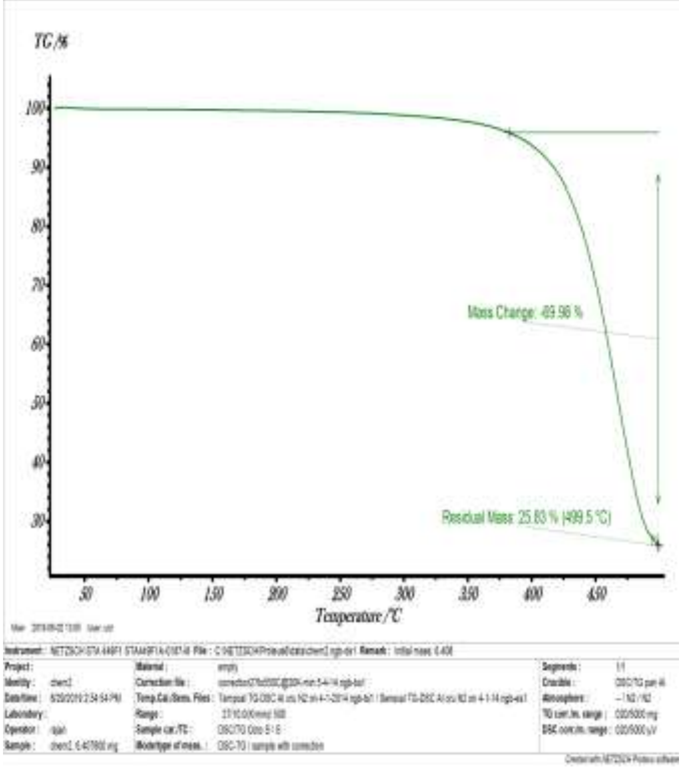

Figure 4.18: TGA plot of 3HDPMB at pH 7.0

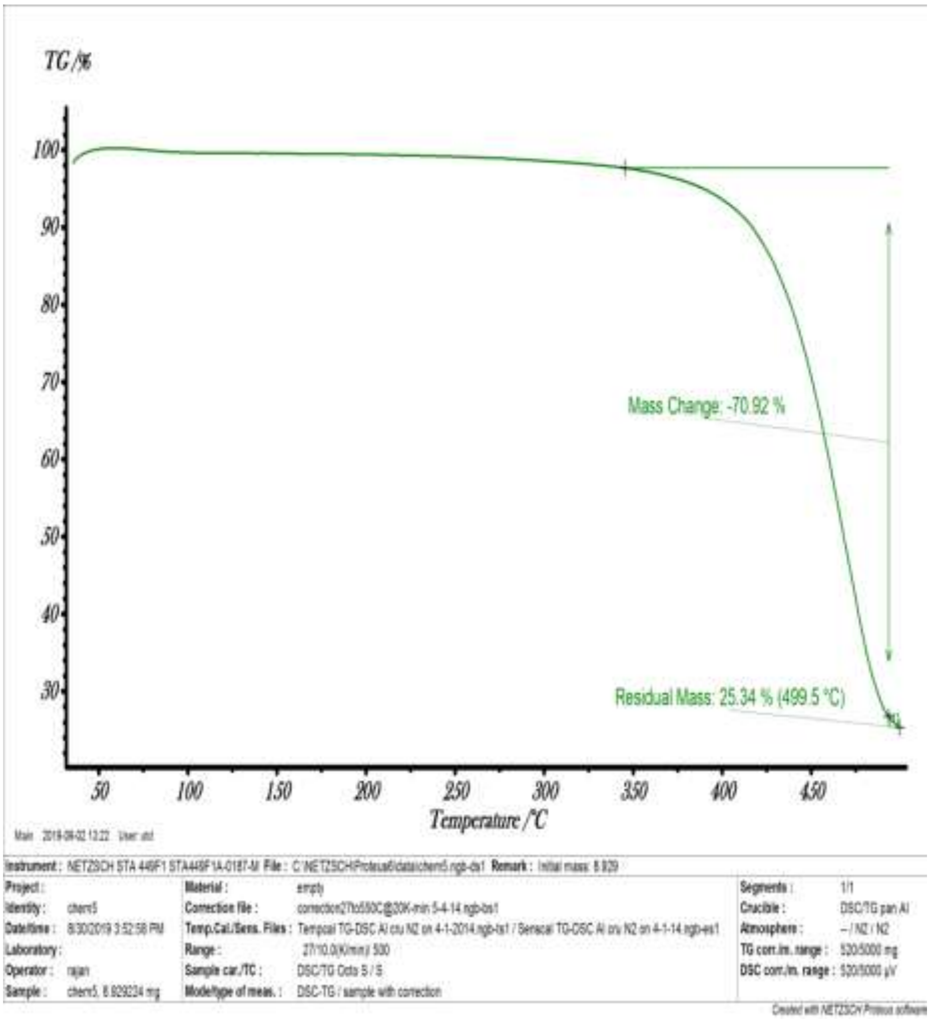

Figure 4.19: TGA plot of 3HDPMB at pH 9.0

Table 4.8: TGA values of bitumen, 3HDPMB and 3HDPMB exposed to pH 5.0, 7.0, 9.0

Samples	**$T_i(^0C)$**	**$T_f(^0C)$**	**Wt. Loss (%)**
Bitumen	200	499.5	76.89
3HDPMB	275	499.5	71.32
3HDPMB at pH 5.0	275	499.5	70.77
3HDPMB at pH 7.0	375	499.5	69.98
3HDPMB at pH 9.0	350	499.5	70.92

Table 4.8 analyses the TGA values of bitumen, 3HDPMB and 3HDPMB which was earlier exposed to environmental conditions of different pH that is pH 5.0, 7.0 and 9.0. The table clearly indicates that pH has very little effect on the thermodynamic stability of 3HDPMB. Rather there is enhancement in the thermodynamic stability of 3HDPMB after exposure to different mediums.

4.10 Conclusion

There is enhancement in physical and mechanical properties of bitumen after modification with HDPE. SEM analyses of the water logged HDPE modified bitumen surface was analyzed, cracks/ holes on the surface of modified bitumen were obtained. To obtain the reason behind these damages on the surface of the modified bitumen, IR spectra of uniform quantity of bitumen/ HDPE modified bitumen (pellets by mixing 1.0 mg of bitumen/modified bitumen with 3.0 mg of KBr) was taken and compared. The important peaks for the expected functional groups are shown in Table (4.3-4.7). The expected functional groups are N-H, C-H, C-C, C=C, C=S etc. The unusual high intensity of the peaks in between 2850-3000 cm^{-1} is worth of analyzing. In almost all of the cases this region is known for the sp^2 or sp^3 C-H stretching band, which is very weak in nature. The high intensity of such peaks indicates high polarity in C-H stretching band. This highly polar C-H stretching band has the tendency to interact with electronegative element like oxygen of H_2O/ H_3O^+/ OH^-. After modification with HDPE we didn’t find any remarkable change in the IR spectrum of modified bitumen compared to unmodified bitumen. Only decrease in C-H stretching band was observed for the modified bitumen at pH 5.0 and pH 9.0 that indicates interaction of acidic or basic water with the polar C-H band. TGA values clearly indicate that on moving from bitumen to HDPE modified bitumen, the temperature of major decomposition shift towards a higher value. This is a positive outcome, because HDPE modified bitumen shows greater thermodynamic stability as compare to unmodified bitumen. When this modified bitumen is exposed to different pH (5.0, 7.0 and 9.0), again the TGA values indicate shifting of major decomposition temperature towards higher side thus confirming that pH has no effect on thermodynamic stability of HDPE modified bitumen. Thus it can be concluded that HDPE modified bitumen is not resistant to pH variations but it is thermodynamically more stable than bitumen.

CHAPTER 5

AN ANALYSIS OF CHANGE IN PHYSICOCHEMICAL PARAMETERS OF BITUMEN AFTER MODIFICATION THROUGH EVA

The last objective of thesis is comparative studies regarding thermal strength, mechanical strength, resistivity towards environmental changes, using various types of plastics. Now, in the first stage, modified bitumen was synthesized using non polar polymers like LDPE and HDPE. But, there is drastic effect of pH on morphological properties of LDPE and HDPE modified bitumen. Hence, a polar polymer modifier was chosen to make the desired changes in bitumen. Morphological analysis of modified bitumen using SEM technique show clear cut indication of effect of pH on the structural behavior and it was found that LDPE and HDPE modified bitumen were not resistant to pH. This is because polyethene being non polar shows only physical interaction with the bitumen as evident from the FTIR study. There is no formation of any new chemical compound. Hence it was expected that polar polymer like EVA can interact with the polar components in bitumen and hence may provide some resistance towards pH variation.

5.1 Penetration Point

Penetration point is one of the basic physical property of bitumen which gives information about the hardness or softness of bitumen. This property depends on intermolecular forces of attraction between molecules of bitumen. If intermolecular forces of attraction are strong, bitumen sample will be more hard and vice versa. Table 5.1 summarized the result of penetration point test for the bitumen and EVA modified bitumen (EVAMB).

Table 5.1 - Penetration test results for bitumen and EVA modified bitumen

% of EVA In bitumen	Penetration point of EVAMB at 25 °C (dmm)	Penetration point of EVAMB at 35 °C (dmm)	Penetration point of EVAMB at 45 °C (dmm)
0	68	68	69
1	50	51	52
3	46	48	49
5	38	38	39
7	36	36	37

First objective of the present research work is to study the effect of temperature variation on physical properties of bitumen. Hence, penetration point of bitumen and EVA modified bitumen at three different temperatures (25 °C, 35 °C , 45 °C) were determined using Penetrometer. Figure 5.1 represents the variation in penetration point of the bitumen and EVAMB at different temperatures versus different percentages of EVA polymer. Table 5.1 indicates that penetration point of bitumen is 68 dmm which is in the acceptable range of VG-30 bitumen. Results of penetration test shows that the penetration value of bitumen decreases after the addition of EVA and it further decreases with the increase in the percentage of EVA polymer (see Figure 5.1). This shows that hardness of bitumen enhances after the modification with EVA polymer. There is sharp decrease in penetration value from 68 dmm for bitumen to 50 dmm for EVA at 1% composition. Then at 3% composition it falls to 46 dmm. For high mass percentage of EVA (5% and 7%), the penetration value for EVAMB falls to 38 dmm, 36 dmm respectively.

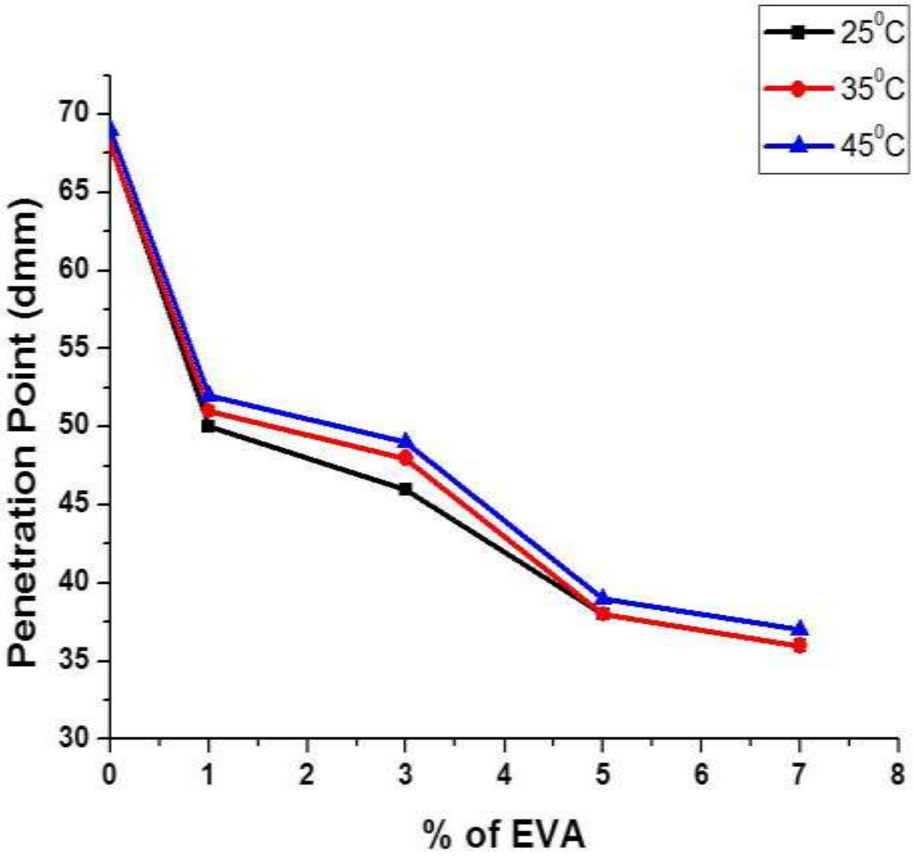

Figure 5.1: Penetration point of EVAMB versus % of EVA at different temperatures

For EVA modified bitumen samples, the penetration value increases with the increase in temperature. However, for particular temperature as compared to bitumen the modified bitumen samples have low penetration. For example, at 45 °C, the penetration value is decreased by 46.38% as compared to bitumen. Overall, these results show that with the incorporation of EVA, the hardness and stiffness of the bitumen increases, which in turn leads to the enhancement in the resistance of modified bitumen towards permanent deformation, rutting at moderate and high temperatures. Due to this improvement in the hardness, the road constructed using modified bitumen can resist the penetration in comparison to the road build from unmodified bitumen and therefore, increase the longevity of the road.

5.2 Softening point

Softening point is also basic physical property of bitumen and depends on intermolecular forces of attraction between molecules of bitumen. If the intermolecular forces of attraction are weak, then the bitumen samples will have tendency to get soften at less temperature and hence have low softening point and vice versa. Softening point of bitumen and EVA modified bitumen samples was determined with the help of ring and ball apparatus.

Table 5.2 summarized the result of softening point test for the bitumen and EVA modified bitumen samples (EVAMB).

Table 5.2 – Softening point test results for bitumen and EVA modified bitumen

Sr. No.	% of EVA in bitumen	Softening point (°C) of EVAMB	Ductility(cm) of EVAMB
1.	0	48	76
2.	1	56	66
3.	3	63	61
4.	5	70	55
5.	7	76	39

Softening point of bitumen is 48 °C. The results of softening point clearly indicate that softening point of bitumen increases after modification with EVA and it further increases with the increase in the percentage of EVA polymer. As the softening point increases bitumen becomes less temperature susceptible. This implies that bitumen becomes resistant towards the effect of heat and it will not soften easily at high temperature. Such modified bitumen can be successfully used in areas with hotter climatic conditions. Figure 5.2 represents the variation in softening point of bitumen and EVAMB with different percentages of EVA polymer. At 1% composition of EVA the increase in softening point is very sharp that is 16.7%. When the percentage of EVA is increased to 3%, the rise in softening point becomes 31.25% for EVAMB. At 5% composition of this polar polymer, the rise in softening point is 45.83% for EVAMB. Softening point increases by 58.33% at 7% composition of EVA.

5.3 Ductility

Ductility of bitumen is a mechanical property which is measure of cohesive strength of bitumen and depends on intermolecular forces of attraction. The bitumen sample will be more ductile if the intermolecular forces of attraction are strong and vice versa. Ductility values of bitumen and EVA modified bitumen samples were determined with the help of ductility testing machine. Table 5.2 summarized the result of ductility test for the bitumen and EVA modified bitumen samples (EVAMB). It is clear from Table 5.2 that ductility of bitumen is 76 cm. Ductility of bitumen decreases after the modification with EVA and with the increase in percentage of EVA polymer. At 1% addition of EVA (by mass of bitumen), ductility decreases by 13.16%. The decrease is 19.74% at 3% mixing of EVA. Decrease in ductility of bitumen is justified because stiffness of bitumen enhances after the modification with EVA. For EVA, ductility decreases by 27.63% at 5% composition and then it falls below the minimum required value of 40 cm. This means bitumen cannot be modified with EVA beyond 5.0% by mass of bitumen. Bitumen which is having very low value of ductility will not act as a good binder because it will not be able to bind the aggregates properly. So, bitumen having percent of EVA greater than 5.0% by mass of bitumen will have poor performance in the pavement, hence should not be used. Therefore, 5.0% EVA by mass of bitumen is the ideal or optimum concentration for the modification of VG-30 bitumen. Figure 5.3 shows the variation in ductility values for the bitumen and EVA modified bitumen samples versus % of EVA polymer.

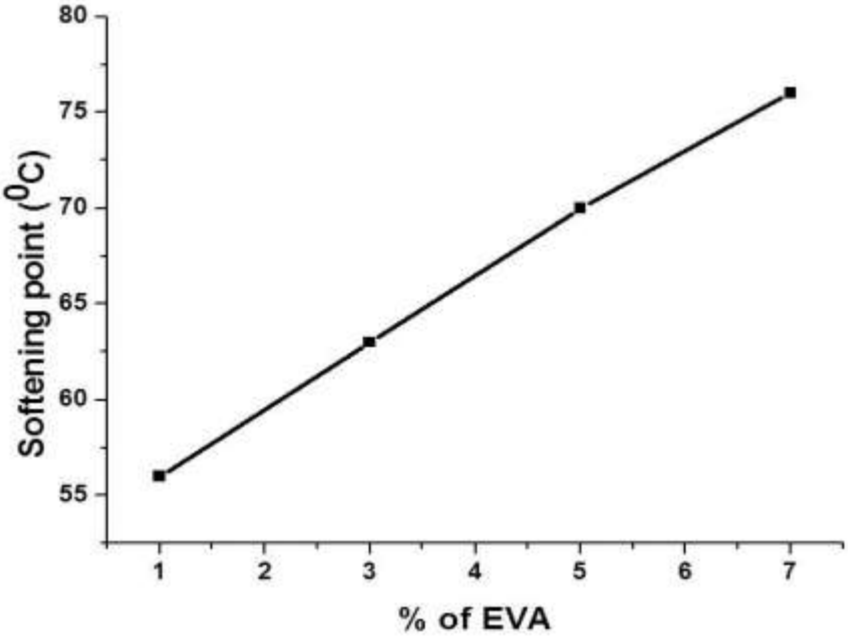

Figure 5.2: Softening point of EVAMB versus % of EVA

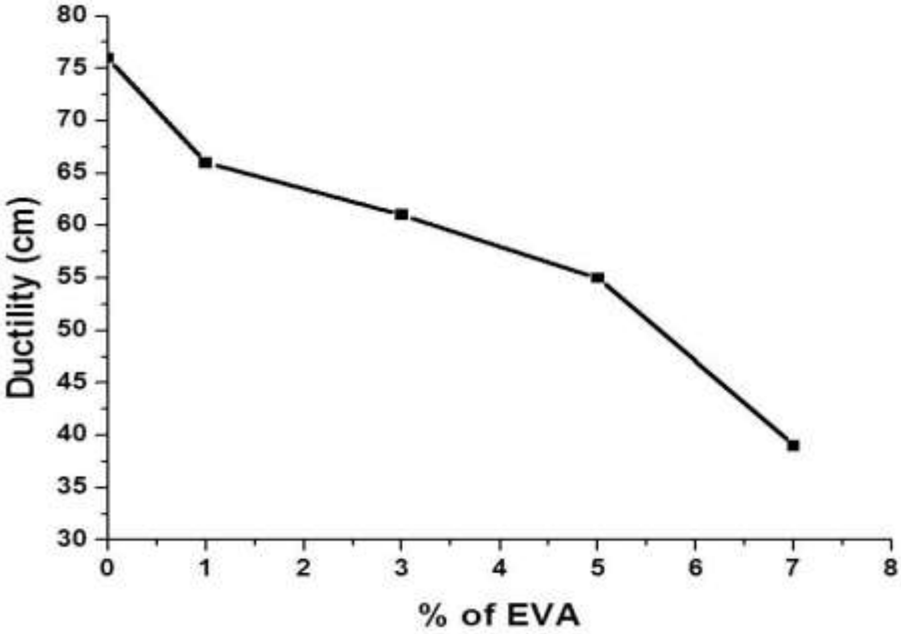

Figure 5.3: Ductility of EVAMB versus % of EVA

5.4 Scanning Electron Microscopy (SEM) analysis of EVA modified bitumen

SEM analysis was performed on bitumen and EVA modified bitumen samples to examine the dispersion of EVA polymer in VG-30 bitumen. Figure 5.4 shows SEM images of bitumen and different compositions of EVAMB. Bitumen, itself is black in color, and doped EVA is uniformly dispersed in it. There is no coagulation of polymers as observed in case of higher percentages of LDPMB and HDPMB. The images clearly suggest that with increase in the percentage of EVA, surface becomes silvery white, uniform and smooth. This shows uniform dispersion of EVA in the bitumen which ultimately results in enhancement in the properties of bitumen.

5.5 SEM analysis of EVA modified bitumen at different pH

Once the SEM analysis of bitumen and different compositions of EVA modified bitumen was performed, similar analysis was performed for EVA modified bitumen samples exposed to different environmental conditions of pH for a particular time interval. Figure 5.5 shows SEM images of 5EVAMB and 5EVAMB exposed to pH 5.0, 7.0, 9.0. From the ductility test results it was clear that 5.0% EVA is the optimum composition for bitumen modification. Hence 5% EVAMB was selected to study the effect of pH using SEM analysis. There is difference in pH of water at different places worldwide; it may vary from slightly acidic to slightly alkaline. So, this was necessary to find the effect of different type of pH on the surface of EVA modified bitumen. The effect of acidic water logging was seen on the EVA modified bitumen surface by dipping the EVAMB sample into acidic water of pH 5.0 for 24 hr and then the morphology of the sample was tested. SEM clearly indicates smooth surface of the bitumen after modification with EVA (Figure 5.5). No crack was found on the surface of EVA modified bitumen as obtained in the case of LDPE and HDPE modified bitumen (in acidic medium). Similarly, tests were performed for checking effect of neutral water and of basic water by dipping EVA modified bitumen in distilled water of pH around 7.0 and dipping in water of pH 9.0 respectively. The surface morphology of these samples again shows smooth surface and absence of any hole which was earlier seen in case of LDPE and HDPE modified bitumen. So the SEM analyses suggest that EVA modified bitumen does not easily deteriorate when the pH of medium is varied and this modifier seems a better solution of problem/damage caused to roads due to water logging especially during rains. But, certainly this needs a cross check by the use of other analytical techniques.

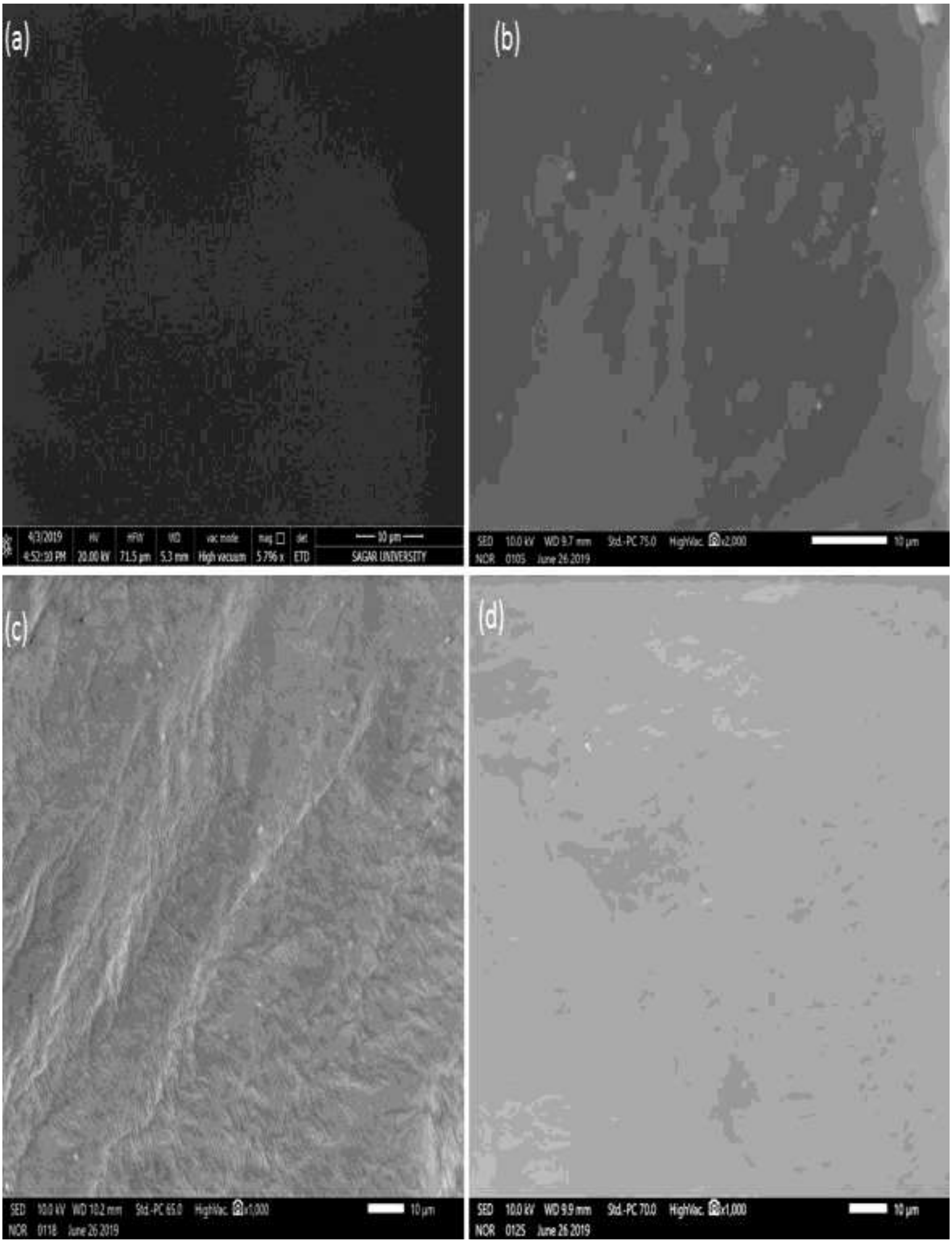

Figure 5.4: SEM images of (a) Neat Bitumen having smooth black surface

(b) 1EVAMB showing few white dots of EVA on bitumen surface

(c) 3 EVAMB having higher % of EVA on surface of bitumen

(d) 5 EVAMB showing uniform, smooth silvery white surface of modified bitumen

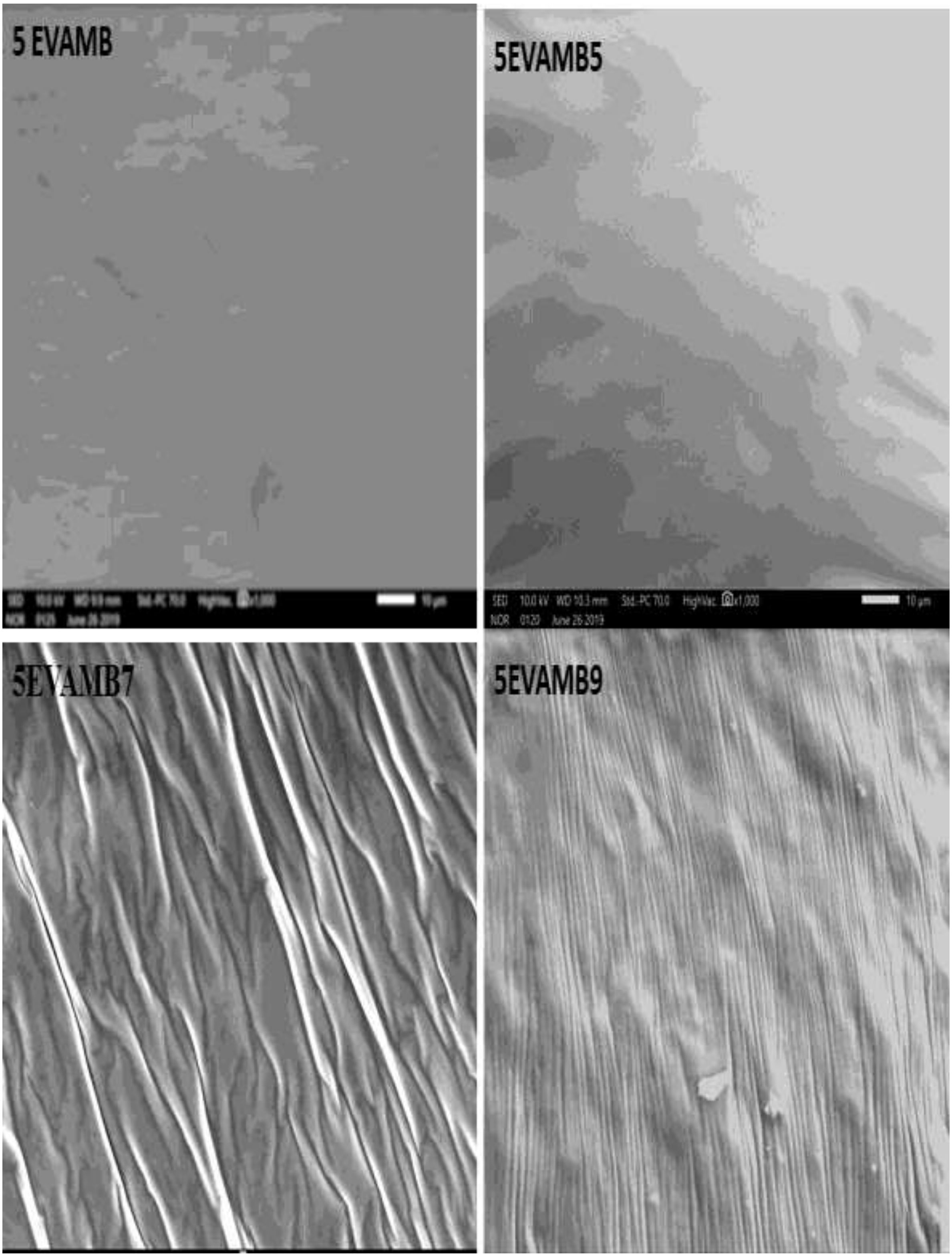

Figure 5.5: SEM images of (a) 5EVAMB showing smooth silvery white surface of bitumen

(b) 5EVAMB at pH 5.0 having uniform surface and no cracks

(c) 5EVAMB at pH 7.0 showing uniform surface

(d) 5EVAMB at pH 9.0 having uniform surface and no holes

5.6 Fourier Transform Infra-Red analysis (FTIR) of EVAMB

Figure 5.6 shows FTIR spectra of bitumen and EVA polymer. Figure 5.7(a) and (b) shows FTIR spectra of 1EVAMB and 3EVAMB respectively. Figure 5.8 shows FTIR spectrum of 5EVAMB. The spectra of VG-30 bitumen show peaks at 2922 cm^{-1}, 2856 cm^{-1} which correspond to C-H aromatic / aliphatic stretching. The high intensity of these peaks is very unusual, which is an indicative of polarity between C-H bonds. This may be due to presence of extreme electron withdrawing group attached to carbon chain in the bitumen. Other peaks which is seen in the spectrum are at 1608 cm^{-1} correspond to N-H bending, peak at 1454 cm^{-1} is due to C=C aromatic stretching, peak at 1371 cm^{-1}correspond to C=S / S=O stretching, peaks at 864 cm^{-1}, 806 cm^{-1} indicates presence of C-H bending band.

In the IR spectrum of EVA, peaks are observed at 2916 cm^{-1}, 2848 cm^{-1} assigned to C-H aliphatic / aromatic stretching, peak at 1737 cm^{-1} which is assigned to ($\upsilon_{C=O}$) of ester, peak at 1238 cm^{-1} which correspond to (υ_{C-O-C}), peak at 1020 cm^{-1} corresponds to C-C stretching,

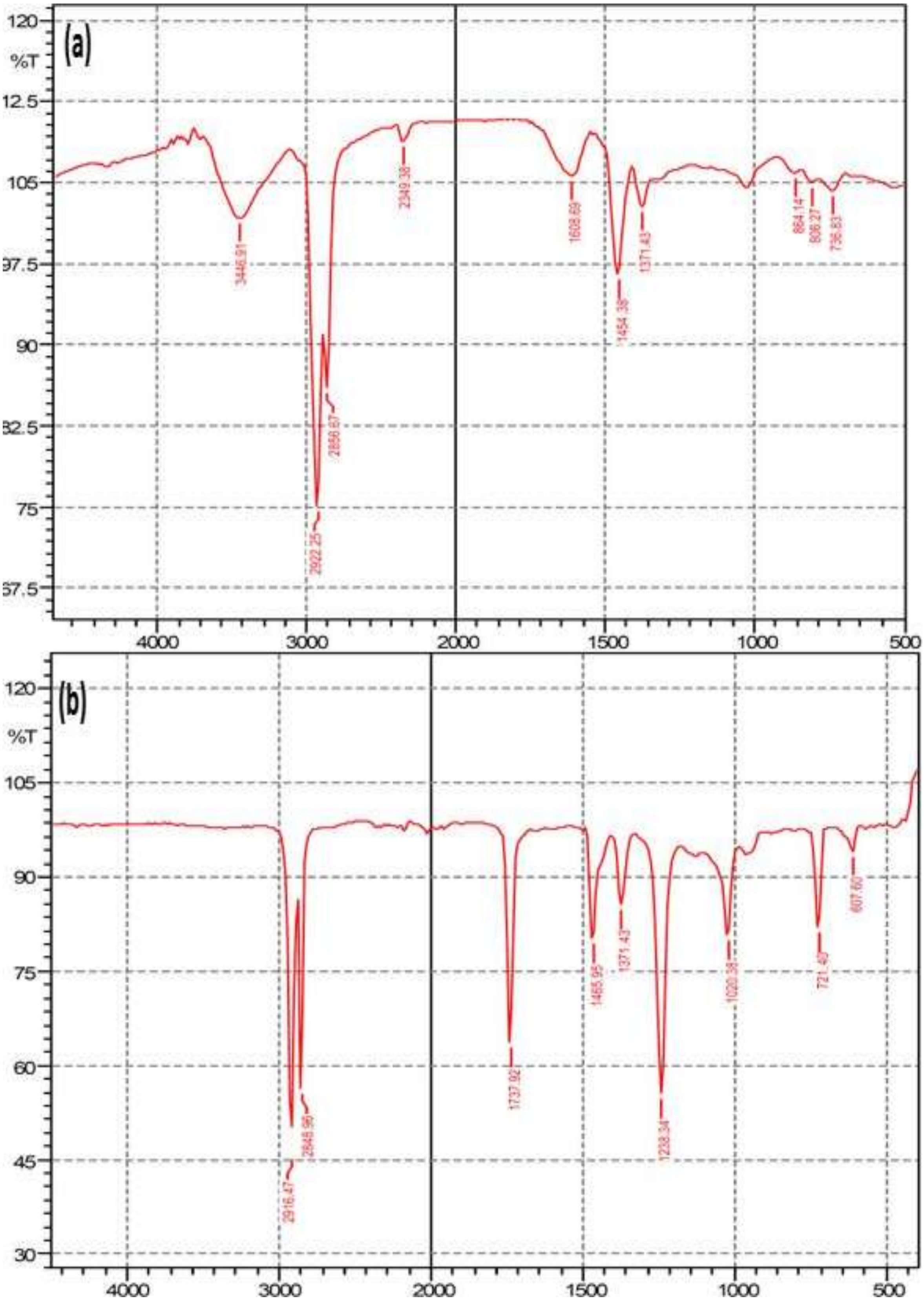

Figure 5.6 : IR spectrum of (a) Bitumen (b) EVA

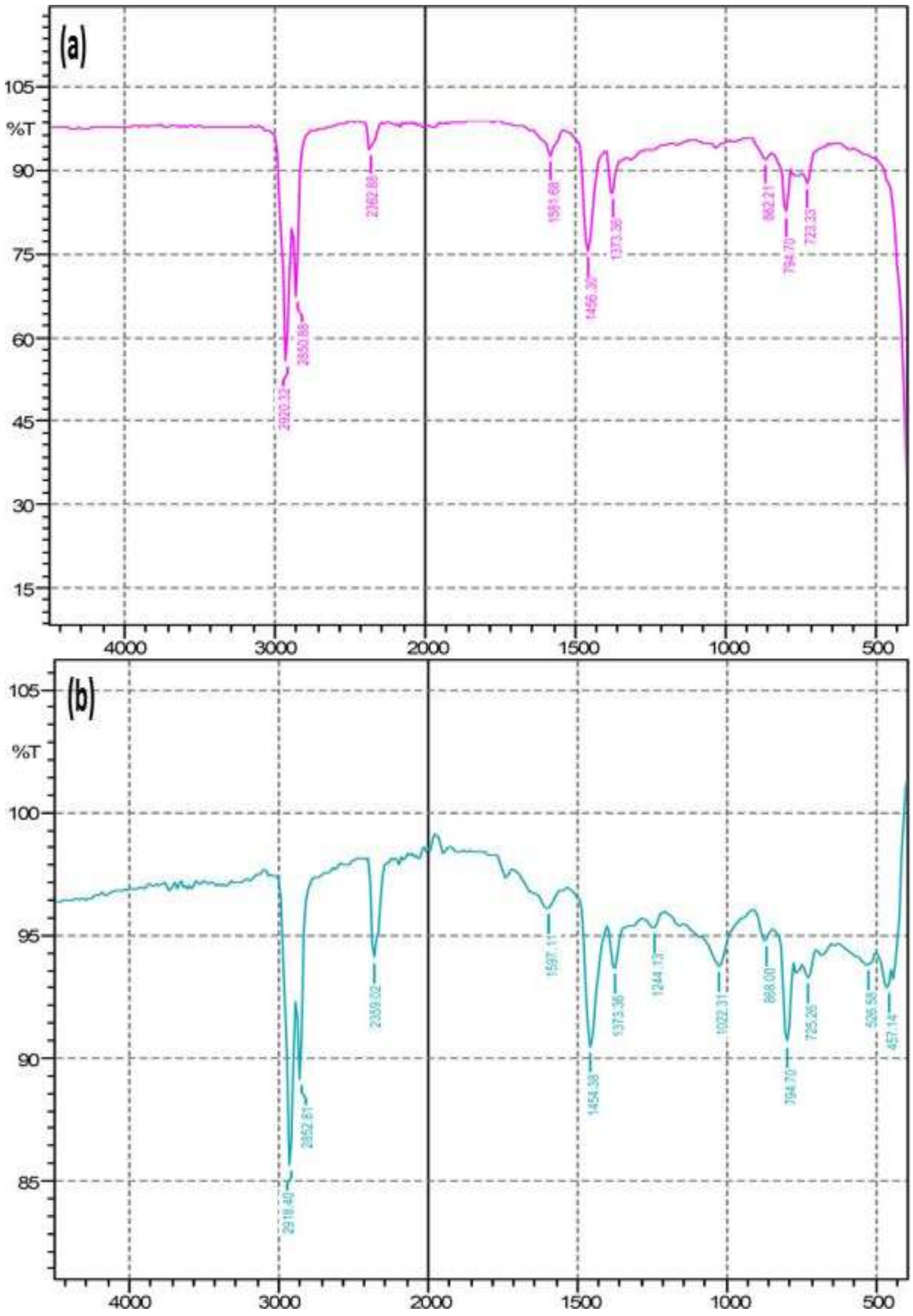

Figure 5.7: IR spectrum of (a) 1EVAMB (b) 3EVAMB

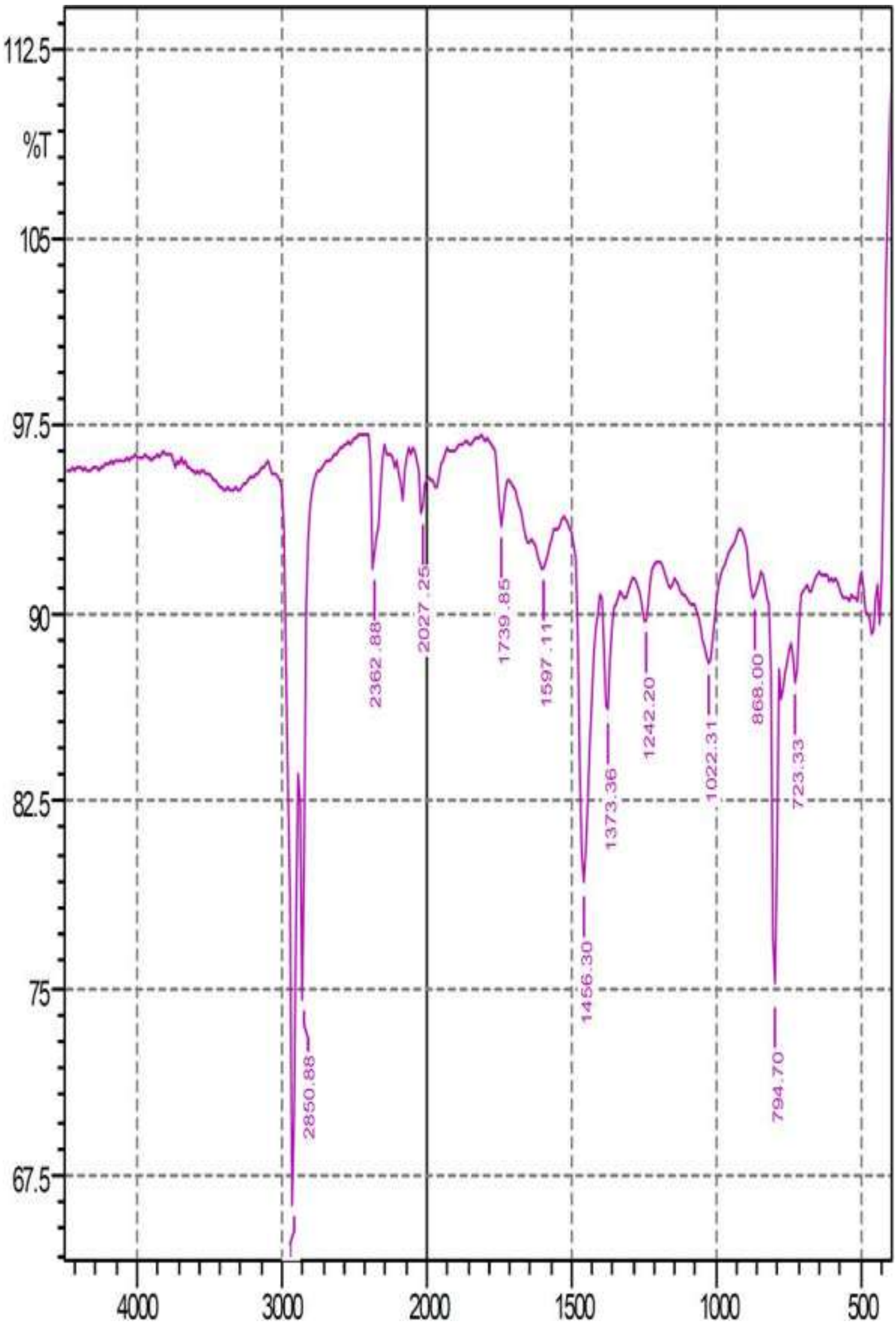

Figure 5.8: IR spectrum of 5EVAMB

Table 5.4 - IR values of bitumen and different compositions of EVAMB

	Wave number (cm^{-1})				
Functional group	**Bitumen**	**EVA**	**1EVAMB**	**3EVAMB**	**5EVAMB**
C-H aromatic / aliphatic stretching	2922, 2856	2916, 2848	2920, 2850	2918, 2852	2920, 2850
C=O stretching	-	1737	-	-	1739
N-H bending	1608	-	1581	1597	1597
C=C aromatic stretching	1454	1465	1456	1454	1456
C=S / S=O stretching	1371	1371	1373	1373	1373
-C-O-C ether	-	1238	-	1244	1242
C-C stretching		1020	-	1022	1022
C-H of CH_3 bending	864, 806	-	862, 794	868, 794	868, 794

Table 5.4 shows important IR peaks of bitumen, EVA and different compositions of EVAMB. Minor shifts in important peaks of bitumen were observed after modification with EVA. Peak of 2922 cm^{-1} (observed in bitumen) shift to 2920 cm^{-1} for 1% and 5% EVAMB and shifts to 2918 cm^{-1} for 3% EVAMB. Peak of 2856 cm^{-1}, shifts to 2850 cm^{-1} for 1% and 5% EVAMB, and to 2852 cm^{-1} for 3% EVAMB. Peak of 1608 cm^{-1}, shifts to 1581cm^{-1} for 1% and 1597 cm^{-1} for 3% and 5% EVAMB. Peak of 1454 cm^{-1} remain unchanged for 3% and shifts to 1456 cm^{-1} for 1% and 5% EVAMB. Peak of 1371cm^{-1}, shift to 1373 cm^{-1} for all the percent mixing of EVA in bitumen. Peak of 1020 cm^{-1}(observed in EVA) shifts to 1022 cm^{-1} for 3% and 5% EVAMB. Peak of 864 cm^{-1}, shifts to 862 cm^{-1} for 1% and to 868 cm^{-1} both for 3% and 5% EVAMB. Peak of 806 cm^{-1}, shifts to 794 cm^{-1} for all modification of bitumen through EVA in bitumen. The IR spectrum of EVA modified bitumen is compared with EVA polymer, this can be interpreted that the intensity of the peak at 1737 cm^{-1} and 1238 cm^{-1} (seen in EVA) decreases in case of EVA modified bitumen. Also the intensity of peak at 2922 cm^{-1}, 2856 cm^{-1} decreases in EVAMB as compare to bitumen. This clearly shows the chemical interaction of polar C-H group of bitumen with C=O group at the EVA polymer. The decrease in intensities of these major peaks is indicative of intermolecular interaction between bitumen and EVA.

5.7 Fourier Transform Infra-Red analysis (FTIR) of EVAMB at different pH

Figure 5.9 (a) and (b) shows IR spectrum of 1EVAMB and 1EVAMB at pH 5.0 respectively. Figure 5.10 (a) and (b) shows IR spectrum of 1EVAMB at pH 7.0 and 1EVAMB at pH 9.0 respectively.

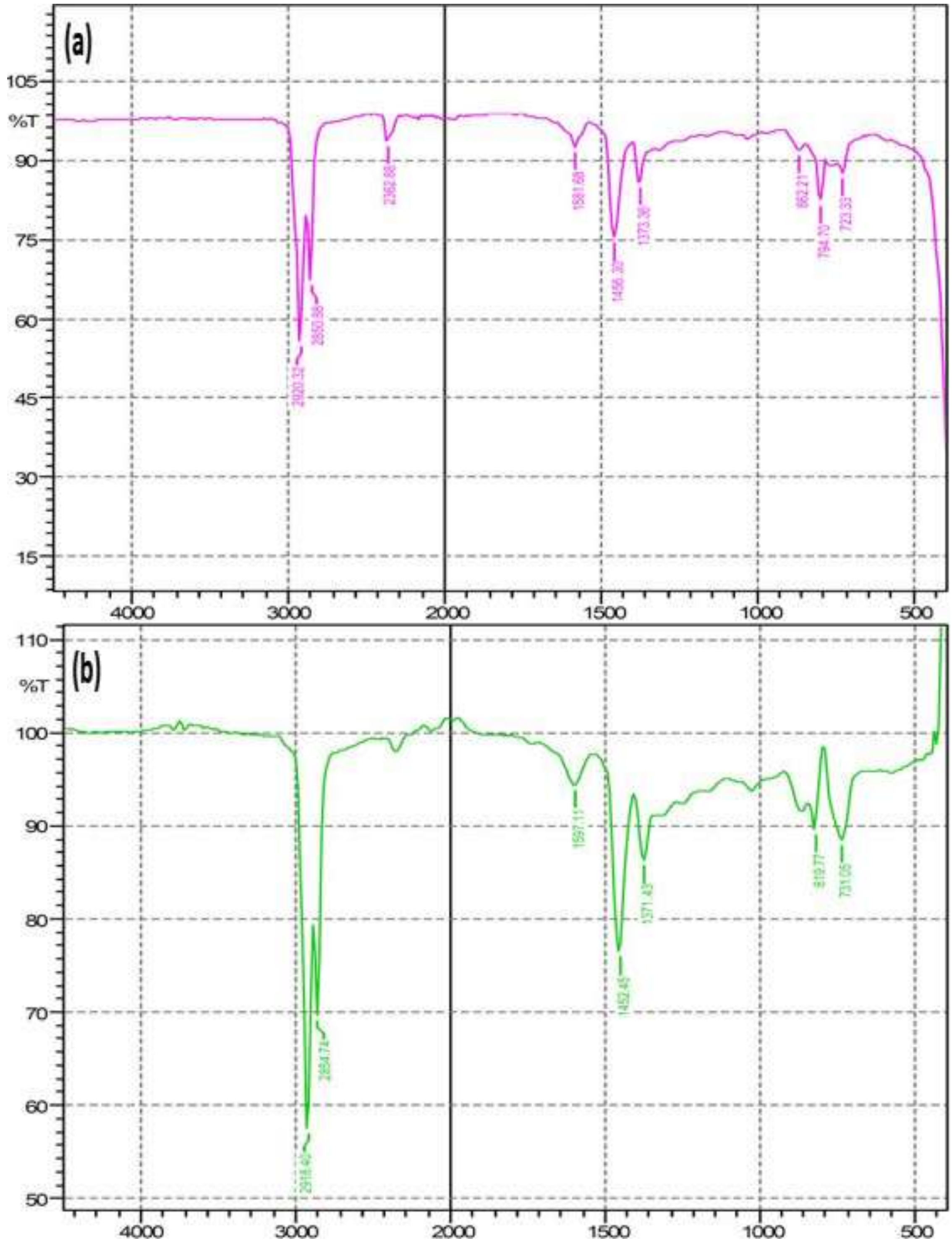

Figure 5.9: IR spectrum of (a) 1EVAMB (b) 1EVAMB at pH 5.0

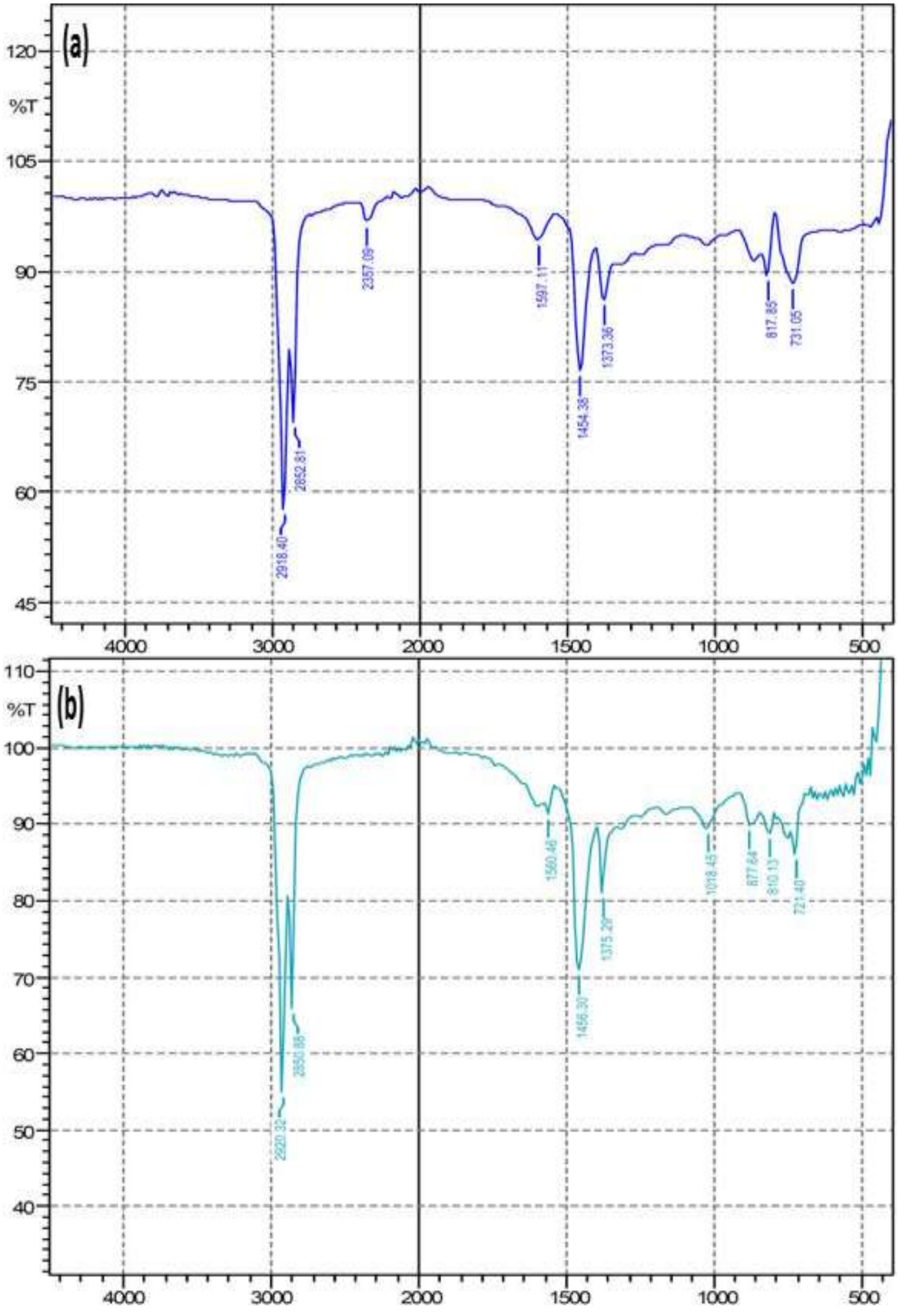

Figure 5.10: IR spectrum of (a) 1EVAMB at pH 7.0 and (b) 1EVAMB at pH 9.0

Table 5.5: IR values of bitumen and 1EVAMB at different pH

	Wave number (cm^{-1})				
Functional group	**Bitumen**	**1EVAMB**	**1EVAMB at pH 5.0**	**1EVAMB at pH 7.0**	**1EVAMB at pH 9.0**
C-H aromatic / aliphatic stretching	2922, 2856	2920, 2850	2918, 2854	2918, 2852	2920, 2850
N-H bending	1608	1581	1597	1597	1560
C=C aromatic stretching	1454	1456	1452	1454	1456
C=S / S=O stretching	1371	1373	1371	1373	1375
C-C stretching	-	-	-	-	1018
C-H of CH_3 bending	864, 806	862,794	819	817	877, 810

Table 5.5 shows IR peak positions of 1EVAMB and 1EVAMB kept at pH of 5.0, 7.0 and 9.0. The IR spectrum of 1EVAMB at different pH is compared with IR of 1EVAMB. Peak of 2920 cm^{-1}, shifts to 2918 cm^{-1} at pH 5.0 and 7.0 but remain unchanged at pH 9.0. Peak of 1581 cm^{-1}, shifts to 1597 cm^{-1} at pH 5.0 and 7.0 and shifts to 1560 cm^{-1} at pH 9.0. Peak of 1456 cm^{-1}, shifts to 1452 cm^{-1} at pH 5.0, and to 1454 cm^{-1} at pH 7.0, but remain unchanged at pH 9.0. Peak of 1373 cm^{-1}, shifts to 1371 cm^{-1} at pH 5.0, shifts to 1375 cm^{-1} at pH 9.0 but remain unchanged at pH 7.0. Peak of 862 cm^{-1}shifts to 819 cm^{-1} at pH 5.0, shifts to 817 cm^{-1} at pH 7.0 and shifts to 877 cm^{-1} at pH 9.0. Figure 5.11 (a) and (b) shows FTIR spectra of 3EVAMB and 3EVAMB at pH 5.0 respectively. Figure 5.12 (a) and (b) shows FTIR spectra of 3EVAMB at pH 7.0 and 3EVAMB at pH 9.0 respectively.

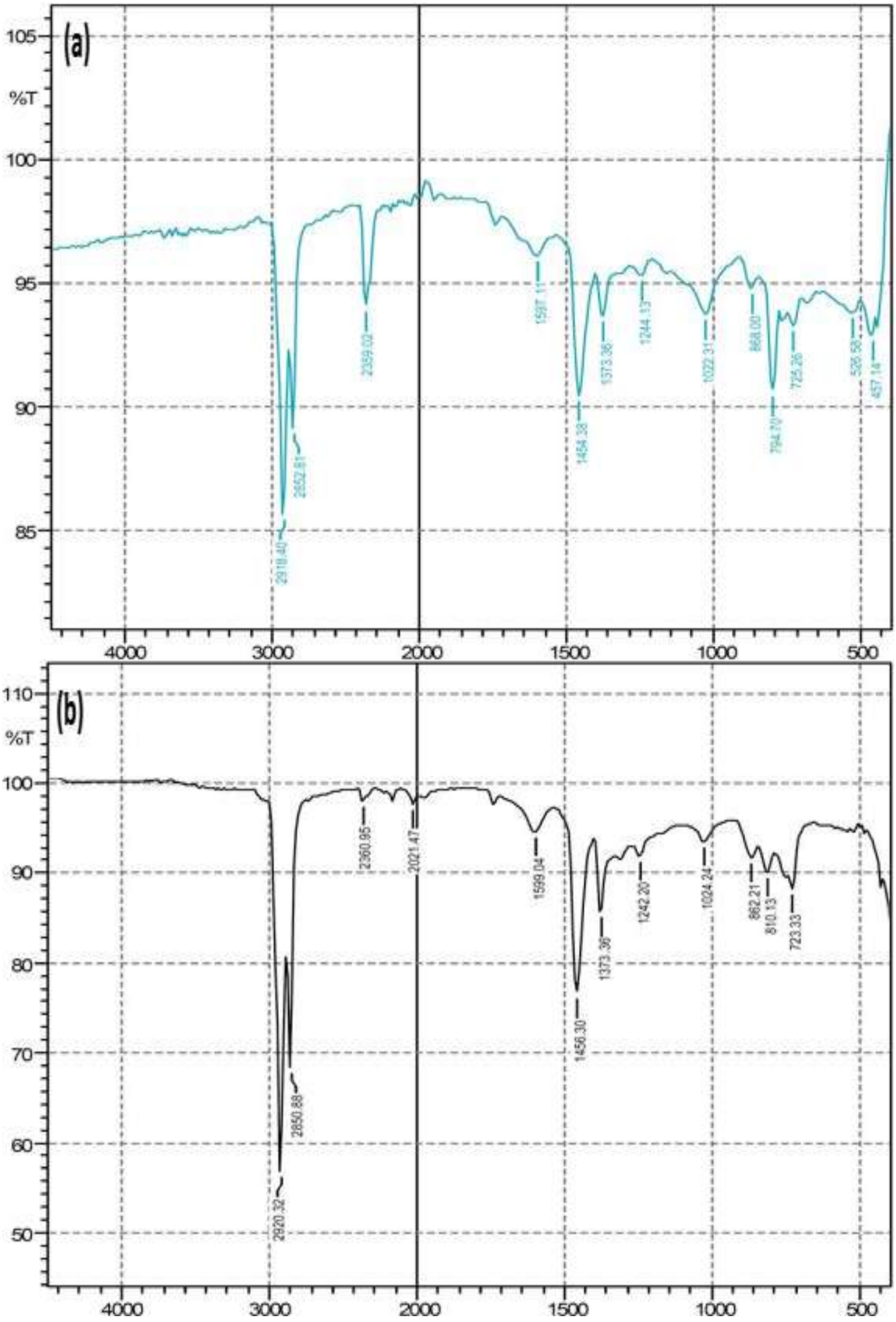

Figure 5.11: IR spectrum of (a) 3EVAMB (b) 3EVAMB at pH 5.0

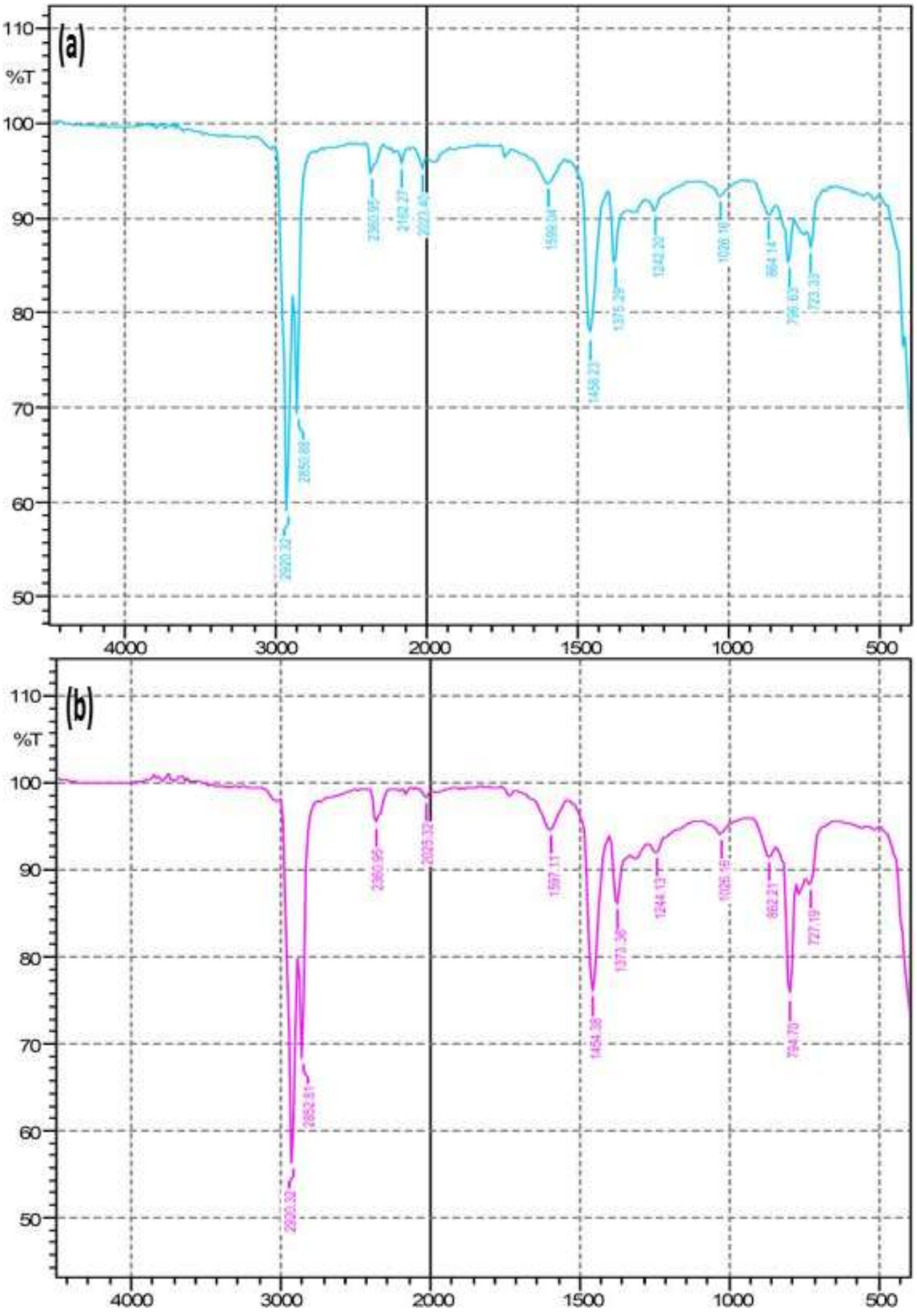

Figure 5.12: IR spectrum of (a) 3EVAMB at pH 7.0(b) 3EVAMB at pH 9.0

Table 5.6: IR spectrum of bitumen and 3EVAMB at different pH

	Wave number (cm^{-1})				
Functional group	**Bitumen**	**3EVAMB**	**3EVAMB at pH 5.0**	**3EVAMB at pH 7.0**	**3EVAMB at pH 9.0**
C-H aromatic / aliphatic stretching	2922, 2856	2918, 2852	2920, 2850	2920, 2850	2920, 2852
N-H bending	1608	1597	1599	1599	1597
C=C aromatic stretching	1454	1454	1456	1458	1454
C=S / S=O stretching	1371	1373	1373	1375	1373
-C-O-C ether	-	1244	1242	1242	1244
C-C stretching	-	1022	1024	1026	1026
C-H of CH_3 bending	864, 806	868,794	862, 810	864, 796	862, 794

Table 5.6 shows IR peak positions of 3EVAMB and 3EVAMB kept at pH of 5.0, 7.0 and 9.0. The IR spectrum of 3EVAMB at different pH is compared with IR of 3EVAMB. Peak of 2918 cm^{-1}, slightly shifts to 2920 cm^{-1} at all the pH (pH 5.0, 7.0 and 9.0). Peak of 2852 cm^{-1} shifts to 2850 cm^{-1} at pH 5.0 and 7.0 but remain unchanged at pH 9.0. Peak of 1597 cm^{-1}, shifts to 1599 cm^{-1} at pH 5.0 and 7.0 and remain unchanged at pH 9.0. Peak of 1454 cm^{-1}, shifts to 1456 cm^{-1} at pH 5.0, shifts to 1458 cm^{-1} at pH 7.0 and remain unchanged at pH 9.0. Peak of 1373 cm^{-1}, shifts to 1375 cm^{-1} at pH 7.0 but remain unchanged at pH 5.0 and 9.0. Peak of 1244 cm^{-1}, shifts to 1242 cm^{-1} at pH 5.0 and 7.0 and remain unchanged at pH 9.0. Peak of 868 cm^{-1}, shifts to 862 cm^{-1} at pH 5.0 and pH 9.0, and shifts to 864 cm^{-1} at pH 7.0. Figure 5.13 (a) and (b) shows FTIR spectra of 5EVAMB and 5EVAMB at pH 5.0 respectively. Figure 5.14 (a) and (b) shows FTIR spectra of 5EVAMB at pH 7.0 and 5EVAMB at pH 9.0 respectively.

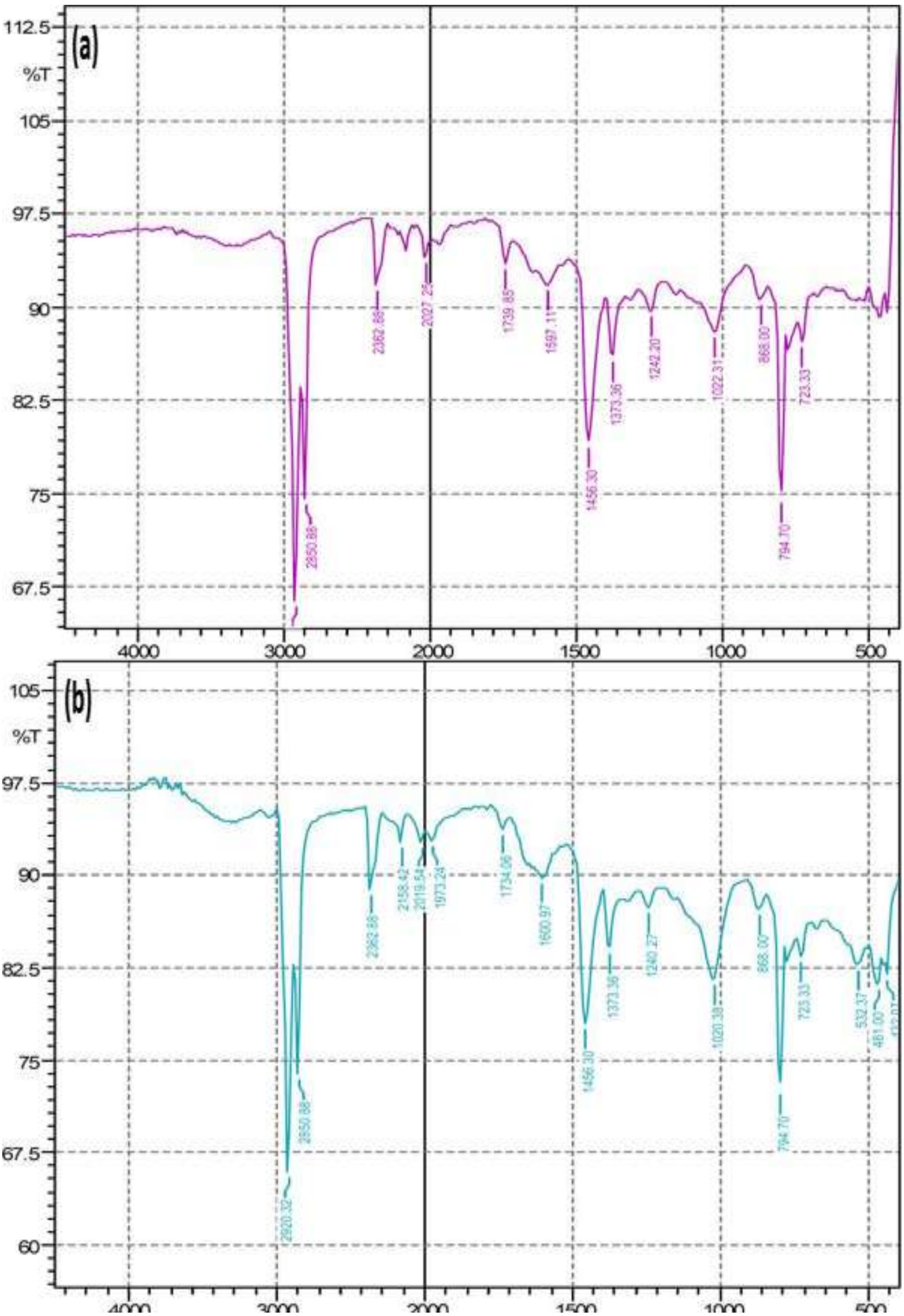

Figure 5.13: IR spectrum of (a) 5EVAMB (b) 5EVAMB at pH 5.0

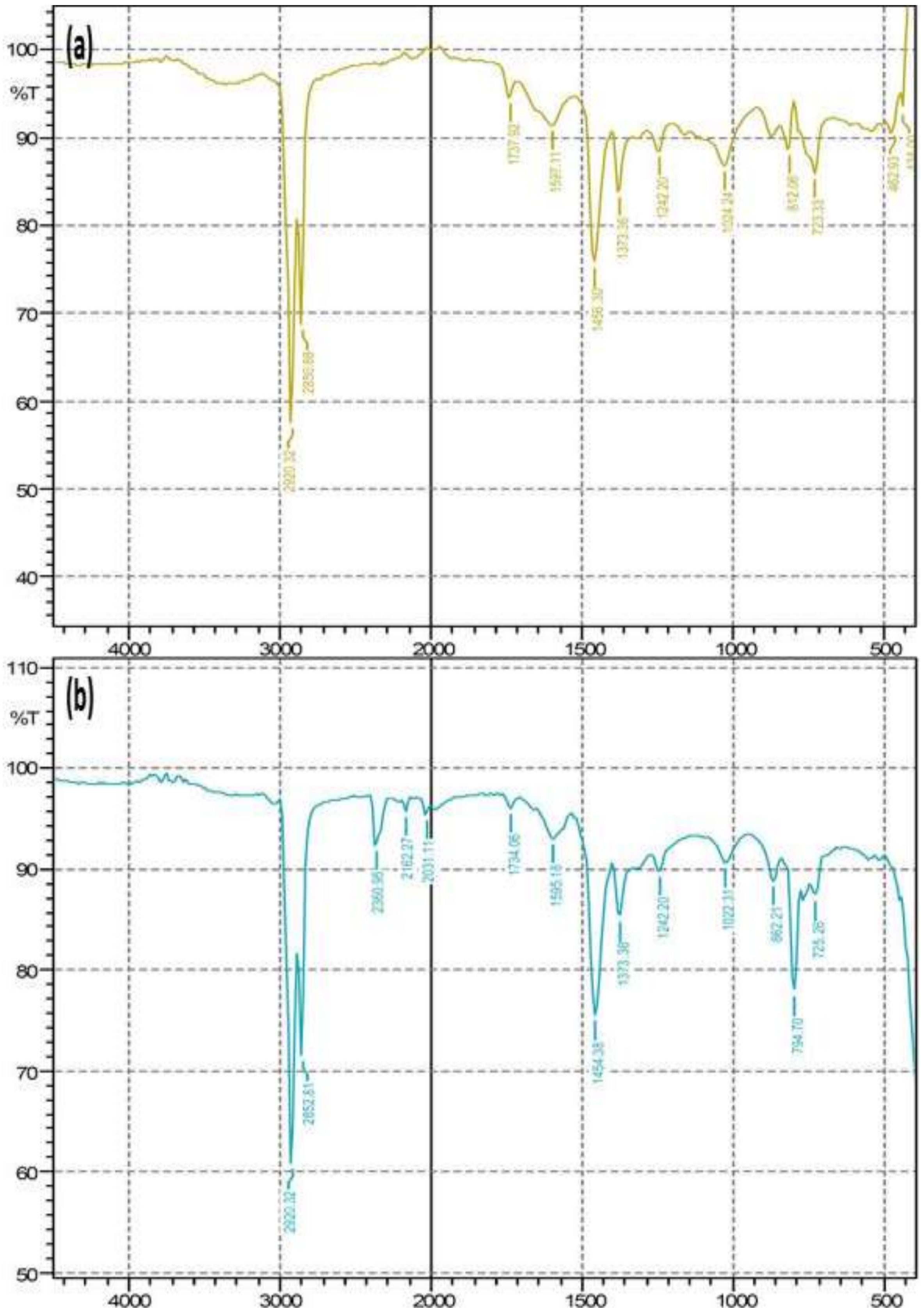

Figure 5.14: IR spectrum of (a) 5EVAMB at pH 7.0(b) 5EVAMB at pH 9.0

Table 5.7: IR spectrum of bitumen and 5EVAMB at different pH

	Wave number (cm^{-1})				
Functional group	**Bitumen**	**5EVAMB**	**5EVAMB at pH 5.0**	**5EVAMB at pH 7.0**	**5EVAMB at pH 9.0**
C-H aromatic / aliphatic stretching	2922, 2856	2920, 2850	2920, 2850	2920, 2850	2920, 2852
C=O stretching	-	1739	1734	1737	1734
N-H bending	1608	1597	1600	1597	1595
C=C aromatic stretching	1454	1456	1456	1456	1454
C=S / S=O stretching	1371	1373	1373	1373	1373
-C-O-C ether	-	1242	1240	1242	1242
C-C stretching	-	1022	1020	1024	1022
C-H of CH_3 bending	864, 806	868	868	812	862

Table 5.7 shows IR peak positions of 5EVAMB and 5EVAMB kept at pH of 5.0, 7.0 and 9.0. The IR spectrum of 5EVAMB at different pH is compared with IR of 5EVAMB. Peak at 2920 cm^{-1} remains unchanged at all the pH studied. Peak of 2850 cm^{-1}, shifts to 2852 cm^{-1}at pH 9.0 and remain unchanged for pH 5.0 and 7.0. Peak of 1739 cm^{-1}, shifts to 1734 cm^{-1} at pH 5.0, 9.0 and shifts to 1737 cm^{-1} at pH 7.0. Peak of 1597 cm^{-1}, shifts to 1600 cm^{-1} at pH 5.0 and shifts to 1595 cm^{-1} at pH 9.0 and remain unchanged at pH 7.0. Peak of 1456 cm^{-1} shifts to 1454 cm^{-1} at pH 9.0, but remain unchanged at pH 5.0 and 7.0. Peak of 1373 cm^{-1} remain unchanged at all the pH of study. Peak of 1242 cm^{-1} shifts to 1240 cm^{-1} at pH 5.0, but remain unchanged at pH 7.0 and 9.0. Peak at 868 cm^{-1}, shifts to 812 cm^{-1} at pH 7.0, 862 cm^{-1} at pH 9.0 and remain unchanged at pH 5.0. The IR spectrum of EVA modified bitumen at different pH (pH 5.0, 7.0 and 9.0) clearly shows that there is very less shift in frequency of different peaks in case of EVA modified bitumen at different pH. This means that

there is very less effect of pH on EVAMB thus indicating that EVA modified bitumen are resistant to pH.

5.8 Thermo-gravimetric analysis of bitumen and EVA modified bitumen

TGA analysis of bitumen, 5EVAMB and 5EVAMB exposed to different medium of pH 5.0, 7.0 and 9.0 was conducted. In case of EVAMB, 5% composition was found as optimum concentration and therefore chosen for the TGA analysis. The thermo-gram of bitumen clearly shows three stage of decomposition. When the temperature is less than 350 °C, aromatics and saturates are expected to decompose. At temperature greater than 350 °C but less than 500 °C asphaltene, resins and aromatics decomposes. When temperature exceeds 500 °C there is major decomposition of asphaltenes and few aromatics as well as resins (136).

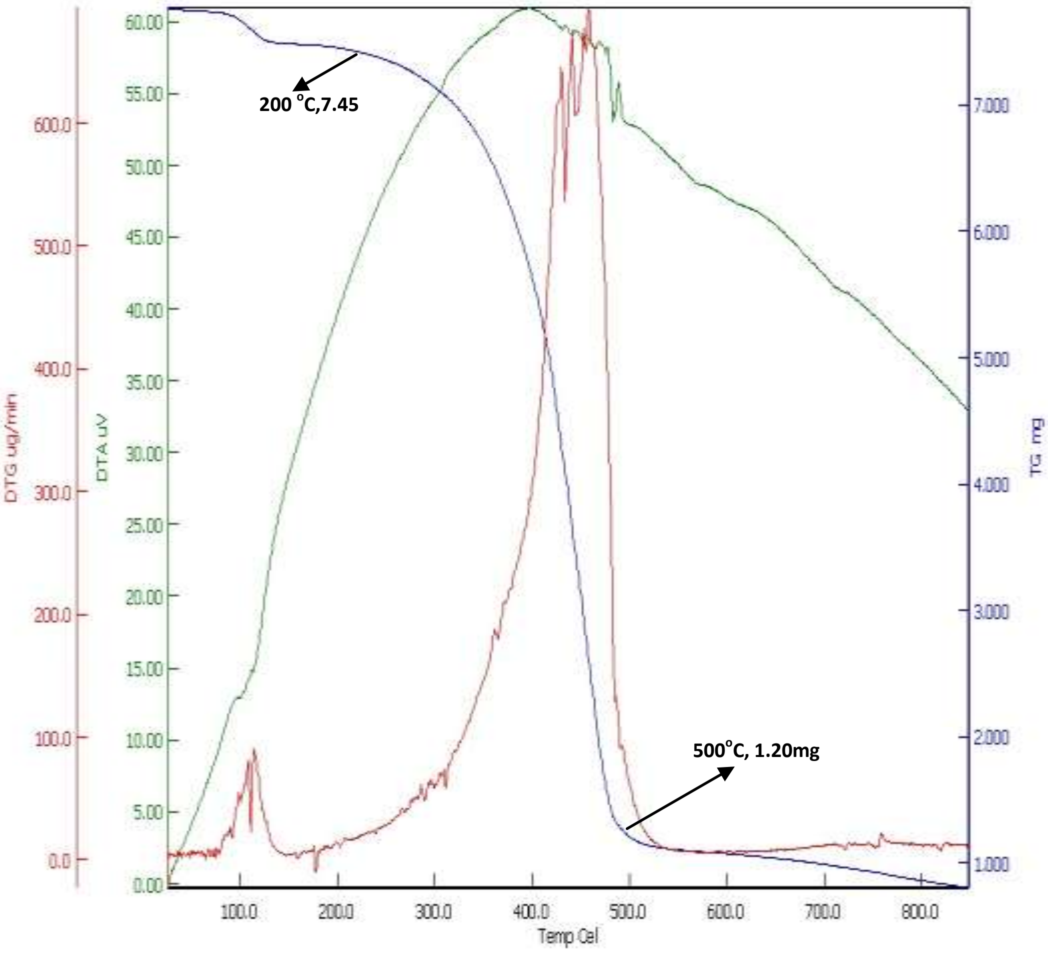

Figure 5.15: TGA plot of bitumen

Figure 5.15 shows TGA plot of bitumen which indicates that major decomposition starts at 200 $^{\circ}$C and ends at 500 $^{\circ}$C with 79.83% weight loss from 7.45 mg to 1.20 mg. The residual mass is 10.23% that is 0.8 mg which is because of presence of some metal ions.

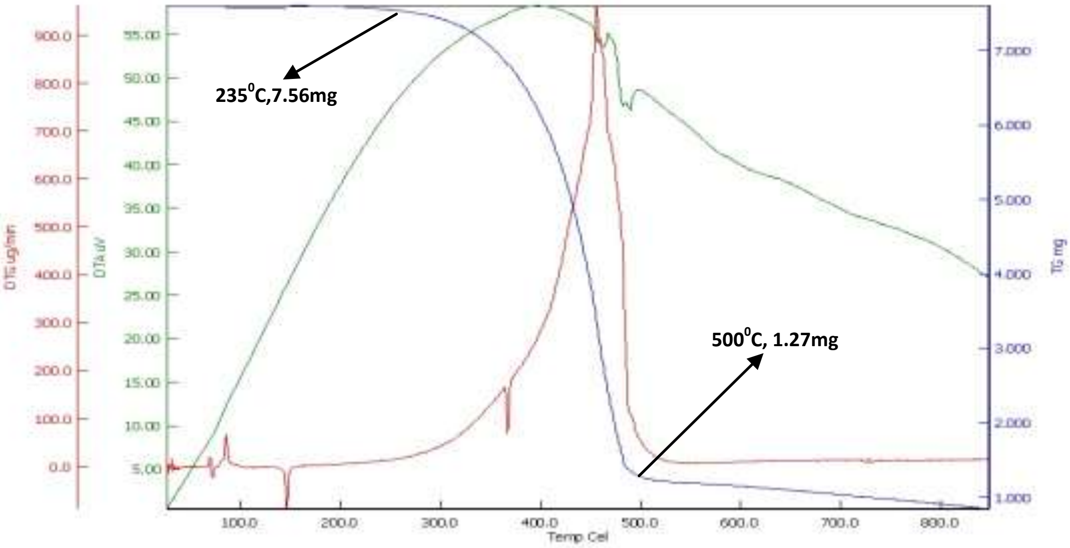

Fig 5.16: TGA plot of 3EVAMB

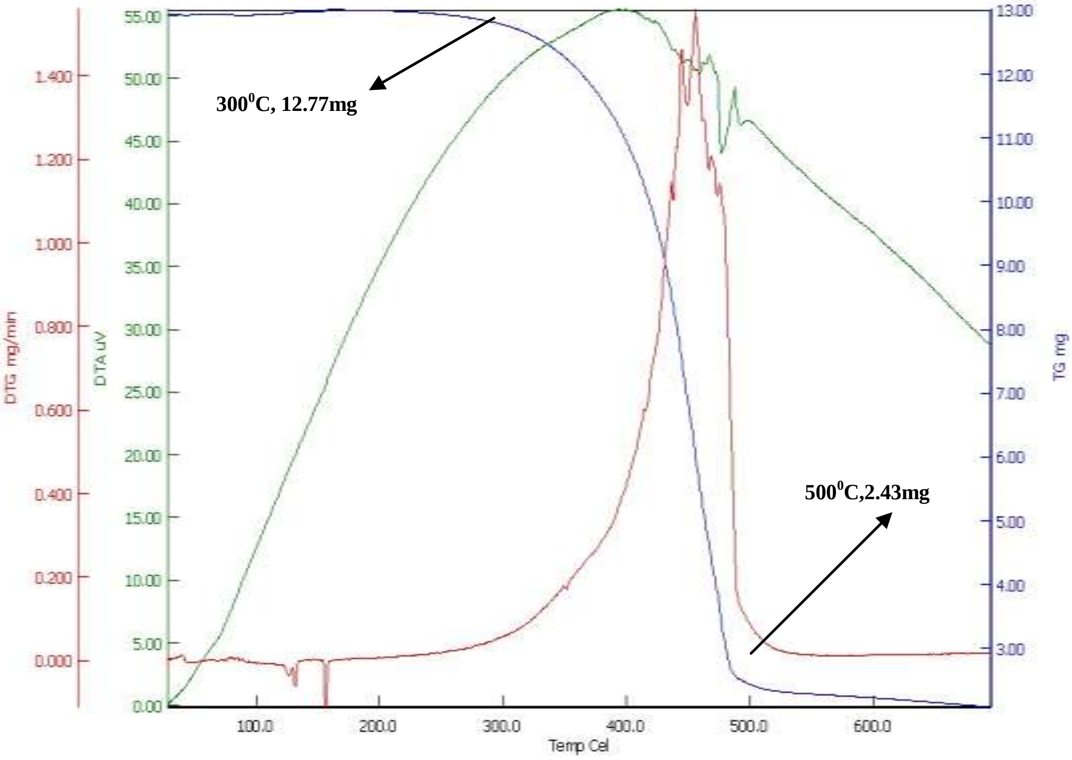

Figure 5.17: TGA plot of 5EVAMB

Figure 5.16 shows TGA plot of 3EVAMB which indicates that major decomposition starts at 235 °C and ends at 500 °C with 81.11% weight loss from 7.56 mg to 1.27 mg. The residual mass is 10.84% that is 0.8 mg which is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 235 °C in case of 3EVA modified bitumen. This means thermal stability of bitumen increases after modification with EVA. Figure 5.17 shows TGA plot of 5EVAMB which indicates that major decomposition starts at 300 °C and ends at 500 °C with 79.73% weight loss from 12.77 mg to 2.43 mg. The residual mass is 16.06% that is 2.08 mg which is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 300 °C in case of 5EVA modified bitumen. This clearly shows that 5EVAMB is thermodynamically more stable than 3EVAMB.

This is evident from TGA plots that EVA modified bitumen are thermally more stable than bitumen as decomposition of bitumen is delayed by adding EVA polymer. Moreover 5EVAMB is more stable than 3EVAMB due to same reasons.

5.9: Thermo-gravimetric analysis of 5EVAMB at different pH

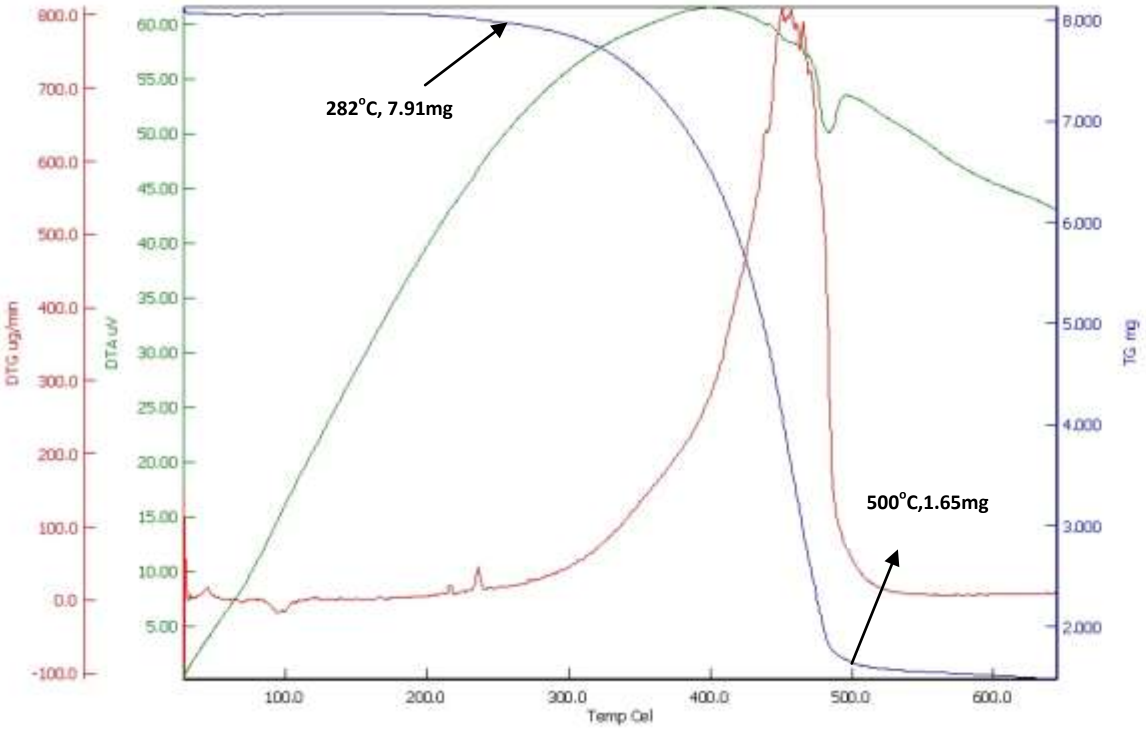

Figure 5.18: TGA plot of 5EVAMB at pH 5.0

Fig 5.18 shows TGA plot of 5EVAMB which is exposed to pH 5.0. This plot indicates that major decomposition starts at 282 °C and ends at 500 °C with 76.5% weight loss from 7.91 mg to 1.65 mg. The residual mass is 18.11% that is 1.48 mg which is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C in case of bitumen to 282 °C in case of 5EVA modified bitumen at pH 5.0.

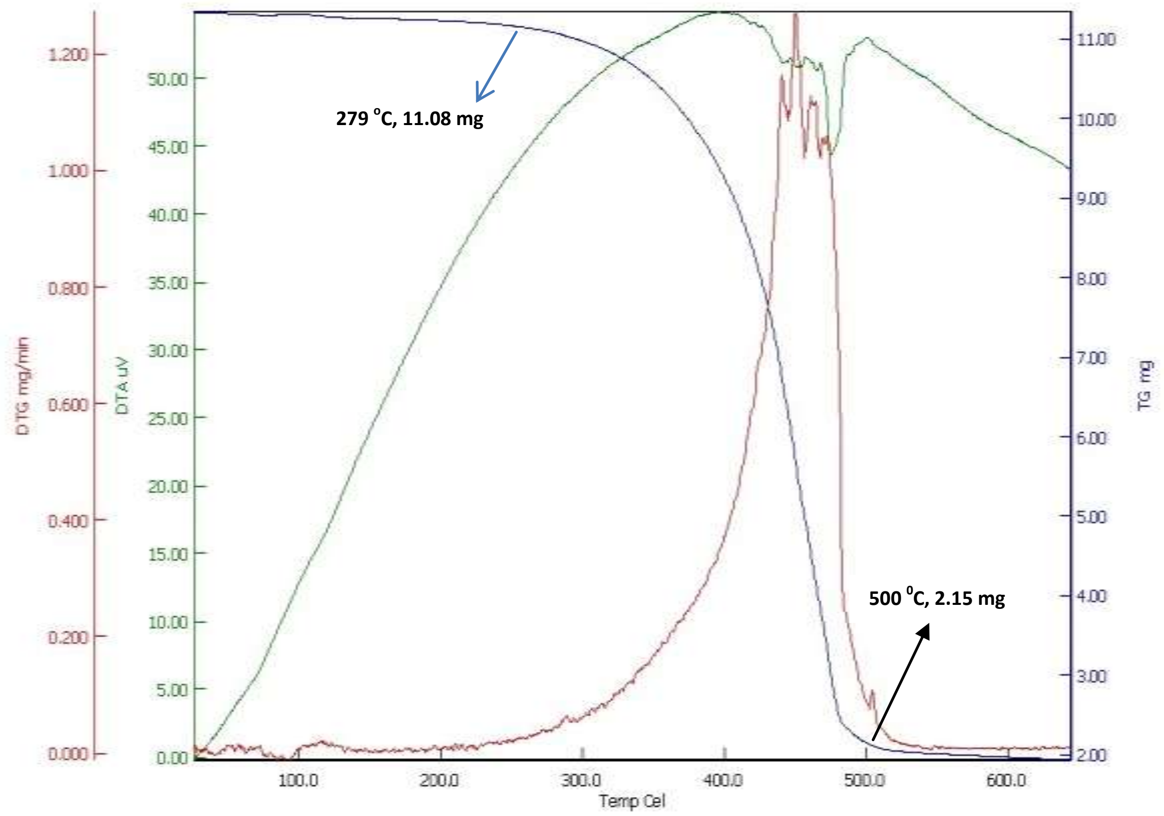

Figure 5.19: TGA plot of 5EVAMB at pH 7.0

Figure 5.19 shows TGA plot of 5EVAMB exposed to neutral water (pH 7.0) for 24 hr. This plot indicates that major decomposition between 279 °C to 500 °C with 76.09% weight loss (from 11.08 mg to 2.15 mg). The residual mass of 16.49% (1.93 mg) is probably due to presence of some metal ions. The starting temperature of decomposition has been increased from 200 °C (in case of bitumen) to 279 °C in case of 5EVA modified bitumen at pH 7.0.

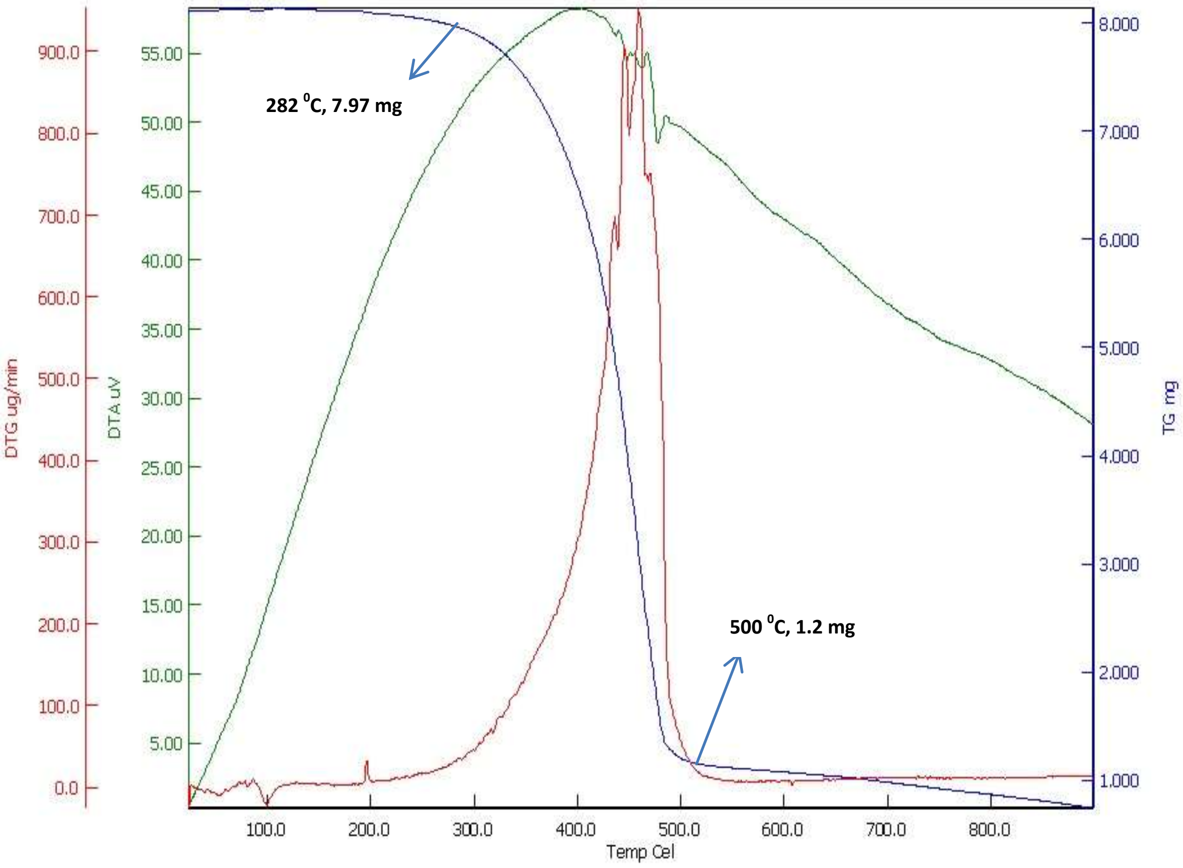

Figure 5.20: TGA plot of 5EVAMB at pH 9.0

Figure 5.20 shows TGA plot of 5EVAMB dipped in water of pH 9.0 (maintained by NaOH). Major decomposition is done in between 282 °C to 500 °C with 79.5% weight loss (from 7.97 mg to 1.2 mg). The residual mass is 8.78% (0.74 mg) is because of presence of some metal ions. The temperature at which decomposition starts has been increased from 200 °C (in case of bitumen) to 282 °C in case of 5EVA modified bitumen at pH 9.0. Table 5.8 gives initial and final temperatures of decomposition of EVA modified bitumen and EVAMB exposed to different pH with percentage loss in weight.

Table 5.8: TGA values of Bitumen, 3EVAMB, 5EVAMB and 5EVAMB kept at different pH

	Step	**T_i(°C)**	**T_f(°C)**	**Wt. Loss (%)**
Bitumen	**1.**	86	125	2.58
	2.	200	500	79.83
	3.	500	848	5.14
3EVAMB	**1.**	235	500	81.11
	2.	500	848	5.58
5EVAMB	**1.**	300	500	79.73
	2.	500	695	2.71
5EVAMB at pH 5.0	**1.**	282	500	76.5
	2.	500	645	2.03
5EVAMB at pH 7.0	**1.**	279	500	76.09
	2.	500	645	1.85
5EVAMB at pH 9.0	**1.**	282	500	79.5
	2.	500	899	5.43

This is clearly depicted by the table that pH has little effect on the thermodynamic stability of EVA modified bitumen hence it is resistant to pH variations.

5.10 Conclusion

There is enhancement in physical, mechanical properties of bitumen after modification with EVA polymer. SEM analyses of the water logged EVA modified bitumen surface was analyzed, no cracks/ holes on the surface of EVA modified bitumen were observed as in case of LDPMB and HDPMB. IR spectra of uniform quantity of bitumen/ EVA modified bitumen (pellets by mixing 1.0 mg of bitumen / EVAMB with 3.0 mg of KBr) was taken and compared. The important peaks for the expected functional groups are shown in Table (5.3-5.7). The expected functional groups are N-H, C-H, C-C, C=C,C=S etc. The unusual high intensity of the peaks in between 2850-3000 cm^{-1} in the spectrum of bitumen is worth of analyzing. In almost all of the cases this region is known for the sp^2 or sp^3 C-H stretching band, which is very weak in nature. The high intensity of such peaks indicates high polarity in C-H stretching band. This highly polar C-H stretching band has the tendency to interact with electronegative element like oxygen of H_2O/ H_3O^+/ OH^-. There was remarkable change in the IR spectrum of EVA modified bitumen as compared to unmodified bitumen. The intensity of the peak at 1737 cm^{-1} and 1238 cm^{-1} (seen in EVA) decreases in case of EVA modified bitumen. Also the intensity of peak at 2922 cm^{-1}, 2856 cm^{-1} decreases in EVAMB as compare to bitumen. The decrease in intensities of these major peaks is indicative of intermolecular interaction between bitumen and EVA. This clearly shows the chemical interaction of polar C-H group of bitumen with C=O group at the EVA polymer. TGA values clearly indicate that on moving from bitumen to EVA modified bitumen, the temperature of major decomposition shift towards a higher value. This is a positive outcome, because EVA modified bitumen shows greater thermodynamic stability as compare to unmodified bitumen. When this modified bitumen is exposed to different pH (5.0, 7.0 and 9.0), again the TGA values indicate shifting of major decomposition temperature towards higher side thus confirming that pH has no effect on thermodynamic stability of EVA modified bitumen. Thus it can be concluded that EVA modified bitumen is resistant to pH variations and also thermodynamically more stable than bitumen.

CHAPTER 6

COMPARISON OF DATA, CONCLUSION AND RECOMMENDATIONS

6.1 Comparison of data

The Individual analysis of the polymers used as bitumen modifiers, is followed by comparative analysis of the polymers for their behavior. Table 6.1 gives a brief comparison of the properties of polymer modifiers used in the present research.

Table 6.1: Comparative table of polymers used as modifier

Property	% of polymer	LDPMB	HDPMB	EVAMB
Penetration point at 25°C	0%	68	68	68
	1.0%	55	52	50
	3.0%	45	43	46
	5.0%	33	41	38
	7.0%	30	40	36
Softening point (°C)	0%	48	48	48
	1.0%	50	52	56
	3.0%	54	55	63
	5.0%	55	58	70
	7.0%	61	63	76
Ductility (cm)	0%	76	76	76
	1.0%	70	68	66
	3.0%	61	58	61
	5.0%	54	39	55

SEM	Doped LDPE is found in white patches in the bitumen. When 5LDPMB is exposed to different conditions of pH, SEM analysis shows crack and holes in acidic and basic medium respectively.	Doped HDPE is found in white patches in the bitumen. When 3HDPMB is exposed to different conditions of pH , SEM analysis shows crack and holes in acidic and basic medium respectively.	Uniform dispersion of EVA in the bitumen is obtained. When 5EVAMB is exposed to different conditions of pH, SEM analysis shows no crack and holes in acidic and basic medium respectively.
FTIR	Physical interaction between bitumen and LDPE.	Physical interaction between bitumen and HDPE.	Intermolecular interaction between bitumen and EVA.
TGA	5LDPMB is thermally more stable than bitumen because major decomposition starts at 265 °C.	3HDPMB is thermally more stable than bitumen because major decomposition starts at 275 °C.	5EVAMB is thermally more stable than bitumen because major decomposition starts at 300 °C.

Penetration point of bitumen decreases with the increase in concentration of LDPE, HDPE as well as EVA. EVA yields maximum hardness out of the three polymers at 1.0% mixing of the polymer. It has been observed that for HDPE decrease in penetration value is more as compare to LDPE/EVA at 3.0% mixing. Hence bitumen becomes harder with the modification of HDPE as compare to LDPE/EVA up to 3.0% mixing by mass of bitumen. The penetration value for LDPMB is lower than HDPMB, EVAMB at high mass percentage of polymer (5.0%, 7.0%), depicts that LDPMB yield more hardness as compare to HDPMB and EVAMB. Softening point of bitumen increases with the increase in concentration of LDPE, HDPE as well as EVA. From the comparative table it is clear that the increase in softening point is more in case of EVA followed by HDPE and LDPE. Ductility of bitumen decreases with the increase in concentration of LDPE, HDPE as well as EVA but bitumen cannot be modified with LDPE or EVA beyond 5.0% mixing otherwise modified bitumen will have very low value of ductility and that is not acceptable. In case of bitumen modification using HDPE, the polymer should not be used beyond 3.0% mixing by mass of bitumen. SEM analysis shows crack and holes in case of LDPMB and HDPMB dipped in acidic and basic medium respectively but in case of EVAMB there is no such observation. Hence EVAMB are resistant to pH variations in the environment. FTIR studies throw light on the type of interaction between bitumen and the three polymers used. There is only physical interaction between bitumen and non-polar polymers which are used in the research that is LDPE and HDPE. The polar polymer that is EVA shows intermolecular interaction with the bitumen. TGA data shows that 5LDPMB, 3HDPMB and 5EVAMB have greater thermodynamic stability than bitumen. Among the three polymers 5EVAMB is thermodynamically most stable followed by 3HDPMB and 5LDPMB.

6.2 Conclusion

The condition of roads is really pathetic in India. After rains, water accumulates on the roads forming potholes, roads break frequently and need maintenance on annual basis thus disturbing national economy, as lot of money is wasted in the process. This problem can be solved by the use of pH resistant modified bitumen. Thus in the present research modified bitumen is synthesized that resist the changes in temperature as well as pH. Important conclusions that can be drawn from the findings of present research work are

1. Penetration point of bitumen decreases after modification with LDPE, HDPE and EVA.
2. Softening point of bitumen enhances after modification with above said polymers and this shows improvement in resistance towards rutting and cracking.
3. Ductility of bitumen decreases after the modification process and these are the acceptable values according to IS specifications up to 5.0% of LDPE and EVA content and 3.0% of HDPE content. Thus the optimum concentration for modification of bitumen is 5.0% in case of LDPE as well as EVA and 3.0% in case of HDPE respectively.
4. These concentrations also have maximum thermal resistance which is indicated by the results obtained from the penetration tests conducted on modified bitumen at different temperatures.
5. Enhancement in properties of bitumen with the addition of HDPE is more as compare to LDPE.
6. FTIR analysis proved that interaction between bitumen and polyethene (both LDPE and HDPE) is a physical process. On the other hand there is chemical interaction between bitumen and EVA.
7. SEM analysis proves that LDPE and HDPE modified bitumen are not resistant to pH variations so these are not good modifiers in case of damage caused to roads due to water logging during rains. EVA modified bitumen can resist the changes in pH and hence act as a solution of damage caused by water logging problem on roads.
8. TGA analysis proves that 5EVAMB is thermally most stable one followed by 3HDPMB and 5LDPMB.

6.3 Future recommendations

1. Effect of UV radiation that is photochemical effect on modified bitumen need to be studied in future.
2. Modified bitumen using different polar polymerase needed to be tested for the effect of different types of pH.
3. Experimental results need to be confirmed by using modified bitumen in the field of application and using other techniques.

4. Modification of other grades of bitumen using non polar and polar polymers can be carried out and the effect of different types of pH on such modified bitumen can be a thrust area of research in this field.
5. Techniques like AFM (atomic force microscopy) can be used to find phase images of modified bitumen in addition to SEM.

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ANNEXURE

LIST OF PUBLICATIONS

1. Sonu Sharma, Sitansh Sharma, Niraj Upadhyay, Composition Based Physicochemical Analysis of Modified Bitumen by HDPE/LDPE, *Oriental Journal of Chemistry*, **2019**, *35(3),* 997-1003.
2. Sonu Sharma, Sitansh Sharma, Niraj Upadhyay, Modifier based Enhancement in Physical and Chemical Properties of Bitumen. *Oriental Journal of Chemistry***, 2019**, *35(3),* 1167-1173.
3. Poster presentation on Polythene as a Modifier in Bitumen in 106th Women Science Congress, on 3-7 January 2019 at Lovely Professional University.
4. Oral presentation on the topic FTIR analysis of LDPE modified Bitumen in an International Multi-stream Conference on Futuristic Approach towards Employability and Enterpreneurship & Industrial Summit on 28th Oct 2018 at Ludhiana, Punjab.
5. Oral presentation on the topic Managing Plastic Waste – An eco-friendly approach towards environment management, in a National Conference on 3rd Nov 2016 at SGHRS College for Women, Chabbewal, Hoshiarpur.
6. Oral presentation on Technological Innovation of using Waste Plastic in Road making Industry in an International Multi-stream Conference on Technology and Life on 8th Nov 2015 at CKD Institute of Management and Technology,Tarn Taran, Punjab
7. Poster presentation on Polythene assisted enhancement of binder property of bitumen in Bhartiya Vigyan Sammelan and Expo on 11-14 Oct 2012 at Lovely Professional University.

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M.Sc. Chemistry from GNDU, Amritsar : 1998-2000(70.5%), IIIrd in University

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10+2 Medical, from Hindu College, Amritsar :1994 (64.8%)

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