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SYNOPSIS

Bitumen is a primary engineering material. Its thermoplastic nature, its water resistance and its adhesion toward most other substances make it unique for roofing applications. Recent developments of modifying bitumen with polymers has resulted in a major change in roofing design and application. The polymer bitumen membrane is a 'composite material' resulting from two elements. The two components work in synergy [10]. Bitumen offers waterproofing capacity, while polymer must improve its resistance to heat, to strain, improve its flexibility at low temperature and resistance against compound ageing and increase in softening point.

Bitumen generally used is Industrial grade and polymeric modifiers used are Atactic polypropylene(APP) and Styrene butadiene Styrene(SBS).

In the present study modification of Paving grade bitumen is studied and evaluated. The modifiers used are APP and SEBS (styrene ethylene butadiene styrene) and the combinations of both. Various compositions of Bitumen-modifier blend were prepared by mixing them in a bitumen mixer at specified conditions. Some formulations were optimized and used for further modifications.

The results show remarkable improvement in physical and mechanical properties as compared to virgin bitumen.

Chapter 1

1.1 INTRODUCTION

Modified bitumen systems are the fastest growing waterproof roofing systems in today's competitive market. Modified bitumen sheets are composed primarily of polymer modified bitumen reinforced with one or more plies of fabric such as polyester, glass fiber or a combination of both [4]. Modified bitumen roofings are generally made from superior grade bitumen. In the present study paving grade bitumen is modified with APP and SEBS and a combination of both. The effectiveness of modification is evaluated by studying various properties. Using this Polymer modified bitumen various formulations with reinforcing fillers, fiber and mats were made to match commercially available modified membranes.

Modified bitumen membranes are attractive for many applications, particularly in climates where roofing systems are exposed to thermal shock or freeze thaw cycles. They offer important advantages over conventional roofing system, including choice of application method , superior strength, durability and moisture protection with fewer plies ,systems engineered for modern as well as traditional building design, attractive, lightweight designs, and composite systems

As long as Bitumens, coal tar pitch and Asphalt have been used for roofing people have tried to improve their properties. Truely effective modified bituminous materials originated in Europe in the late 1950s when several organic chemists made a breakthrough discovery that polymers could be blended with asphalt to create materials with waterproofing properties of Asphalt and the flexibility, elongation, and recovery properties of Rubber or Plastic compound.[11]

Over the last two years, USA is the country where most of the research is done, followed by China, Canada and some European countries (France, Italy, Great Britain and

Spain). Among the companies that have been filing patents on PMA over the last two years, Marathon Ashland Petroleum LLC is the leading one.

The Goodyear Tire & Rubber Company, Fina Technology, Polyphalt LLC, BASF Corporation and Ergon Incorporated are also reported. There have been lots of movements in the marketing area.

The interest for PMA technology has been increasing, and so the number of companies which commercialize it, and their earnings. For example, Canada based Polyphalt, which develops and markets polymer modified asphalt reports its revenues (from royalties and license fees)increased 119 percent in the nine-month period ended on December 31, 2001 New PMA plants have also been opened.

In the most recent study (February, 2000) from the Freedonia Group on Asphalt Products and Markets US demands for asphalt products is forecasted to advance three percent per annual through 2003, and so will do the adoption of the Superpave program's performance based specifications for road projects. This will generate a greater demand for polymer modified asphalts.

1.1.1) MEMBRANES

The use of Built-up roofing (BUR) for over a century has made this a class by itself. It is still the single biggest type of roofing installed. The new materials introduced as alternatives to BUR are products of different chemical formulations. Although no panacea, they do provide a wide range of options that meet required performance characteristics. The first generation of these materials suffered some setbacks due to lack of design and performance criteria and lack of experience. However, improvements in their compositions, reinforcing, and lap joint techniques have resulted in a second generation of products with better and progressively improved performance characteristics. The development and promotion of new materials were prompted by the following factors:

- *The energy crisis of the early 1970's resulted in an increase in the cost of petroleum-based products. The unpredictability of the sources of oil supplies meant that the quality of asphalt was not consistent. This, in turn, affected the quality of roofing materials.*

- *Energy-induced inflation raised the cost of labour intensive BUR, thus making the alternatives economically more viable.*

- *Advances in polymer chemistry and technology resulted in the development of many polymer-based synthetic materials that could be used for roof coverings.*

- *During the 1960's new structural design principles gave rise to lightweight structures that caused problems for conventional roofing assemblies owing to their increased structural movement.*

- *Highly insulated roofs and decks with unusual architectural configurations allowed innovative designs of roof systems that only the new materials could meet.*

- *The aesthetics of roofs in terms of color and pattern presented the architect with attractive alternatives that would complement the architecture of other elements like flooring and carpeting in the building as well as other exterior elements of the building.*

As a consequence, literally hundreds of new roofing materials have appeared on the market. Most of them are polymeric in nature. They are reinforced with a variety of woven and nonwoven fabrics of synthetic and glass fibres.

1.1.2)MEMBRANE TYPES

In addition to BUR there are many different types of new membranes that are mostly prefabricated sheets or liquid applied materials that cure to form waterproof sheets or closed cell foams. They are made from a wide variety of synthetic organic materials *(polymers) with various chemical compositions and additives. In some cases natural materials such as bitumen, organic fibers, etc. are compounded with them.*

A brief generic list of roofing membranes is given in Table I. In each type there is a long and growing list of products. No two products are identical even if they consist of the same predominant polymer. A manufacturer may have a number of different products: unreinforced , or reinforced with different fabrics, for protected or exposed application, with different seaming techniques and different attachment methods, availability in different colours, etc.

Table I Types of roofing membranes

Classification	***Membrane***
Conventional roofing	*Bituminous built-up roofing (BUR)*
Prefabricated sheets	*Thermoplastic sheets*
	• *PVC and blends*
	• *EIP (ethylene interpolymer)*
	• *CPA (copolymer alloys)*
	Elastomeric (synthetic rubber) sheets
	• *Vulcanized:*
	EPDM (ethylene-propylene-diene monomer)
	Neoprene (polychloroprene)
	• *Non-vulcanized:*
	CSPE (chlorosulfonated polyethylene)
	CPE (chlorinated polyethylene)
	PIB (polyisobutylene)
	NBP (butadiene-acrylonitrile)

	Modified bituminous sheets • *Polymer modifiers:* *SBS (styrene-butadiene-styrene)* *APP (atactic polypropylene)* *IPP (isotactic polyproylene)*
Cast in situ	*Hot applied rubberized asphalt* *Cold applied liquid compounds* • *Various polymeric and bituminous materials* *Polyurethane foam roof with protective coating*

The terms sheet and membrane tend to be interchangeable. By definition, a membrane refers to the finished built-up waterproofing layer comprising one or more prefabricated sheets. As such, a sheet becomes a membrane in a single-ply application and a modified bituminous membrane may have two sheets, base and cap.

1.1.3) MEMBRANE CHARACTERISTICS

a) Bituminous built-up roofing

Bituminous materials used in BUR include (a) asphalt, obtained in petroleum processing, and (b) coal-tar pitch (CTP) or just tar or pitch, obtained as a residue from the distillation of coal tar. This and asphalt impregnated glass fiber felts are used as plies in the construction of BUR. Heated asphalt is mopped on each felt layer to bind them together into the finished multiply membrane.

Many problems in BUR, like blistering, are related to moisture and air voids in the membrane. The organic felts absorb moisture from improper storage and the lack of protection from rain during installation and as a result lose strength due to wetness.

Sometimes moisture is trapped where there are shippings in the mopping of asphalt under the felt. Also, synthetic fibers from rags sometimes get included in the felts during manufacture, resulting in poor asphalt saturation. Glass fiber felts are quite porous and provide good adhesion. Their use in flashing is not recommended. During installation, walking over felt on hot asphalt causes the asphalt to squeeze out, which could result in a void and lack of adhesion in the membrane, a potential source of moisture problems.

A very common source of problems is overheating asphalt. This apparently makes the mopping easy, but it hardens the asphalt and reduces both its softening point and coefficient of linear thermal expansion. The surface shows shrinkage cracks and alligatoring. Some other problems in BUR include shrinkage of the membrane that pulls flashings away, caused by a lack of adhesion of the roofing system to the deck. Membrane slippage occurs if the softening point of the asphalt is too low with respect to the roof slope, or the amount of interply asphalt is excessive.

b)Thermoplastic sheets

As the name implies, thermoplastic polymers soften when heated and thus can be easily extruded or molded. They are distinguished from thermosets by the fact that there is no cross-linkage or vulcanization of the molecules. Welding together using heat or a solvent is easy and creates new molecular linkages during service life.

Poly(vinyl chloride) is one of the most versatile thermoplastics in use today. Its use in roof covering started in the sixties. In a PVC sheet, the compounded plastic is the key element that determines the final characteristic of the product and acts as a binder for the system. Plasticizers are added to impart flexibility to the sheet and improve processing. Fillers and extenders (such as calcium carbonate) are used primarily to lower the cost of the compound. They also improve processing and affect other mechanical properties, such as the hardness and dimensional stability of the finished product. Stabilizers protect PVC against heat during processing and against ultraviolet radiation during service. Pigments are added to color the plastic material.

Loss of plasticizers was once a major concern, as it caused embrittlement in the PVC sheets. This is now considerably improved by using high molecular weight plasticizers that have less of a tendency to volatilize or migrate out of PVC resin.

PVC sheets are produced by three basic methods, calendering, extruding and coating. There are three types of sheets: unreinforced, lightly reinforced with fibres or fabrics that act as carriers, and reinforced sheets that contain glass and/or polyester fibres or fabrics. The carrier facilitates manufacturing and adds to the dimensional stability of the sheet. Reinforcement provides tensile and other properties.

PVC sheets have good resistance to industrial pollutants, bacterial growth and extreme weather conditions. Minor damage to the sheet during installation or in service can be easily repaired by patching the hole using heat or solvent.

c)Elastomeric sheets

There are many types of elastomers or synthetic rubbers used in roofing, including EPDM, neoprene, hypalon, butyl, nitrite, etc. They are compounded with polymers and ingredients such as fillers, anti-degradants, processing oils and processing aids, to impart the required properties. Polymers provide the muscle and fillers provide bones to the materials. Anti-degradants improve weathering properties of the membranes. The most commonly-used elastomer in roofing is EPDM. The compound contains 30-50% polymer (ethylene-propylene-diene monomer), 20-30% carbon black and 30-50% extender oil, sulfur, accelerator and antioxidant. Sheets are produced by laminating two plies with or without reinforcing.

Vulcanization or curing is an irreversible process during which an elastomeric compound is converted through chemical cross-linking from a soft, tacky thermoplastic to a partially thermoset material having improved elastic properties. Vulcanization is the result of heating the compound with sulfur or another cross-linking agent.

The non-vulcanized or uncured rubber sheets that are self-curing are gradually cured on the roof by heat from the sun. Once they are cured, their behaviour is similar to that of cured elastomers. If they are not self-curing, they remain uncured and exhibit properties similar to thermoplastics during their service life. In general, elastomeric sheets have good tensile and other mechanical properties and excellent resistance to UV, ozone, many oils, and solvents.

Field seaming of some vulcanized sheets, known to cause some problems, is progressively being improved. Doing the maximum possible seaming in the factory reduces the amount of field seaming and the probability of problems. Some aspects have been discussed above in the section on lap joint integrity. Proper choice of adhesives, care in the preparation of the seam area, skillful application, and adequate curing time could result in a durable joint.

d)Polyurethane foam

Polyurethane rigid foams (PUF) were first developed in the late thirties and used during the war to strengthen aircraft wings. Commercial use in different industries started only in the late fifties. The sprayed-in-place PUF roofing system was introduced in the early 1960's.

This system is made up of three components: PUF, a protective cover and a vapour barrier. PUF forms a closed cell waterproofing barrier and provides insulation. The foam is made from the combination of two materials, a resin (containing polyol, catalyst, blowing agent, surfactant, etc.) and a polyisocyanate component. Their combination during application from a two-head spray gun produces a polymeric structure and a vapour that forms bubbles before the foam becomes rigid. During the chemical reaction it expands 20 to 30 times its original volume within seconds. Minimum thickness of the foam layer is 25 mm.

The use of PUF in roofing faced many problems in early years, that were related to the ambient temperature. On hot days the foam reacted too rapidly leaving a rough texture, while on very cold days it did not react leaving the material in a liquid form. Accordingly, attention to environmental conditions (temperature, wind, moisture on deck) is necessary. PUF, once considered only as a reroofing alternative to BUR, is now being used in a wide range of new construction projects.

Since urethane foam is very sensitive to UV radiation, it must be protected in some manner. Various elastomeric coatings and latex paints have been used for this purpose. In some cases, mineral roofing granules are sprinkled into the coating when wet. They improve abrasion resistance, weathering characteristics and fire resistance. Coatings must have high tensile strength, elongation, and water transmission resistance, since water is foam's prime enemy

e)Modified bituminous (MB) sheets

This class of sheets is made from bitumens and modifying polymers (synthetic rubbers or plastic materials), together with fillers and special-property additives. Since the process is basically mixing components, the amount of modifier can be varied according to the required characteristics. The two most widely used bitumen modifiers are SBS (styrene-butadiene-styrene) and APP (Atactic polypropylene). The average SBS content in the formulation is 12-15%. Generally, more SBS means greater low temperature flexibility and fatigue resistance as well as a higher softening point and wider temperature use. There are about a dozen different SBS grades that accentuate one or the other property required for processing and performance of the membranes. APP is a by-product of the manufacture of IPP (Isotactic polypropylene). It comprises 25-35% of the modified compound, its primary function being to improve the mechanical properties of the finished membrane. The APP-modified product has higher strength and lower elongation compared to the SBS modified type. A small quantity of filler provides rigidity to the *compound but large quantities reduce flexibility and adhesion. Consequently, the best products have the least filler.*

Proper modification of bitumen results in a product whose performance characteristics are far superior to those of normal bitumen. Various types of reinforcements, particularly glass and polyester composites incorporated in the membrane, provide improved properties. Granules protect the surface from the degrading effect of UV. In some membranes a light glass mat laminated to the surface protects the surface from cracking and acts as a replacement for granules. The number of reinforcing fabrics and their positioning depends on the design of the product. The sheets are up to about 5 mm thick.

These membranes are frequently applied by torching (open-flame melting) the underside as the sheet is being unrolled. Others have self-adhesive backing, or they may be adhered with a mopped-on adhesive. Since open-flame torching is considered a fire hazard, some manufacturers have introduced an electric heat-welding process. Overheating modified bitumen degrades the mastic and leads to poor adhesion and weak lap joints.

1.1.4) INSTALLATION

Hot-applied rubberized asphalt

Hot-applied rubberized asphalts consist of proprietary blends of asphalt, mineral fillers, elastomers (natural, synthetic, or a blend of both), virgin or reclaimed oil and a Thermoplastic resin. It is applied hot in such a manner as to form an impermeable monolithic membrane over the surface to be waterproofed, which may be concrete, gypsum board or wood. Improved versions of this type of system consist of two coats of rubberized asphalt with a polyester mat in between, called the fully reinforced or two-ply system.

Cold-applied liquid compounds

This category of material comprises a number of different products in the market. They consist of emulsions and solutions of (a) various resins or elastomers such as polyurethanes, silicones, acrylics, etc., and (b) bitumens and modified bitumens. The material left after the evaporation of volatiles (water or organic solvents) forms the waterproofing layer. Their surface coatings may contain white pigment or aluminum flakes or they may be vinyl films for protection from solar radiation. These liquids are generally applied by spraying or with rollers. The emulsions cure slowly at low temperatures and they cannot be applied below water's freezing temperature. The solution forms a film much faster under these conditions.

Also, the cutbacks (solutions) and emulsions (water dispersions) of asphalt and coal tar pitch are used in various types of cold applications of BUR. Polyester mats are used as alternatives to conventional felts for plies. The market share of cold-applied BUR's is small. From the point of view of economy and availability, asphalt is more commonly used in this type of roofing product [11].

FIG:1 [25]

1.1.5) PERFORMANCE CONSIDERATIONS OF ROOFING MEMBRANES

In general, performance or durability is related to the fulfillment of the user's requirements and the desired attributes of materials, and is considered the most important factor. Performance means the actual functioning of a building system or element in service. Every roofing membrane, irrespective of the material it is made of or who the manufacturer is, must be capable of doing the following:

- *Remain waterproof.*
- *Withstand all weather factors (such as wind, rain, snow, hail, solar radiation, temperature extremes, and thermal shocks) during its intended service life.*
- *Resist various stresses from internal or external causes during manufacture, application and service.*

It may be appropriate to define some of the terms related to the performance of building materials or components in general. They apply to roofing sheets and membranes as well.

- *Performance requirement is a qualitative statement describing what the system or element is to accomplish.*
- *Performance criterion is a quantitative aspect of the acceptable and/or adequate performance level.*
- *Characterization method means a method for evaluating the compliance with performance criteria.*

It should be noted that requirement and criterion are interchangeable and, to some, one means both, i.e. the qualitative aspect is implied in the statement of the quantitative *aspects. The selection of a roofing membrane, like any other building component, must be based on its ability to meet the performance requirements for proper functioning throughout its life.*

1.1.6) PERFORMANCE REQUIREMENTS

The performance of roofs, as mentioned above, is related to numerous variables concerning weather factors and stresses. Other variables are the chemical composition of materials, the quality control of the constituent materials and products during manufacture, storage, transportation, installation and maintenance. Most of these conditions vary from one situation to another, so that a large number of performance requirements and criteria are identifiable. One way to predict the performance of a membrane is to identify the physical, chemical and mechanical properties essential for its performance and to quantify them either arbitrarily on the basis of experience or by testing many products in the same generic class. These values constitute the performance criteria for the specific class of product tests. These criteria may be projected with or without modifications to other generic types of membranes. Similar requirements can be developed for a specific product if desired. Quantification of the requirements can be accomplished by comparison or experience with other products[11].

1.2) NEED FOR MODIFICATION:

As a result of changes that have come about in the roofing industry, many times (several recently) have been asked about the modifications of roofing bitumen. "Why modify bitumen? Isn't it a good enough waterproofing material already? Certainly. But because of the improvements that can be made in a bituminous material's durability and extensibility (especially at lower temperatures) by adding polymers (rubbers and plastics), the physical properties of the resulting polymer modified bitumen surpass any other material for the cost .By combining bitumen with a polymer (the modifier), new and advantageous physical properties are obtained- when the formulation is done at the correct material ratios, controlled temperature and mixing speed and are always *different, depending on the bitumen, the modifier and the proportions that are used. Some of these advantages over blown bitumen systems are indicated :*

- *Improved elasticity, making them capable of accommodating the repeat-ed thermal movements of the roof*
- *Improved flexibility at low temperatures, enabling contractors to lay roof felts in colder weather.*
- *Improved strength, allowing a reduction in the number of plies of felt by completely or partly replacing a blown bitumen coated felt by an elastomeric coated system with the resultant economic advantages.*
- *Better fatigue resistance*
- *To improve fatigue resistance of blends*
- *To improve oxidation and aging resistance*

1.2.1) BITUMEN :

The terms asphalt and bitumen are synonymous .The ASTM defines bitumen as a generic class of amorphous, dark colored cementitious substances, natural or manufactured composed principally of high molecular mass hydrocarbons, soluble in carbon disulfide. The primary source of bitumen originates in or is derived from petroleum crude oil It naturally occurs in rock strata of certain of certain geological formulations, from which it is produced by drilling, then recovered by natural flow or by natural flow or by pumping.

Distillation is a necessary first step in the separation of a bitumen-containing residuum from crude petroleum. Distillation separates the more volatile fractions, generally first an atmospheric fractionator and then a second vacuum stage in order to remove the distillable fractions from the bitumen –containing residuum. The temperature shown in figure approximates the boiling ranges of the fractions being separated. A final cut point *temperatures of 450℃ is necessary to separate the bitumen containing residumm from the crude. As indicated in the fig the most direct means of manufacturing is by straight reduction to bitumen of grade AC 2.5 to AC 40 [12].*

1.2.2) COMPOSITION OF BITUMEN

Bitumen is composed of following fractions as given in Table 2 [12]:

Fraction	***Low viscosity flux***	***Paving cement***	***Hard pitch***
Saturates wt%	*16.7*	*13.0*	*3.7*
Naphthene aromatics, wt%	*41.4*	*34.7*	*27.2*
Polar aromatics, wt%	*29.8*	*37.4*	*45.8*
Asphaltenes wt%	*11.5*	*14.6*	*23.0*
Softening point, ℃	*28*	*46*	*85*
Penetration at 25℃	*>300*	*89*	*5*

1.2.3) BITUMEN GRADES

- ***Industrial bitumen (IS 702-1988)*** *: The material shall be prepared from petroleum residue by air blowing at atmospheric pressure or under pressure with or without catalyst .This grade of bitumen is generally used for following:*

a) Manufacture and fixing of roofing and damp proofing felts.

b) *Manufacture of plastic bitumen for leak stops.*

Properties:

Softening point / Penetration point---85/40, 85/25 ,90/15, 115/15, 135/10, 155/6

- ***Cutback bitumen (IS 217-1988)*** *: This grade of bitumen is produced by fluxing bitumen with distillates of petroleum or coal tar for use in roads.*

  Grades:

  a) Rapid curing

  b) Medium curing

  c) Slow curing

- ***Paving Bitumen (IS 73:1992****) : This grade of bitumen is produced by destructive distillation of petroleum and is provided for road paving.*

Grades*:*

	a) A35	*b) A55*	*c) A65*	*d) A90*
Softening Pt.	*55to70*	*45to60*	*45to60*	*35to50*
Penetration Pt.	*30to40*	*50to60*	*60to70*	*80to100*

Grades:

a) S35 b) S45 c) S55 d) S65 e) S 90 f)S200

Softening Pt.	*50to65*	*45to60*	*45to60*	*40to55*	*35to50*	*30to45*
Penetration Pt.	*30to40*	*40to50*	*50to60*	*60to70*	*80to100*	*175to225*

1.2.4) POLYMERS:

Polymers are giant molecules of different chemicals. A polymer or a macromolecule is made up of many (poly) molecules ('mers') or monomers linked together like wagons in a train, for example poly(vinyl chloride), poly(ethylene), etc. Figure2 shows the polymerization of vinyl chloride (VC), which represents some 500 to 2000 molecules of VC linked together to make a giant molecule of commercial PVC. Monomers may have the same or different chemical compositions.

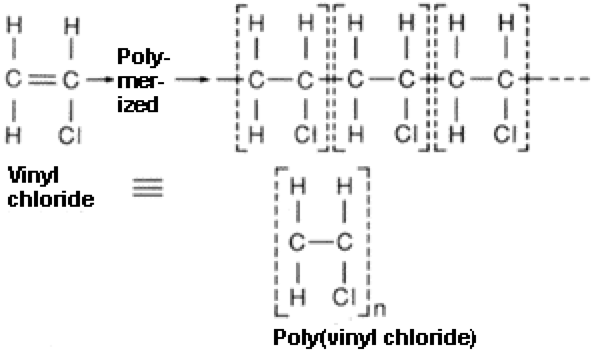


Fig 2. Polymerization of vinyl chloride

Similarly, esters constitute a family of chemicals whose macromolecules are known as polyesters that are used in synthetic fibers, filaments, threads, fabrics, etc. (Their use in reinforcing roofing sheets and membranes is discussed later). Polyurethanes include rigid, semi-rigid, flexible and integral skin foams used in interiors of automobiles and many everyday products.

Elastomers are another group of polymers that stretch under low stress to at least twice their original length and recover after the removal of the stress.

In the field of polymer chemistry there are many terms related to internal structure such as monomers (as in EPDM), co-polymers as in vinylidene chloride (saran wrap), block co-polymers (as in SBS) and interpolymers (as in EIP), etc [11].

1.2.5) POLYMERS USED FOR MODIFYING BITUMEN

Many polymers have been used as binder modifiers, and they can be classified into five groups:

Thermoplastics :	*Polythenes* *Polypropylenes (app, atactic and ipp ,isotactic)* *Ethylene Vinyl Acetate* *PVC, PS*
Natural and synthetic rubbers:	*Natural rubber* *SBR* *Polybutadiene* *Polyisoprene*
Thermoplastic rubbers :	*SBS* *SIS*

Summary of these polymers and their advantages and disadvantages as asphalt modifiers : table 3

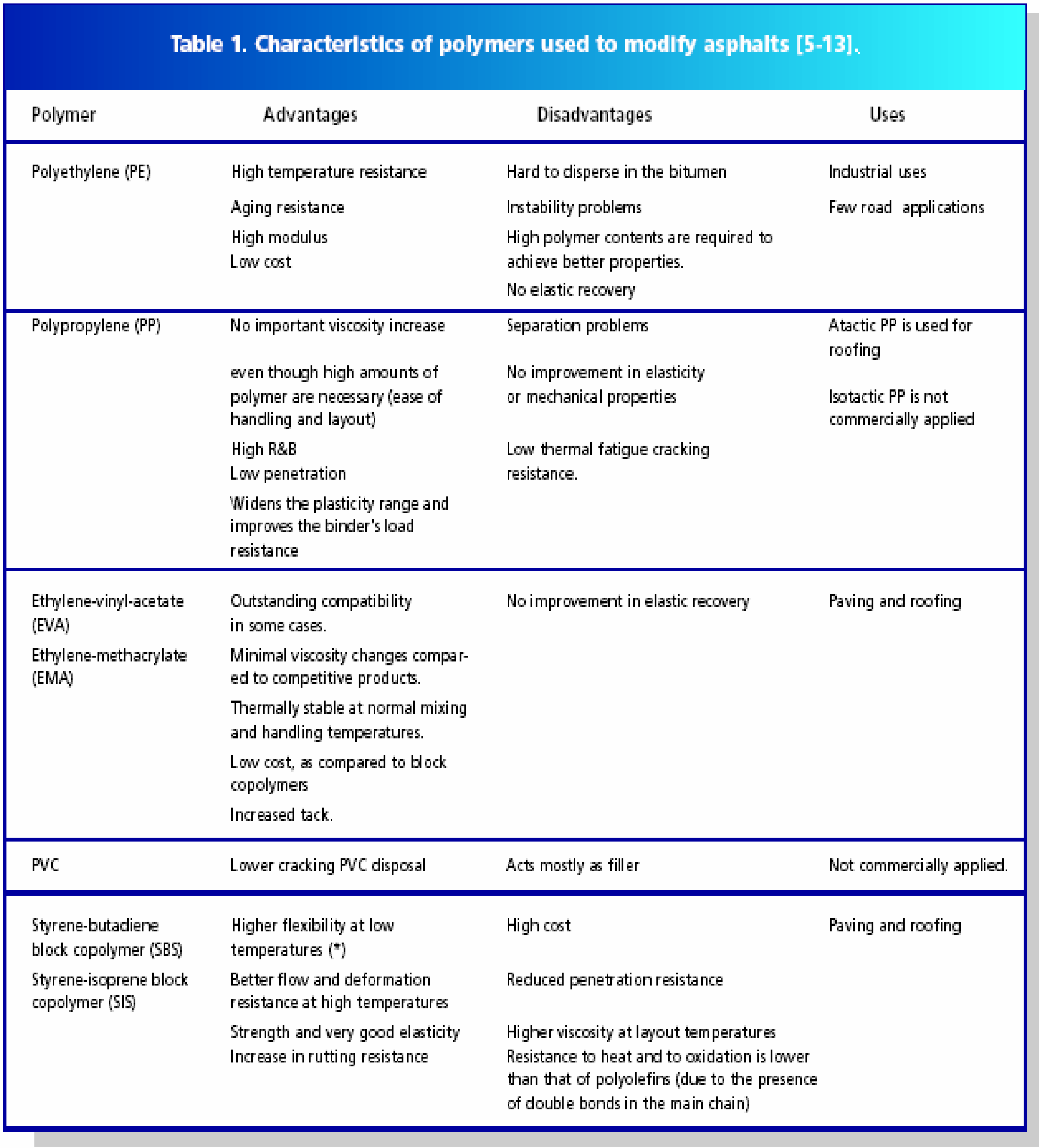


Table 1. Characteristics of polymers used to modify asphalts [5-13].

Polymer	Advantages	Disadvantages	Uses
Polyethylene (PE)	High temperature resistance Aging resistance High modulus Low cost	Hard to disperse in the bitumen Instability problems High polymer contents are required to achieve better properties. No elastic recovery	Industrial uses Few road applications
Polypropylene (PP)	No important viscosity increase even though high amounts of polymer are necessary (ease of handling and layout) High R&B Low penetration Widens the plasticity range and improves the binder's load resistance	Separation problems No improvement in elasticity or mechanical properties Low thermal fatigue cracking resistance.	Atactic PP is used for roofing Isotactic PP is not commercially applied
Ethylene-vinyl-acetate (EVA) Ethylene-methacrylate (EMA)	Outstanding compatibility in some cases. Minimal viscosity changes compared to competitive products. Thermally stable at normal mixing and handling temperatures. Low cost, as compared to block copolymers Increased tack.	No improvement in elastic recovery	Paving and roofing
PVC	Lower cracking PVC disposal	Acts mostly as filler	Not commercially applied.
Styrene-butadiene block copolymer (SBS) Styrene-isoprene block copolymer (SIS)	Higher flexibility at low temperatures (*) Better flow and deformation resistance at high temperatures Strength and very good elasticity Increase in rutting resistance	High cost Reduced penetration resistance Higher viscosity at layout temperatures Resistance to heat and to oxidation is lower than that of polyolefins (due to the presence of double bonds in the main chain)	Paving and roofing

Many different polymers are used to modify asphalts and each has their own associated physical properties. For example, ethyl vinyl acetate (EVA) stiffens the asphalt, much like a hard plastic, so it is considered a plastomer. Styrene butadiene (SB) and styrene butadiene styrene (SBS) block copolymers can increase the elasticity of the asphalt, much like a rubber band, so they are considered elastomers. Another group of elastomeric polymers ,styrene butadiene rubber (SBR) latex polymers, increases the ductility of asphalt cements

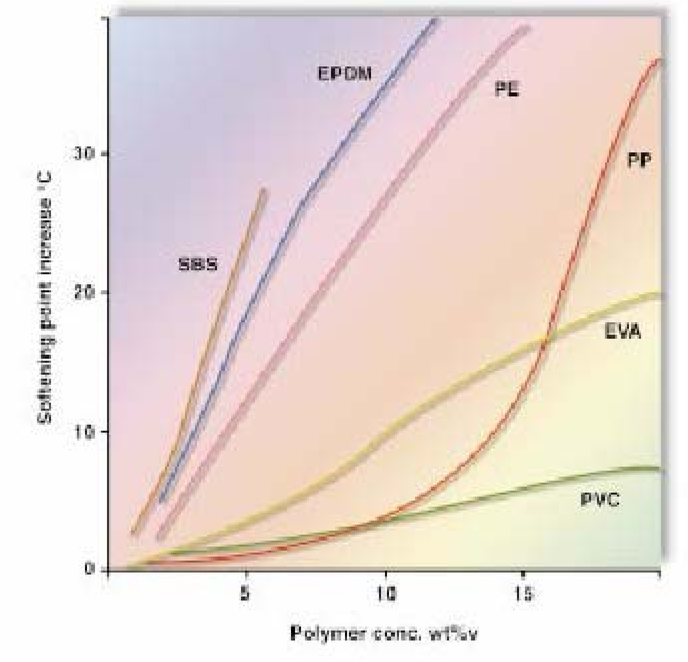


Fig.3 above shows how the softening point of specific asphalt changes with different polymers at different concentrations.

1.3) RHEOLOGY OF MODIFIED ASPHALT

The rheological behavior of asphalt-polymer blends is of great interest because it is closely related to the performance of roofing. Furthermore, the addition of small amounts of polymer dramatically changes the rheological properties of the asphalt. The addition of polymer introduces an additional difficulty to the asphalt complexity , because of its high molecular weight. The formation of a homogeneous system is not easy and incompatibility problems arise. Since a modified binder consists of two distinct phases, three different cases must be considered for modified systems

Low polymer content

In this case, the bitumen is the continuous phase of the system, and the polymer phase (less than 4%) is dispersed through it. Due to its lowered oil content, the bitumen phase has a correlatively higher asphaltene proportion. As a result, both the cohesion and elasticity of the asphalt are enhanced. In addition, the polymer phase is dispersed through the bitumen matrix. At high service Temperatures (around 60°C), the stiffness modulus of the polymer phase is higher than that of the matrix. These reinforcing properties of the polymer phase improve the mechanical performance of the binder. At low temperatures, the stiffness modulus of the dispersed phase is lower than that of the matrix, and reduces its brittleness. Briefly, the dispersed polymer phase enhances the properties of the binder both at low and at high service temperatures. In otherwords, the polymer extends the useful temperature range for the asphalt. In this case, the choice of bitumen is determining factor.

Polymer content around 5%

This system may show microstructures in which the two phases are continuous and interlocked. Such systems are generally difficult to control and pose stability problems (their micro morphology and properties often depend on temperature history).

Sufficiently high polymer content

More than 7% in general, if the bitumen and polymer are correctly chosen. The polymer phase is the matrix of the system. This is in fact not a bitumen , but a polymer plastified by the oils in the bitumen in which the heavier fractions of the initial asphalt cement are dispersed. In this case, the polymer is the continuous phase and the asphalt is there in dispersed. The properties of such a system are fundamentally different to those of bitumen, and depend essentially on those of the polymer. One should speak not of a polymer modified bitumen, but of a thermoplastic adhesive. These materials are usually employed for roofing.

1.3.1) INCORPORATION OF POLYMERS INTO ASPHALT

Two methods are commonly used to incorporate polymers into asphalt:

- *Addition of latex polymer to the asphalt. This method is relatively easy and trouble free.*

- *Addition of solid polymers to asphalt. This method normally requires substantial mixing and shearing in order to uniformly disperse the polymers, particularly when SBS or SEBS block copolymers are used.*

At room temperature, SBS materials show similar behavior to that of a crosslinked network, because the polystyrene (PS) end blocks aggregate into rigid domains, whereas the polybutadiene (PB) or polyisoprene (PI) blocks act as elastic amorphous unions between them .

Because their "tridimensional" network is only physical, unlike other crosslinked materials, they become fluid at high temperatures, thus facilitating their mixing and processing .When adding a polymer such as SEBS to asphalt, specific interactions between asphalt and the polymers, can take place.

Volume of polymer increases up to 9 times
after contact with asphalt

Fig. 2. Scheme of SBS molecules blended with asphalt [5].

Fig.4

1.3.2 ASPECTS THAT INFLUENCE THE PROPERTIES OF POLYMER-ASPHALT BLENDS

Polymer characteristics

To be effective, a polymer must be blended with the bitumen and increase its resistance at high temperatures without rendering it too viscous for the mixing procedure or too brittle at low temperatures. It should also be capable of being processed in asphalt conventional equipment. The modifying polymer should be sufficiently compatible with the asphalt as not to cause phase separation during the storage, transportation, application and service .Moreover , the modified polymer must be cost effective, i.e. the polymer should improve the rheology and strength of the asphalt .Polymer content ranges of different proportions are used. Sometimes waste materials (due to their low cost they might be added in higher proportions), or mixes of two different polymers (as mentioned before) are being used. Polymer parameters affecting the modification process include

- *polymer content,*
- *chemical composition,*
- *structure,*
- *average molecular weight,*
- *molecular weight distribution,*
- *degree of branching,*
- *crystallinity*

Asphalt characteristics

Asphalt nature greatly influences the binder micro morphology, as well as some of its properties, such as penetration and mechanical properties. It has also a very large influence on the stability of the blend .As it has been mentioned numerous times, the polymer must be compatible with the bitumen and maintain this compatibility during storage and use. This is a difficult task , because the PMA constituents are very different in molecular weight and structure, viscosity and density .Moreover, bitumen differences depend not only on the composition of the original crude, but also on the production process . In all cases, there is a close connection between polymer type and bitumen composition, especially with the content of bitumen components, which act as solvents or swelling agents for the modifier.

For low polymer content, the continuous asphalt phase is enriched with resins and asphaltenes , thus leading to an increase in the consistency and the elastic properties of the binder. In general, a thermoplastic polymer modified asphalt (resulting from physical mixing of the constituents without chemical interactions between them) can consequently be regarded as a diphase system made up of a swollen polymer and a phase grouping the constituents of the asphalt not intervening in the solvation. If the polymer content is increased, the inversion point is observed. This transition is accompanied by a major modification in the physical properties of the blend. This results essentially in a significant increase in the plasticity interval, in tensile strength and elastic properties, and a reduction in thermal sensitivity over the utilization temperature range Studies by Vonk and Bull have shown that when a thermoplastic rubber copolymer is in contact with bitumen, the elastomer absorbs, almost proportionally, all the bitumen components, with the exception of the asphaltenes. The asphaltenes, however, require support from the presence of the maltenes to avoid their precipitation.

Thus, if the asphaltene content of the bitumen is too high, addition of a thermoplastic rubber can result in asphaltene precipitation or gelation and the blend becomes unworkable. Conversely, if the asphaltene content is low the polymer is able to absorb *more maltenes after which even a single phase blend may be obtained. When phase separation occurs in a bitumen-SBS material ,the thermoplastic rubber phase rises to the surface of the bitumen and the asphaltene phase falls to the bottom. The top section of the mixture thus becomes soft and elastic, while the bottom becomes hard and brittle. The ratio of penetration at the top/penetration at the bottom quantifies the extent to which separation of the binder has taken place.*

The softening point of the bitumen-thermoplastic rubber blends is largely governed by the aromaticity and average molecular weight of the base bitumen and tend to be little influenced by the hardness of the base bitumen. The viscosity of the blends at 180°C is predominantly affected by the average molecular weight of the base bitumen The asphaltene content of the bitumen-thermoplastic rubber blend must also be carefully balanced as, at low concentrations, the asphaltenes interact with the thermoplastic rubber molecules forming beneficial associations ,which result in higher flow resistance and higher softening points. Conversely, a too high asphaltene content will result in phase separation leading to a lower proportion of the thermoplastic rubber being available in the continuous phase. The permissible level of the asphaltene concentration is dependent upon:

- *polymer content*
- *polymer molecular weight*
- *asphaltene molecular weight*
- *aromaticity.*

Careful balancing of the aromatic content and the aromaticity in relation to polymer content is necessary in order to produce a bitumen-thermoplastic rubber blend which is stable, and in which the thermoplastic rubber is present as a continuous phase to the maximum extent possible, in order to achieve the maximum possible benefit from the polymer. Such blends are termed as "compatible" blends

1.3.3)FACTORS AFFECTING MIXING CONDITIONS

The parameters influencing the mixing process include:

- ***Nature of the polymer***

The time required to achieve a homogeneous blend of the polymer and the asphalt will vary with the type of polymer, its molecular weight, and(for thermoplastic rubbers) with the chemical composition of the polymer. A higher molecular weight will give rise to longer blending times, and vice versa

- ***Physical form of the polymer (powder, crumbs, pellets).***

The physical form of the polymer influences the blending process in two ways. The smaller the particle size of the polymer, the lesser it has to be reduced in order to achieve a good dispersion. In addition, since smaller particle size means larger surface area per unit mass of polymer, penetration of the bitumen and swelling of the polymer is facilitated, and thus more rapid dissolution is completed. Powdered polymers will therefore disperse and dissolve more rapidly than porous pellets.

- ***Nature and grade of the bitumen**.*

Bitumen plays a complex role in the mixing process as both its composition and viscosity affect the blending process in more than one way. The way constituents affect the mixing process has not very extensively been studied, as has been mentioned before. General observations drawn included that an asphalt should contain big oil fractions to dissolve and expand the polymer, and a high content of condensed ingredients in order to guarantee the PMA blends endurance .On the other hand, low viscosity bitumen is beneficial in aiding pre-dispersion of the polymer in the bitumen, and will subsequently speed the penetration and swelling of the polymer particles. A low bitumen viscosity at *the blending temperature will improve the disintegration of the polymer at the mill and result in a more rapid particle size reduction .*

- ***Type of mixing equipment.***

Two main methods exist for the dissolution of polymer in the bitumen, high shear and low shear mixing. For low shear mixing a simple mixing tank with a paddle stirrer can be used with powdered modifier ,the action being confined to the swelling and dissolving by the bitumen. The mixer serves to maintain homogeneity of composition and uniformity of temperature, proving little or no heat input itself.

In high shear mixing, polymer particles are physically reduced in size by mechanical and hydrodynamic shear in a rotor-stator combination accompanied by significant in put of heat energy to the mix.

- ***Time-temperature profile during mixing.***

The ideal mixing process should be undertaken at the lowest possible temperature for the shortest possible time, corresponding to the complete incorporation of the polymer into the bitumen both from an economic standpoint and to minimize any thermal effect on the polymer. In practical terms however , the time-temperature profile is a function of the bitumen chosen, and its requirement to achieve mobility and initial swelling of the polymer. For SBS, for example, temperatures higher than 190°C should be avoided to minimize thermal effects on the polymer .Blending conditions have an important impact on the structure and properties of modified binders: the longer the mixing time, the finer the microstructure. There is however, a starting point beyond which polymer degradation leads to a decrease in mechanical properties and, more precisely , in low temperature deformation possibilities .The higher the temperature, the more rapidly this threshold is reached

1.3.4)COMPATILBILTY AND STABILITY

A polymer may be incompatible, slightly compatible or compatible with bitumen.

- *Incompatible polymers, when mixed with asphalts ,result in heterogeneous mixtures without cohesion or ductility. The polymer affects the colloidal equilibrium of the asphalt and, therefore, the cohesion of the material.*

- *Slightly compatible polymers require special mechanical, thermal or chemical processes to successfully improve asphalts.*

- *Compatible materials yield physically stable blends, using conventional mixing techniques, and they may or may not improve the physical properties of the asphalt .A proper degree of compatibility between polymer and asphalt is necessary in order to avoid separation during storing , pumping and application of the asphalts and to achieve the expected properties in the pavement. Poor storage stability will render the polymer modified asphalt unsuitable for use in paving binder applications, roofing applications , and other industrial specialty products .The extent to which a stable system is formed when the bitumen is modified by the addition of thermoplastic rubber is dependent upon a number of factors which include:*
  - *the amount and size of the asphaltenes*
  - *the amount and size of the polymer molecules*
  - *the aromaticity of the maltene phase.*

The compatibility and stability of the polymer-asphalt blends can be improved considerably by certain commercial compatibilization processes, such as the one patented by Exxon Research and Engineering Co. (Florham Park,NJ), where both the asphalt and the polymer are in contact with sulfonate or sulfonic acid groups and then blended.

TexPar Energy, Inc. uses an additive called ButaphaltTM, among many others; for *compatibility purposes, considers the addition of an acid after the polymer has been added to the asphalt. It has also been stated that the storage stability of asphalt can be improved, if the acid is added to the asphalt before the polymer. One example where an acid is added to improve the stability of the asphalt-polymer blend, is a technology patented by Ergon Incorporated.*

It is also known that the stability of polymer-bitumen compositions can be increased by the addition of crosslinking agents such as sulfur, frequently in the form of elemental sulfur. It is believed that the sulfur chemically couples the polymer, and the bitumen through sulfide and/or polysulfi-de bonds. The addition of extraneous sulfur is required to produce the improved stability, even though bitumen naturally contain varying amounts of native sulfur .UV microscopy is used to determine the completeness of blending and compatibility of polymer-modified asphalts. Samples are taken every hour as seen under a fluorescence microscope in order to see the degree in which polymer is incorporated in the asphalt. As mentioned before, finely dispersed polymer grains in the asphalt matrix would be considered a homogeneous (and therefore compatible) system[28].

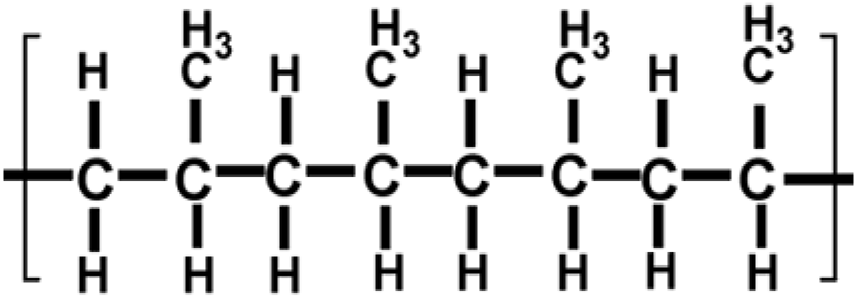
1.3.5) POLYMERIC MODIFIERS USED IN THE PRESENT STUDY

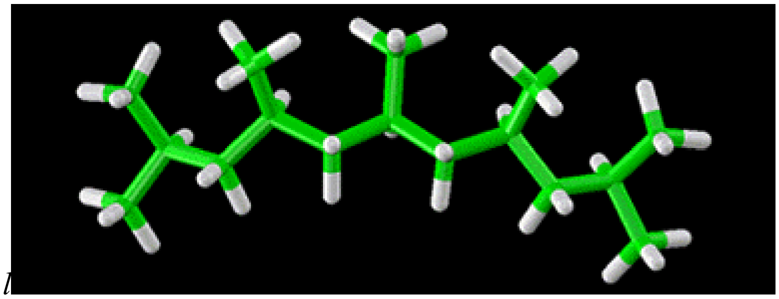
a) ATACTIC POLYPROPYLENE

Atactic polymers are characterized by their tacky, amorphous behaviour and low molecular weights. They provide the same effect as Plasticizers, by reducing the crystallinity of the polypropylene. A small amount of atactic polymers in the final polymer can be used to improve certain mechanical properties. This provides properties to the final polymer such as improved low temperature performance, elongation, processibility and optical properties but sacrifices flexural modulus or stiffness and long term heat aging properties.

Manufacturing process:

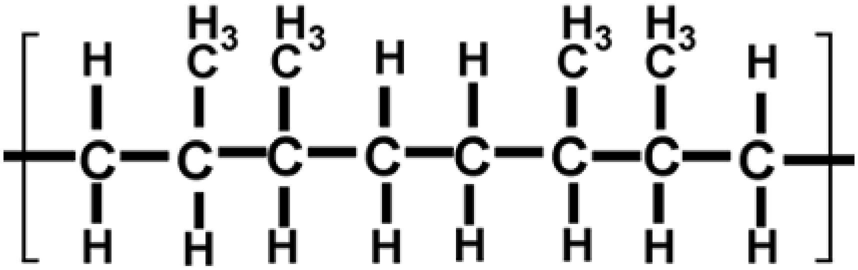
When ethylene is polymerized into linear chains, only one arrangement of atoms is possible. However, the incorporation of substituents into the olefin monomer introduces the opportunity for some structural variability. For example, when propylene is polymerized, the monomers can arrange themselves along the chain in three different ways. If we call the CH_2 *end of the propylene the "head" and the* $CH(CH_3)$ *end the "tail", then a head-to-tail polymerization would lead to a polymer chain with a methyl group (*CH_3*) located on every other carbon .On the other hand, if the polymerization occurred in a head-to-head, tail-to-tail fashion, methyl groups would be located on adjacent carbons in pairs. A third possibility involves random orientation of monomer units along the polymer chain. These three different structural forms of polypropylene would be expected to have different physical properties. Generally, the head-to-tail polymer is produced using heterogeneous Ziegler-Natta or homogeneous cyclopentadienyl-zirconium catalysts. The reason for this result should become apparent in figures below [13].*

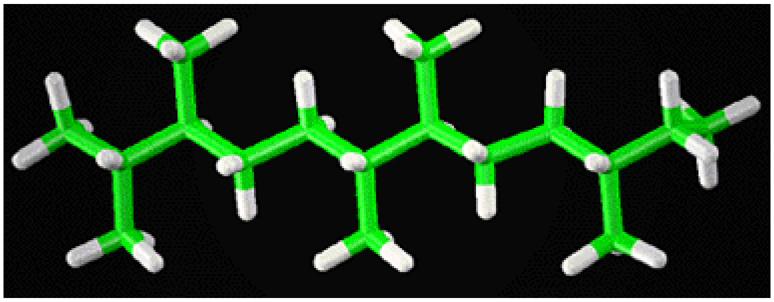




Head to Tail

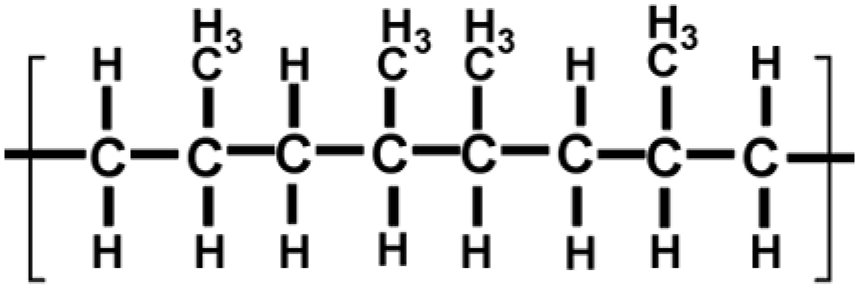
Fig.5: Head-to-tail polymerization of Polypropylene

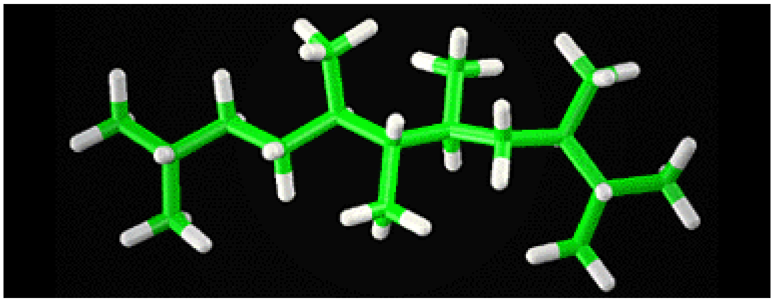




Head to Head, Tail to Tail

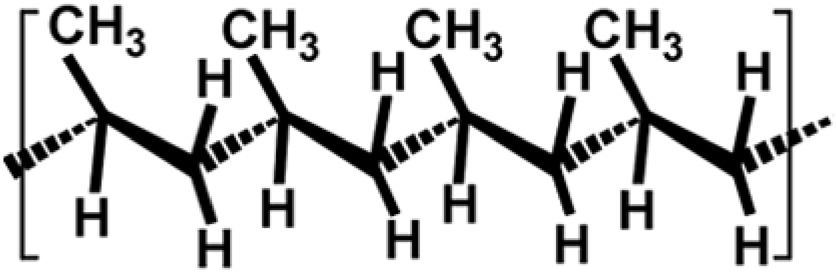
Fig.6: Head to Head, Tail to Tail Polymerization of Polypropylene

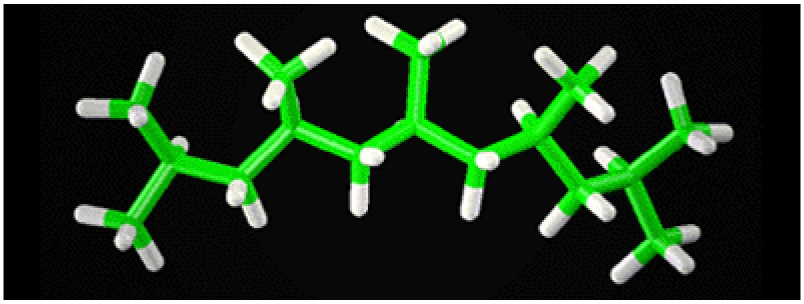




Random

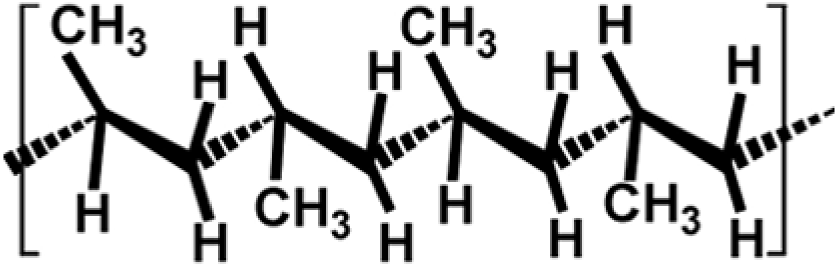
***Fig.7**: random orientation of Polypropylene*

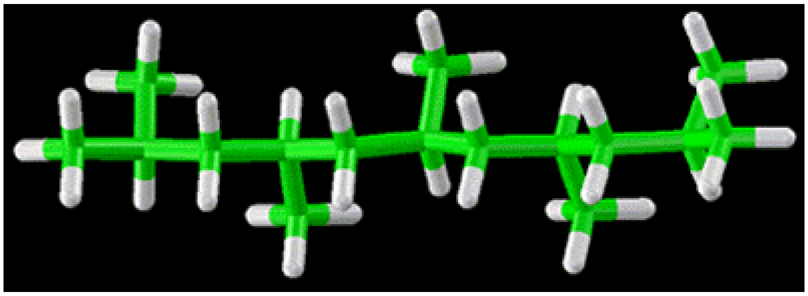




Isotactic

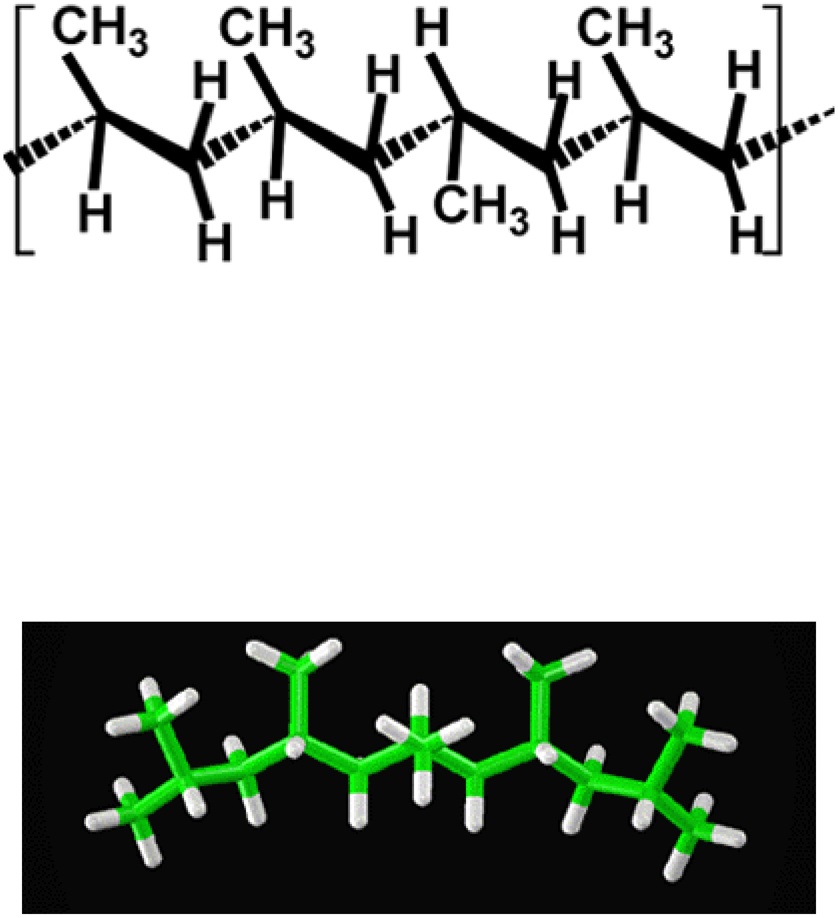
Fig8: Isotactic orientation of Polypropylene





Syndiotactic

Fig.9**: **Syndiotactic orientation of Polypropylene



Atactic

Fig.10**: **Atactic orientation of Polypropylene

Two-dimensional representations of portions of linear polypropylene that result from different arrangements of monomer units along the polymer chain.

Corresponding 3D stick representations are shown above. The hydrogens are shown in white and the carbons are in green. The polymer is terminated by hydrogens.

There is another kind of structural variability in polypropylene that is perhaps a bit more subtle. The groups around each carbon atom in a polyolefin chain are tetrahedrally oriented. Hence, the chain has three-dimensional structure. Even if we assume a regular head-to-tail polymerization pattern for polypropylene, the methyl groups (which will be situated on alternating carbon atoms) can adopt different relative orientations with respect to the polymer backbone

If all the methyl groups lie on the same side of the chain, the polymer is called Isotactic. If the methyl groups alternate in a regular fashion from one side of the chain to the other, the polymer is Syndiotactic. Finally, if the orientation of the methyl groups is random, the polymer is given the name Atactic. The tacticity of a polymer can have a dramatic effect on its physical properties. For example, the melting points of isotactic, syndiotactic, and atactic polypropylene are 60-170 ^oC,125-131 ^oC, and <0 ^oC, respectively. Atactic polypropylene is a soft, rubbery polymer, while isotactic polypropylene is strong and hard with excellent resistance to stress, cracking, and chemical reaction. Syndiotactic polypropylene has only recently been made on a large scale. It is somewhat softer than the isotactic polymer, but also tough and clear. It is stable to gamma radiation and will therefore find applications in medicine.

ATTRIBUTES OF APP:

- *Compatibility .APP is uniquely compatible with a wide range of bitumens*
- *Chemical Stability APP is fully saturated polymer and hence it has no double bonds such as SBS that are vulnerable to UV attack*
- *Oil absorption bitumen losses stability by losing its oils over time. Because APP has a randomly branched non crystalline molecular structure ,it absorbs more than its own weight of bitumen oils when it is blended with bitumen[7].*

STYRENE-ETHYLENE-BUTYLENE-STYRENE

The molecular structure of SEBS thermoplastic rubber is that of a block polymer, where the intermediate block is formed by a flexible elastomeric chain of poly(ethylene-butylene). To the ends of this chain are coupled terminal polystyrene blocks. The production of SEBS is carried out in two stages. In the first stage, a SBS precursor is manufactured in the medium of a hydrocarbon solvent using anionic polymerization. SEBS itself is obtained during the second stage through the total hydrogenation of the SBS. The precise composition of the intermediate polyolefin that forms the midblock of the SEBS depends on the microstructure of the polybutadiene component of this SBS precursor. The cis or trans forms of the polybutadiene will hydrogenate to create the polyethylene chain of the molecule, whilst the vinyl elements are converted to polybutylene .

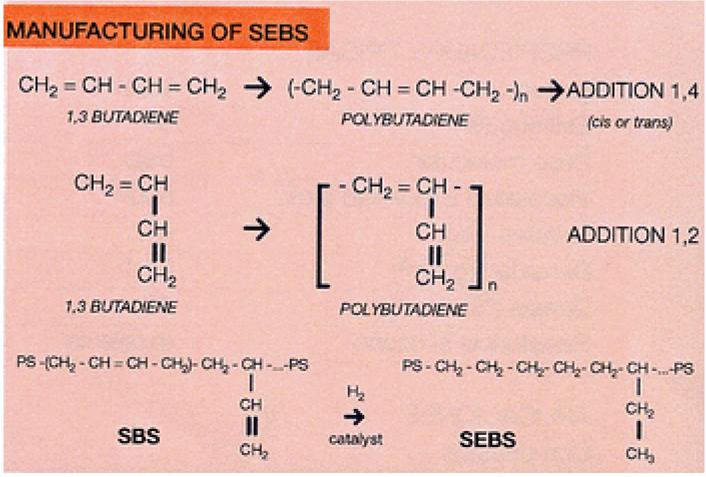


Fig. 11

Characteristics

The polystyrene endblocks of SEBS are thermodynamically incompatible with the poly(ethylene-butylene) mid block. There are two distinct phases with separate and different glass-transition temperatures or 95°C for the polystyrene and -50°C for the *poly(ethylene-butylene) mid block. Furthermore, the various molecules that make up the polystyrene block are joined, creating polystyrene domains. In this way, a three-dimensional molecular network is formed, which confers the elastic and self-reinforcing properties characteristic of vulcanized rubbers or other cross-linked elastomers*

When the temperature of the SEBS is raised above the polystyrene glass-transition temperature, the rubber softens, the molecules uncouple and the material flows when pressure or shearing forces are applied. This process is reversible and when the polymer is cooled, the molecules join together again and the three-dimensional network is re-established. The rubber will then remain flexible and elastic across the entire range of temperatures above the glass-transition temperature of poly(ethylene-butylene). Owing to their saturated structure, these polymers display a high level of resistance to degradation from exposure to oxygen, ozone and ultra-violet light, even under severe conditions. Additionally, they are resistant to heat degradation at temperatures up to 275°C.

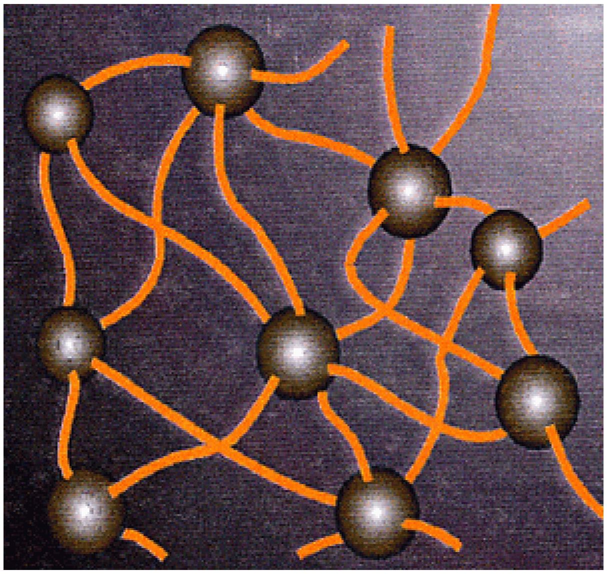


Fig.12:Three-dimensionalMolecularNetwork

SEBS is another rubber polymer compound, which is used to modify asphalt for roofing applications. Adding styrene-ethylene-butylene-styrene (SEBS) to asphalt uniquely alters the properties of roofing asphalt at the molecular level so that the enhanced asphaltic systems shows a significant improvement in overall performance. SEBS polymer modified asphalt increases the roof life and in place performencs of the systems .

SEBS modified asphalt is an elastomeric material with improved fatigue resistance and cohesive strength compared to conventional ,non polymerized asphalt bitumen. Its thermal stability , tensile strength and low temperature flexibility are superior to traditionally available products[14].

The flexibility of the bitumen at colder temperatures is a key factor in a membranes ability to withstand the stresses typically experienced in roofing applications.

1.3.6) REINFORCEMENTS USED IN PRESENT STUDY :

Conventional roofing felts are made of organic fibers and are impregnated with asphalt. They act as binders and as reinforcement in the waterproofing component in the BUR. In recent years non woven fabrics have made significant in roofing, in addition to many other fields, such as the geotextile and medical fields.

Most of the reinforcements used in roofing are woven fabrics or mats and scrims of nonwoven glass fibers and synthetic fibers. They are placed within the body of the membrane. In some cases, a lightweight reinforcing mesh is incorporated to act as a carrier during manufacture. Some exposed modified bituminous membranes without granule surfacing have a light glass mat embedded in the top surface to make it crack-resistant. The main requirements for the reinforcing fabrics include tensile strength, high initial elastic modulus, tear strength, puncture resistance, flexural stiffness, absorption and fatigue resistance. These and other properties such as dimensional stability are required during the manufacture of the membrane as well as during the performance in the field. The tensile strength and elongation properties can be varied as dictated by the *design requirements. A number of reinforced single-ply sheets were tested for load and elongation at break. The results show variations. Similarly, samples of modified bituminous membranes were tensile tested.*

FILLERS

Fillers have been considered especially by their manufacturers to be cheap extenders or diluents and have not been used correctly to obtain the full measure of their benefits. If their primary use is to reduce the cost of a compound it is our purpose to show the most efficient way to this end. There are some limitations also where the effect of fillers are not neglected.

- **Carbon black:** *carbon black is usually thought of as a reinforcement for elastomers. Although the greatest volume of carbon black does find its way into transportation products ,millions of pounds of black are consumed annually by the inks, coatings, and plastic industries. Generally carbon black does not provide the reinforcing characteristics associated with rubber in most plastics polymers. It is used however as a filler for economy .At the same time ,carbon black provides desirable end performance properties, the most important being ultraviolet and thermal protection protection , control of electrical conductivity and improved compound processing. The coarsest products provide the least blackness and the least ability to provide U.V protection they are however the least costly and because of low surface area, allow for the greatest loadings. Carbon black prevents ultraviolet degration of many polymers by two mechanisms. First, the carbon ,because of its blackness absorbs the damaging radiation . Second the carbon black acts as free radical trap catching the breakdown products of degradation which would likely catalyze additional degradation. U.V protection is best achieved when carbon blacks in the 16-20m particle dia range are dispersed well at concentrations between 2-3% by weight.*

In the simplest terms, carbon black is essentially elemental carbon in the form of extremely fine particles having an amorphous molecular structure. Buried within the amorphous mass is an infrastructure of microcrystalline arrays of condensed rings. These arrays appear to be similar to the layered condensed ring form exhibited by graphite, which is another form of carbon. The orientation of the arrays within the amorphous mass appears to be random, consequently a large percentage of arrays have open edges of their layer planes at the surface of the particle. Associated with these open edges are large numbers of unsatisfied carbon bonds providing sites for chemical activity. In use, particles remain largely intact and many of the useful properties of carbon black stem from their morphological characteristics while others result from surface activity.

Other than carbon, also present are very small quantities of other elements such as oxygen, hydrogen, and sulfur occurring in various function groups bound to the carbon mass. In addition, small quantities of condensed hydrocarbons are adsorbed onto the particles surface of most rubber grade carbon.

- **Talc:** *There are several forms of ore from which talc products can be made. However the talc of major interest to plastics users is a finely ground product consisting of thin platelets and is preferably white in color. Due to the platy nature of this special form of talc it is considered to be a reinforcing filler in many plastic applications. Its low cost qualifies the talc as an extender while its platyness or high aspect ration ,further qualifies the talc as a reinforcing filler. White ,platy fine ground talc s having ,dry brightness are readily available from certain suppliers. Composites filled with a platy talc always exhibit a higher stiffness and creep resistance ,both at ambient and elevated temperatures, when compared with composites filled with a particulate filler such as calcium carbonate. Talc, Steatite and soapstone are terms used in the trade for the same material. The chemical name for Talc is Magnesium Silicate. In its ground form, steatite has a large variety of industrial applications.*

Features

The value of industrial talc lies in its extreme softness, smoothness, slip & lubricating properties, high luster and sheen, chemical inertness, high fusion point, low conductivity to heat & electricity and hiding power as a pigment extender.

- **Calcium carbonate:** *Calcium carbonate fillers have high volume usage in plastics due to their unique advantages, including following:*

- *Their cost is among the lowest of the fillers.*
- *They are non toxic ,non-irritating, odorless*
- *They are white with low refractive index,easily colored to any desired shade.*
- *Their softness*
- *Their dryness*
- *They are easily mixed into formulations, sometimes aiding the mixing of other ingredients.*
- *They are stable over a wide temperatures between about 800-900℃*
- **Calcium Carbonate Synonyms**

Limestone, calcium carbonate, precipitated calcium carbonate, ground / pulverized calcium carbonate, PCC, GCC, calcite, limestone, crushed marble, ground limestone, lime, chalk, whiting, champagne chalk, French chalk.[15]

1.3.7) PRESENT STUDY

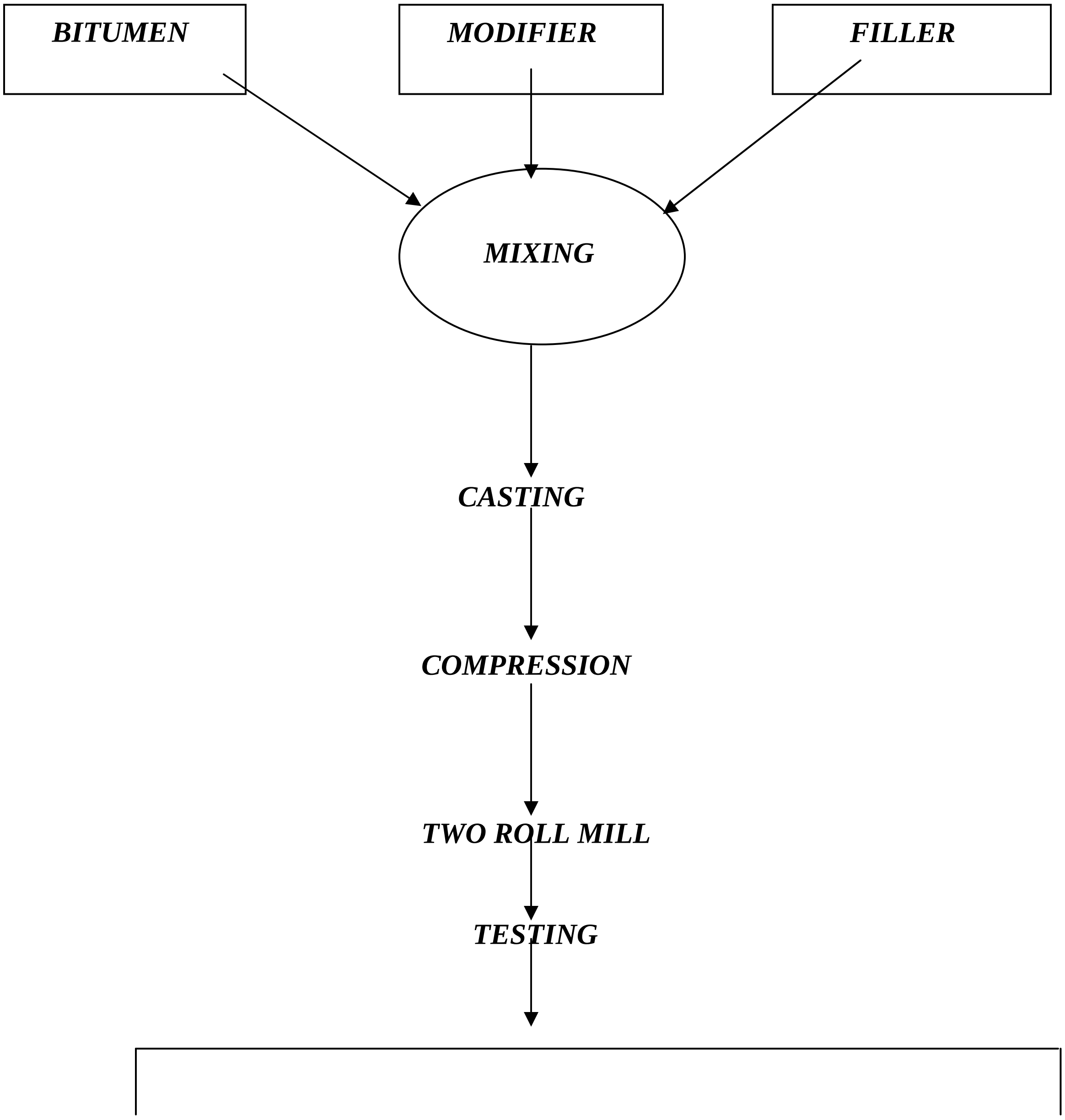
In the present study we have selected SEBS and APP as modifiers to improve the properties of Paving Grade Bitumen for application in waterproof roofing . Paving grade bitumen is selected because of its ease of availability and its reduced cost as compared to Industrial grade bitumen.

Raw bitumen behaves as thermoplastic i.e it softens on heating and hardens on cooling. Initially it is hard and brittle , it has inherent waterproofing property but lacks flexibility and strength. Here polymeric modifiers were used to improve the properties of raw bitumen. Different compositions for Reinforced and Non-Reinforced membranes were made using these two modifiers and their properties were Studied and compared with each other in order to study the effect of the material in waterproof roofings and similar applications.

Chapter-2

EXPERIMENTAL

FLOW CHART OF ASPHALT AND MODIFIER BLENDS



Softening point---- ASTM D 36
Penetration point--- ASTM D 5
Tear strength --- ASTM D 5147

Tensile strength ---ASTM D 5147
Heat Stability ---- ASTM D 5147
Cold Flexibility --- ASTM D 5147

2.1 RAW MATERIALS USED

a) BITUMEN:

Properties of virgin bitumen used:

- *Softening point-46℃*
- *Penetration point –40 to 400 dmm at 25℃*
- *Viscosity _ 600 to 3000 poise at 60℃*

b) TALC

Very fine white to greyish white odourless tastelass powder, insoluble in water but slightly soluble in dilute mineral acids.

- SiO_4 *: 61.5*
- *MgO : 29.5*
- Fe_2O_3 *: 0.15*
- *Cao : 0.375*

c) Calcium Carbonate : *Precipitated* $CaCo_3$ *powder granulations are available down to nanoparticles as fine as 30 nanometers*

Molecular Weight (g/mol.)	*100.09*
pH (saturated solution)	*9.3 to 9.8*
Loose Bulk Density (lbs/ft^3)	*~35-58*
Loose Bulk Density (lbs./cu. ft^3)	*50 to 90*
Tapped Density (g/cm^3)	*0.43 to 0.98*
Specific Heat (Btu/lbs./deg.F)	*0.19*
Mohrs Hardness @20°C	*3.0*
Merck	*11,1657*
Specific Gravity (solids)	*2.70- 2.71*
Index of Refraction	*1.6*
Crystallography	*hexagonal*

d) Glass fiber Strands: *Glass fiber strands are used in blending to improve the initial strength of the blend.*

Features: *Superior control on nominal weight,*

Uniform fiber distribution

Good handling characteristics

Easier mouldability

Lower resin consumption

Fast wet out results in lower cost.

Specifications:

Make—*Twiga*

Strand Length----*3mm to 51mm*

Density,g/m2----*300*

Application----*Reinforcement of thermoplastic for Engineering plastics*

e) ***Glass fiber Mat:*** *Glass fiber mat is used to reinforce two modified bitumen sheets to give this membrane high strength and improved mechanical properties.*

Specifications:

Make---*Twiga*

Filament Dia ,m---*11*

Glass to resin ratio---*1:1.7 to 1:2.2*

Mean Strand Tex, mm---*29*

Compatibility---*Polyester*

Density,g/m2---*300,450,600*

Width, mm----*1500*

Roll weight ,Kg---*50*

Application: *Contact molding, Cold press molding, Hand lay-up ,Sheet molding compound*

2.2) PROCEDURE FOR PREPARATION OF MODIFIED BITUMEN SHEETS:

To study the effect of various polymeric modifiers on bituminous membranes based on different formulations bitumen sheets were prepared and various properties were studied. The procedure for blending of polymer with bitumen and other ingredients and making of sheets is described below.

Blending:

The ingredients were weighed as per the formulation and are mixed in paddle type blender, under conditions given below. The bitumen is added to the mixer first and it is agitated under temperature till it becomes a low viscous melt. Then the polymer is added in small quantities. SEBS is available in powder form, which is added as such. But in the case of APP, which is in the lump form, was added after softening small pieces of the polymer. This procedure helps in better dispersion of polymer in bitumen matrix. The remaining ingredients are added one by one after a uniform melt is formed. The ingredients were added in the order of Talc, Calcium Carbonate, Carbon black and glass fiber.

Conditions:

Temperature: 200℃
Volume of the material used : 3000gms
Speed of motor: 50-150rpm

The mixture is cooled to the temperature where it can be easily poured out of the vessel on the casting mould.

Casting:

The mould consists of two metallic sheets called glaze sheets and one metallic frame with inside dimensions of 6.0 x 6.0 inch and 3mm thickness. The surfaces coming in contact with material are coated with silicon mould release agent to prevent sticking of bitumen to its surface. The hot formulation was then poured in to the mould cavity. After solidification of the sheet it is removed from the mould.

Compression Moulding:

The bitumen sheet is covered with a thin PET film on both sides before compression moulding for easy mould release. The sheet/composite laminate is then compressed between the platens under pressure and heat, so that the material softens and a sheet of uniform thickness is obtained.

Moulding conditions

Temperature : 85 °

Pressure: Increased from 0to 100 Kg/cm^2 in the intervals of 5Kg/cm^2 per 5 minutes.

Process time: 1 hrs including cooling

Cooling: Till temperature drops to 30℃(approx.)

Sheeting on Two roll mill:

This is to make the sheet still compact and of uniform thickness. The sheet after compression molding is passed between the rolls of two-roll mill to produce a thickness of 2 to 3 mm at 45℃ temperature

2.3)FORMULATIONS PREPARED

Various formulations of bitumen, modifiers and fillers were prepared by weighing and mixing in a mixer to get uniform mixture.

Various formulations were made based on following combinations of Bitumen, Polymer and other additives like carbon black, talc, and calcium carbonate and chopped glass fiber strands.

1. *In the first case Bitumen is modified with SEBS. Other ingredients were carbon black, talc, calcium carbonate and chopped glass fiber*

2. *The optimized blend from the Bitumen SEBS blend was chosen for further modifications. Here the Bitumen to polymer ratio is kept similar to that of optimized formulation. The polymer modifier used here were*

    1. *A combination of SEBS and APP. The ratio between SEBS and APP only was varied*

    2. *A combination of APP and PP. The ratio between APP and PP only was varied.*

3. *The optimized formulations of Bitumen with SEBS- APP combination and APP-PP combination were further modified by reinforcing with a glass fiber mat. The sheets of membranes made by casting were compressed together by keeping the glass fiber mat between them. The evaluation of this composite sheet was done by studying various mechanical and physical properties*

Each formulation is prepared for a batch of 3000gms

➢ *1) Formulations with SEBS*

Non-reinforcing formulations were made with varying ratios of bitumen and polymer and with fixed quantity of filler. The ratios of bitumen and polymer used were 90:10, 80:20 and 70:30. The quantity of filler was 20 percentage of the total weight of bitumen and polymer. The total filler includes carbon black, talc, calcium carbonate and chopped glass strands in the ratio of 22: 22: 45.75: 1.2

In the first case the bitumen and SEBS were blended. The formulations are given in table.4

	BITUMEN(gm)	*SEBS(gm)*	*FILLER(gm)*	*BITUMEN TO POLYMER RATIO*
Formulation A	*2160*	*240*	*600*	*90:10*
Formulation B	*1920*	*480*	*600*	*80:20*
Formulation C	*1680*	*720*	*600*	*70:30*

Table.4 Formulations for Bitumen- SEBS Blends

- ***Formulations with SEBS –APP combination***

The bitumen was blended with two polymeric modifiers i.e. SEBS and APP, in these formulations. The ratio between bitumen and polymer was constant i.e. 80:20 in all the formulations. Here the quantity of SEBS and APP were varied with in the fixed amount of 20 percent of total quantity of bitumen and polymer. The ratios of APP to SEBS used were 10:10, 15:5, and 5:15. Here also the quantity of filler and ratio of constituents were same as in the previous case of bitumen SEBS blends.

Formulations (BITUMEN TO POLYMER RATIO)	*Bitumen(gms)*	*APP(gms)*	*SEBS(gms)*	*Filler(gms)*
(B1)80:(10:10)	*1920*	*240*	*240*	*600*
(B2)80: (15:5)	*1920*	*360*	*120*	*600*
(B3)80: (5:15)	*1920*	*120*	*360*	*600*

Table 5: Formulations SEBS –APP combination

- ***Formulations with APP-PP combination***

Here the bitumen was modified with APP and PP combination with keeping the bitumen polymer ratio 80:20. The ratios of APP to PP were 10:10, 15:5, 5:15. The quantity of filler and ratio of constituents were same as the above cases.

Formulations (BITUMEN TO POLYMER RATIO)	*Bitumen(gms)*	*APP(gms)*	*PP(gms)*	*Filler(gms)*
(B4)80:(10:10)	*1920*	*240*	*240*	*600*
(B5)80: (15:5)	*1920*	*360*	*120*	*600*
(B6)80: (5:15)	*1920*	*120*	*360*	*600*

Table 6: Formulations with APP-PP combination

- ***Glass fiber mat reinforced formulations***

Here the optimized blends of Bitumen with APP-PP combination were further modified by reinforcing with a lass fiber mat between two layers of cast modified bituminous sheets.

Formulation B1 (BITUMEN TO POLYMER RATIO)	*Bitumen(gms)*	*APP(gms)*	*PP(gms)*	*Filler(gms)*
(B7)80:(10:10)	*1920*	*240*	*240*	*600*
(B8)80:(15:5)	*1920*	*360*	*120*	*600*
(B9)80:(5:5)	*1920*	*120*	*360*	*600*

Table 7: Glass fiber mat reinforced formulations

- ***Glass fibre reinforced formulations based on formulation 'B'***

Here the optimized blends of Bitumen with APP-SEBS combination were further modified by reinforcing with a lass fiber mat between two layers of cast modified bituminous sheets.

Formulations (*BITUMEN TO POLYMER RATIO)*	*Bitumen(gms)*	*APP(gms)*	*SEBS(gms)*	*Filler(gms)*
(B10)80:(10:10)	*1920*	*240*	*240*	*600*
(B11)80:(15: 5)	*1920*	*360*	*120*	*600*
(B12)80:(5:15)	*1920*	*120*	*360*	*600*

Table 8:Glass fibre reinforced formulations

CONCLUSION AND FUTURE PROSPECTS

This study was to analyze the effect of various polymeric modifiers on paving grade Bitumen and to evaluate various characteristics of the membrane made from bitumen modified with these polymers. The improvement in properties of paving grade membrane is evaluated by studying softening point and penetration point. The membrane made out of this modified bitumen is evaluated by studying performance properties like tensile strength, elongation, tear strength, heat stability and cold flexibility. From the results obtained following conclusions can be drawn

- *20 % polymer content in the formulation was found to be more suitable for modification on the basis of improved softening point, lower penetration point and consideration of economical factors*
- *Among various polymeric modifiers used the combination of APP- SEBS polymers in the ratio 10:10 was found to be the best. This combination was chosen for fabricating a commercially competent membrane using glass mat reinforcement.*
- *The glass fiber reinforcement improved physical and mechanical properties.*
- *The study shows that the paving grade bitumen can be used to make bituminous membranes for roofing application by modifying with common polymeric modifiers.*

This study about modification of paving grade bitumen for water proof roofing application requires further consideration in several aspects. The future scope of this project includes the commercialization of the economical process for the manufacture of roofing membranes using paving grade bitumen, the study about other important parameters like water impermeability, resistance to environmental factors etc., and utilization of recyclable polymeric materials for modification.

2.3 CHARACTERIZATION AND TESTING

INSTRUMENTS USED

- ***Bitumen Mixer:*** *This mixer is used to blend all the ingredients to form a homogenous blend . Mixing is the most important factor in manufacturing of membranes. All the ingredients are dispersed well in this mixer.*

Specifications:

Temperature Range---- *0-300°c*

Vessel Volume---*30Kg approx.*

Speed of motor(with controller)---*1440 rpm*

Power---*2HP*

Agitator---*Paddle Type*

- ***Compression Molding Machine:*** *This is used to compress the material to give it a required shape and thickness under specified pressure and temperature.*

Specification:

Make---*Santec(India)*

Temperature Range---*0-400°C*

Pressure---*0-280Kg/cm2*

- ***Two roll mill:*** *Two roll mill is generally used for mixing or compounding.*

Specification:

Make---*Slach Industries(India)*

Temp. Range---*0-200°C*

Roll dimensions ---*300mm length and 150mm dia*

- ***Universal Testing Machine:*** *This instrument is used for testing various mechanical properties of plastics.*

  Specification:

  Make ---*Instron*

  Model---4302

  Load capacity----*10KN tension or compression*

  Load weight accuracy*---+ 1% of reading*

  Cross head speed *----0.5-500mm/min*

  Return speed*----500mm/min*

  Max Load/speed capability*----10KN at 250mm/min*

  5KN at 500mm/min.

TESTING OVERVIEW

Performance Properties

- ***Tensile Strength and Elongation (ASTMD 5147)***

<u>Scope:</u>

Tensile Elongation measurements are among the most important indication of strength in a material and are the most widely specialised properties of plastic materials .Tensile test in a broad sense is measurement of the ability of the material to withstand forces that tend to pull it apart and to determine to what extent the material stretches before breaking.

This test method covers the determination of the tensile –elongation properties of *polymer modified bituminous sheets*

Testing Procedure

Before testing every test specimen is conditioned at specified temperature and humidity as specified in the standard.

- **Conditioning:** *test specimens are conditioned for a minimum of 4hrs.at 23±3 ℃ and 50+ 5 % relative humidity prior to testing.*
- **Specimens:** *Five specimens are prepared in both longitudinal and transverse direction for each temperature to be tested.*
- **Specimen size:***25mm wide and 150mm length*
- **Procedure:** *Each sample is conditioned for a minimum of 2hrs.and then tested on a Universal Testing Machine. The initial clamp separation shall be 75±2mm . Maintain a rate of separation of 50mm/min .Record the percent elongation at specimen break and also at maximum load using an extensiometer, or calculate the percent elongation at specimen break and also at maximum. Record the breaking load and maximum load of each specimen.*

Report the average load(KN/m) and percent elongation.

❖ Tear Strength (ASTM D 5147)

Scope

This test method covers the determination of the tensile –tear strength of bituminous roofing membranes

Testing Procedure

Before testing every test specimen is conditioned at specified temperature and humidity as specified in the standard.

- **Conditioning:** *test specimens are conditioned for a minimum of 4hrs.at 23±3 °C and 50+ 5 % relative humidity prior to testing.*

- **Specimens:** *Five specimens are prepared in both longitudinal and transverse direction for each temperature to be tested.*

- **Specimen size:***75mm wide and 200mm length ,notched*

- **Procedure:** *Each sample is conditioned for a minimum of 2hrs.and then tested on a Universal Testing Machine. The initial clamp separation shall be 75±2mm . Maintain a rate of separation of 50mm/min .Record the maximum load at specimen break, Report the average load (KN/m).*

- ***Low temperature Flexibility (ASTM D 5147)***

Scope

This test method determines the low temperature flexibility of polymer modified bituminous sheets. Low temperature flexibility is defined as the lowest temperature recorded at which no visual signs of cracking in the membrane are observed after bending 180+ 5 at the desired temperature around a 25+2mm diameter mandrel in approx. 2+1s.

Testing Procedure

- **Conditioning:** *Condition the specimens at 23+ and 50% relative humidity before testing.*

- **Specimens:** *Five specimens are prepared in both longitudinal and transverse direction for each temperature to be tested.*

- **Specimen size:***25mm wide and 150mm length*

- **Procedure:** *Each sample is tested at a temperature where the sheet is supposed to resist with the mandrel placed in the chamber for 2hrs. check the samples for each 3+1c increments and the record the temperature.*

❖ Heat Stability(ASTM D 5147)

Scope: *This test method determines the high temperature stability of polymer modified bituminous sheets.*

Testing Procedure:

- **Conditioning:** *Condition the specimens at 23+ and 50% relative humidity before testing.*

- **Specimens:** *Five specimens are prepared in both longitudinal and transverse direction for each temperature to be tested.*

- **Specimen size:***50 mm wide and 75mm length*

- **Procedure:** *Clamp each specimen on the 50mm edge with a clamp. Suspend the specimen via the clamp in the forced air oven with the 75mm edge of the specimen set vertically. After the specimens have been conditioned for at least 2h 15min at the specified temperature observe each specimen for signs of flowing ,dripping or drop formation on the lower edge of the specimen. If these signs are not observed ,increase the oven temperature by 14±3 °c .Maximum temperature shall not exceed 121±3 °c.Report the test temperature at which these signs are observed.*

❖ Softening point (ASTM D36)

Scope: *Bitumens are viscoelastic materials without sharply defined melting points they gradually become softer and less viscous as the temperature rises. For this reason softening point must be determind by an arbitrary and closely defined method .This test* *method covers the determination of the softening point of bitumen in the range from (30℃ to 157℃) using the ring and ball apparatus immersed in distilled water, glycerin(above 80 to 157℃ or Ethylene glycol(30 to 110℃)*

Apparatus:

Rings--- *Two square shouldered brass rings forming to the dimensions shown in Fig*

Pouring Plate--- *A flat smooth brass plate approx 50 by 75mm*

Balls---*Two steel balls ,9.5mm in dia each having a mass of 3.50±0.05gm*

Ball-centering Guides--- *Two bras guides for holding the steel balls on for each ring conforming to general shape as in fig below*

Bath--- *A glass vessel ,capable of being heated not more than 85mm in inside diameter and not less than 120mmin depth from the bottom of the flare.*

Ring holder and assembly--- *A brass holder designed to support the two rings in a horizontal position ,conforming to the shape and dimensions given in fig3. The bottom of the shouldered rings in the ring holder shall be 25mm above the upper surface of the bottom plate, and the lower surface of the bottom plate shall be 16±3mm from the bottom of the bath.*

Thermometers: *Low softening point Thermometer having a range from –2 to +80 prescribed in specification E1. High softening point Thermometer Having a range from 30 to 200℃ prescribed in specification E1.*

Release Agents: *To prevent adhesion of the bitumen to the pouring plate when casting disks ,the surface of the brass pouring plate may be thinly coated just before use with silicone oil or grease.*

Test procedure:

Specimens: *Heat the bitumen sample with care,stirring frequently to prevent local over heating until it has become sufficiently fluid to pour .Stir carefully to avoid incorporation of air bubbles in the sample. Take no more than 2h to heat an asphalt sample to its pouring temperature. Pour a slight excess of the heated bitumen into each ring and then allow the specimens to cool in ambient air for at least 30min. When the specimens have cooled cut away the excess bitumen cleanly with a slightly heated knife or spatula ,so that each disk is flush and level with the top of its ring.*

Procedure: *Select one of the following bath liquids and thermometers appropriate for the expected softening point. Assemble the apparatus in the labhood with the specimen rings ,ball-centering guides and thermometer in position and fill the bath so that the liquid depth will be 105±3mm ith the apparatus in place .Using forceps place the two steel balls in the bottom of the bath so they will reach the same starting temperature as the rest of the assembly. Heat the bath from below so that the temperature indicated by the temperature rises at a uniform rate of 5C. Protect the balls from drafts using shields if necessary. Record for each ring and ball the temperature indicated by the thermometer at the instant the bitumen surrounding the ball touches the bottom plate.*

- ***Penetration point(ASTM D 5)***

Scope: *Consistency of a bituminous material expressed as the distance in tenths of a millimeter that a standard needle vertically penetrates a sample of the material under known conditions of loading ,time, and temperature.This test method covers determination of the penetration of semi-solid and solid bituminous materials. The penetration is measured with a penetrometer by means of which a standard needle is applied to the sample under specified conditions.*

Apparatus: *Any apparatus that permits the needle holder to move vertically without measurable friction and is capable of indicating the depth of penetration to the nearest*

0.1mm will be acceptable. The weight of the spindle the weight of the spindle shall be 47.5+_0.05g.The total weight of the needle and spindle assembly shall be 50.0+_0.05g.Weights of 50+_0.05g and 100+_0.05g shall also be provided for total loads of 100g and 200g ,as required for some conditions of the test. The surface on which the sample container rests shall be flat and the axis of the plunger shall be approximately 90 to this surface. The spindle shall be easily detached for checking its weight.

Penetration needle: *The needle shall be made from fully hardened and tempered stainless steel, grade 440-c or equal , HRC 54 to 60 . It shall be approximately 50mm (2in.)in length and 1.00 to1.02 mm (0.0394 to 0.0402 in.) in diameter. It shall be symmetrically tapered at one end by grinding to a cone having an angle between 8.7 and 9.7 over the entire cone length. The cone should be coaxial with the straight body of the needle. The total coxial variation variation of the intersection between the conical and straight surfaces shall not be in excess of 0.2mm. The truncated tip of the cone shall be with in the diameter limits of 0.14 and 0.16mm and square to the needle axis within 2. The entire edge of the truncated surface at the tip shall be sharp and free of burs.*

Specimens: *Heat the sample with care until it becomes sufficiently fluid to pour . Pour the sample in to the sample container to adapt such that when cold to the temperature of the test . The depth of the sample is at least 10mm greater than the depth to which the needle is expected to penetrate*

Test Condition:

Where the conditions of test are not specified the temperature, load and time are understood to be at 25 C , 100gm, 5s respectively .

Procedure: *Place the sample container under the needle in a position so that by slowly lowering the needle until its tip just makes contact with the surface of the sample. Note the reading of the penetrometer dial or bring the pointer to zero. Quickly release the needle holder for the specified period of time and adjust the instrument to measure the distance penetrated in tenths of a millimeter.*

Chapter-3

RESULTS AND DISSCUSSIONS

3.1) Bitumen modified with SEBS :

The blends made by modifying Bitumen with SEBS were evaluated by studying various physical and mechanical properties. The important properties studied were softening point, penetration point, tensile strength and elongation, tear strength, heat ageing and cold flexibility.

a) Softening Point:

Softening point of different formulations is given in the table. The softening point of the bitumen, which was 46 °C, has improved tremendously after blending with the polymer. This is due to the formation of new morphology after blending with the polymer and due to the higher softening point of the SEBS. And also it is observed that the softening point increased with increasing polymer content.

S.No.	Code	Softening Point °c
1	Unmodified Bitumen	46
1	A	110
2	B	125
3	C	133

Table 9: Softening points of unmodified and SEBS modified bitumen

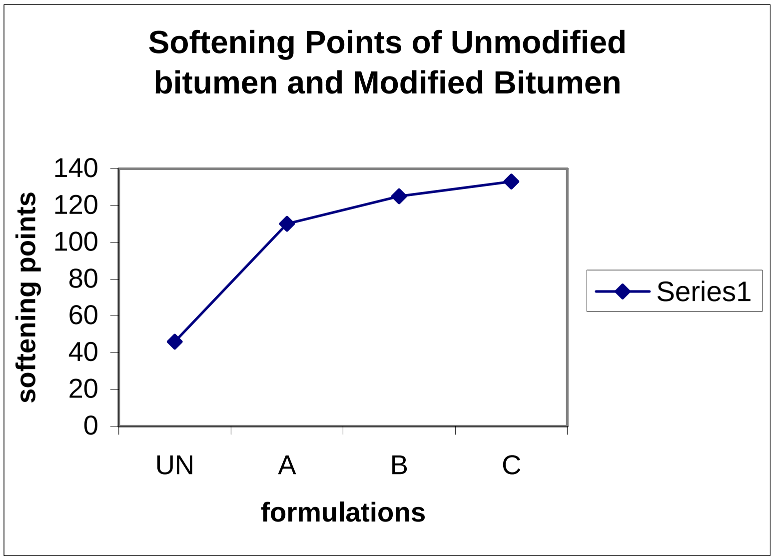


Fig: 13: Softening points of unmodified and SEBS modified bitumen

b) Penetration Point

Penetration point of unmodified bitumen and various formulations is given in table 2. Penetration point decreased with increasing content of SEBS. The penetration point of Unmodified Bitumen was 40, which showed a sharp decrease after blending with polymer. This is due to the improvement in stiffness of the blend because of the formation of physical bonding of polymer and bitumen. A three dimensional network is formed between the bitumen and the polymer due to physical bonding.

S.No.	*Code*	*Penetration Point(mm)*
1	*Un modified Bitumen*	*40*
2	*A*	*15*
2	*B*	*10*
3	*C*	*9*

Table10: Penetration points of unmodified and SEBS modified bitumen

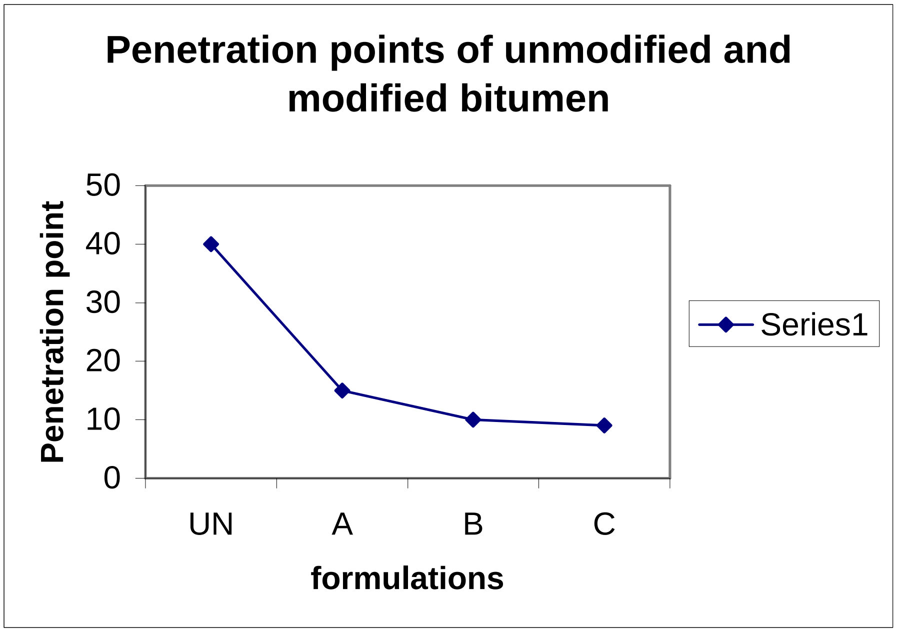


Fig: 14 Penetration points of unmodified and SEBS modified bitumen

b) Tear Strength

Tear strength of Bitumen modified sheets with various ratios of SEBS in longitudinal and transverse directions is given in table 3. The longitudinal direction is the direction of milling in the two-roll mill and direction perpendicular to this is transverse. As the unmodified bitumen has no integral properties the tear strength cannot be found. But the tear strength was found to be improving with increasing polymer content in both directions. On comparing tear strength in both directions it is found that tear strength is higher in the longitudinal direction. The improvement in tear strength also can be attributed to the improvement in strength and stiffness of the bitumen sheets on modification with polymer. The higher value of tear strength in longitudinal direction is presumed to be due to the alignment of chopped glass fiber strands in the milling direction.

S.No.	*Code*	*Direction*	*Tear strength KN/m*
1	*A*	*Longitudinal*	*2.78*
2	*B*	*Longitudinal*	*3.75*
3	*C*	*Longitudinal*	*4.08*
4	*A*	*Transverse*	*1.05*
5	*B*	*Transverse*	*2.2*
6	*C*	*Transverse*	*3.45*

Table 11: Tear strength of SEBS modified bitumen

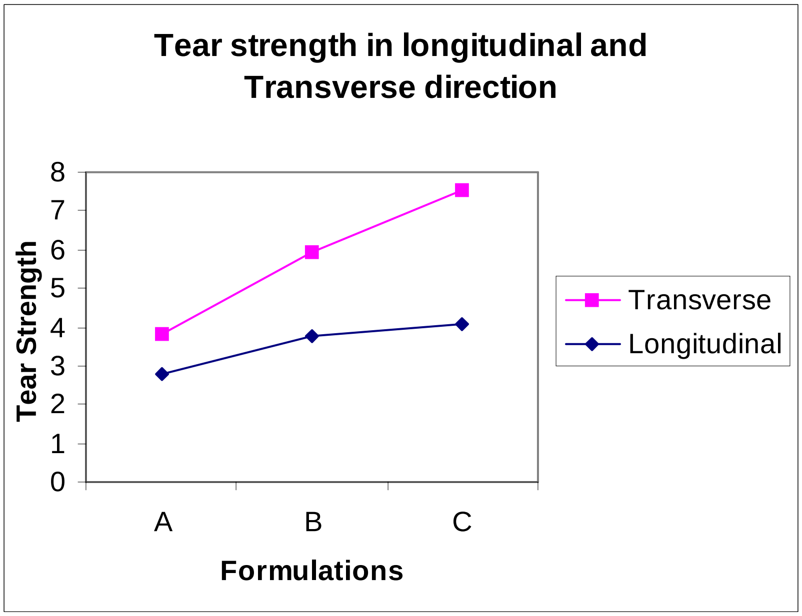


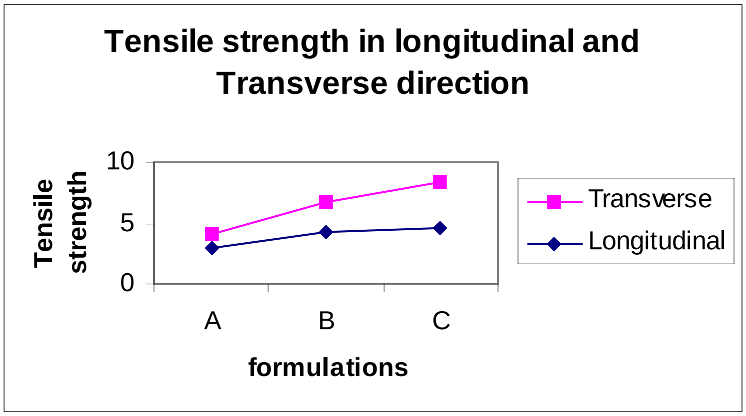
Fig: 15 Tear strength of SEBS modified bitumen

b) Tensile Strength and Elongation

Tear strength of Bitumen modified sheets with various ratios of SEBS in longitudinal and transverse directions is given in table 4.The results show the increase in tensile strength up to certain % this is because the modifiers improves the mechanical properties of the bitumen. Adding SEBS to asphalt uniquely alters the properties of roofing asphalt at the molecular level so that the enhanced asphaltic systems shows a significant improvement in overall performance.

S.No.	Code	Direction	Elongation %	Tensile strength N/25mm
1	A	Longitudinal	42.81	2.98
2	B	Longitudinal	45.13	4.25
3	C	Longitudinal	48.32	4.59
4	A	Transverse	52.38	1.15
5	B	Transverse	50.41	2.4
6	C	Transverse	53.21	3.76

Table 12: Tensile strength and elongation of SEBS modified bitumen



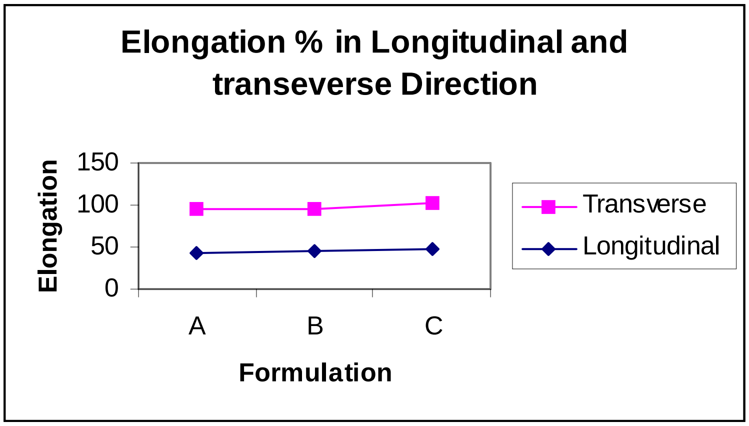


Fig: 16 Tensile strength and elongation of SEBS modified bitumen

e) Cold Flexibility

The table below shows cold flexibility temperatures of formulations:

The table reveals the cold flexibility temperatures of all the formulations increasing with the increase in the modifiers ratio .Raw bitumen initially used becomes brittle at low temperatures , as the amount of polymer is added to it its low temperature properties are also enhanced it may be because the polymeric modifier used has its initial low temperature flexibility . Polymeric modifier improves the morphology of the bitumen and hence improves its capability for various applications.

S.No.	*Code*	*Cold Flexibility, ° C*
1	*A*	*-2*
2	*B*	*-5*
3	*C*	*-10*

Table 13: Cold Flexibility temperature of SEBS modified bitumen

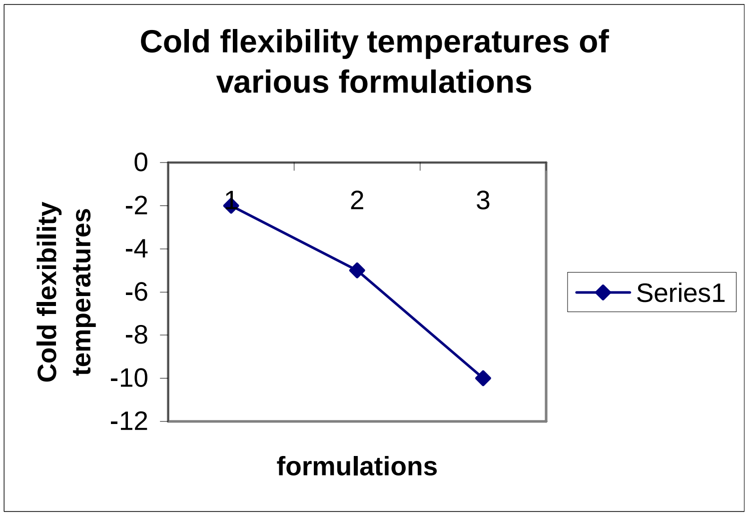


Fig: 17 Cold Flexibility temperature of SEBS modified bitumen

f) **Heat Aging:** *Heat aging is an important property of the modified bitumen roofings as it has to withstand high temperatures . the table below shows the heat stability temperatures increasing with the increasing amount of modifier. Bitumen initially used has no heat stability ,it tends to soften and liquify on heating but with the in corporation of polymers its heat aging properties improved.*

S.No.	*Code*	*Heat Aging°C*
1	*A*	*50*
2	*B*	*60*
3	*C*	*60*

Table 14: Heat aging temperature of SEBS modified bitumen

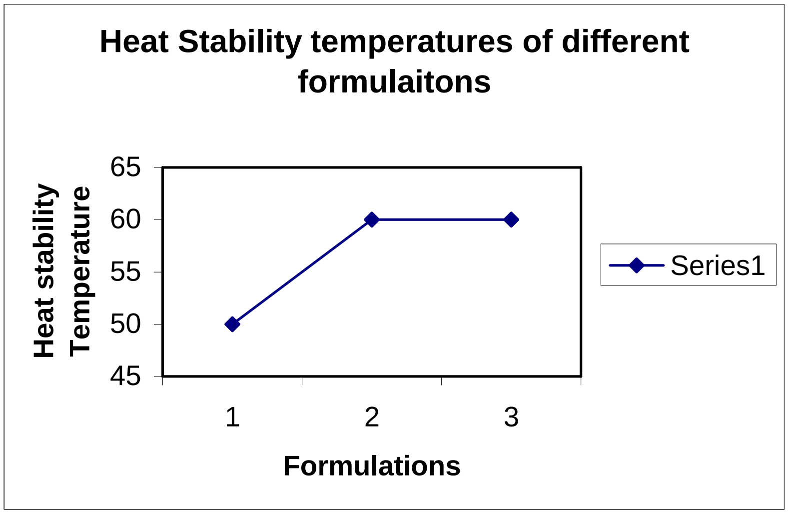


Fig: 18 Heat aging temperature of SEBS modified bitumen

CONCLUSION: *from above discussions it was observed that the addition of polymeric modifiers changes the bitumen rheology. The properties of this system were totally different to those of a bitumen and that it essentially depends on the polymer concentration.*

It was observed that as the polymer concentration was increased there was a significant change in the physical and mechanical property of the bitumen. Three cases were observed here:

- *Initially, Formulation A , a low polymer content was used ,here the polymer phase is dispersed through the bitumen matrix.The dispersed polymer phase enhances the properties of the binder both at low and at high service temperatures. In otherwords, the polymer extends the useful temperature range for the asphalt. In this case, the choice of bitumen is determining factor.*

- *Formulation B In this case, the polymer is the continuous phase and the asphalt is there in dispersed. The properties of such a system are fundamentally different to those of a bitumen, and depend essentially on those of the polymer. One should speak not of a polymer modified bitumen, but of a thermoplastic adhesive. The properties are better than formulation A.*

- *Formulation C ,this was based on very high polymer content although the properties are better than previous formulations but very high polymer content increases the cost of the membrane.*

Based on these studies Formulation B was selected as optimized formulation and was used as bases for further modifications.

3.2) MODIFICATION OF OPTIMIZED FORMULATIONS:

The optimized formulation from initial batches was selected for further study . Here a combination of polymers was used to study the effect on bitumen. The quantity of polymers were varied in fixed amount of 20 percent of the total quantity of bitumen and polymer. These ratios were 10:10, 15:5, 5:15.

Two types of systems are formed :

- *Non-reinforced formulations with APP- SEBS and APP –PP*
- *Glass fiber mat reinforced formulations with APP- SEBS and APP –PP*

Bitumen modified with APP-SEBS and APP - PPcombination:

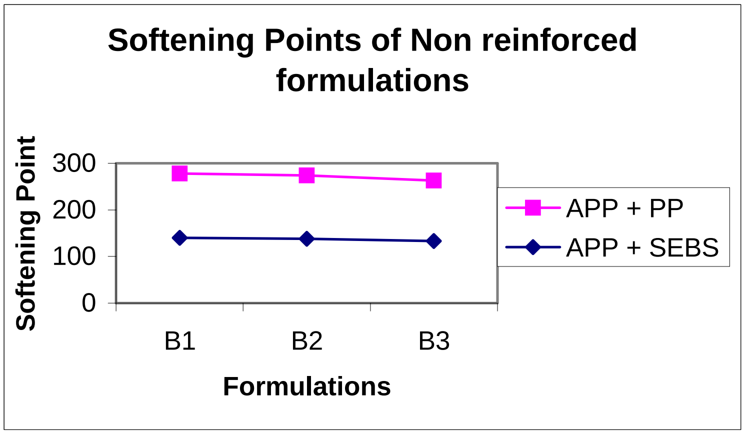
a) *Softening Point:*

As it was observed that the percentage of modifier in the ratio of 10: 10 gives better results ,there is an increase in the softening point of the blend this may be due to the combination of modifiers forming a good network with the bitumen and both have initial high softening points .

- *Miscibility of Bitumen and Modifier increases with increasing shear forming a homogenous blend .*
- *The increase in softening point is due to the modifier molecules forming physical bonding with the bitumen and improves its high temperature flexibility.*
- *The Bar-graphs show the comparison of various formulations modified with APP – SEBS and APP -PP*

S.No.	*Code*	*Softening Point ◦c*
1	*B1*	*140*
2	*B2*	*138*
3	*B3*	*133*
4	*B4*	*138*
5	*B5*	*136*
6	*B6*	*130*

Table 15(a): softening points of APP-SEBS and APP - PPcombination



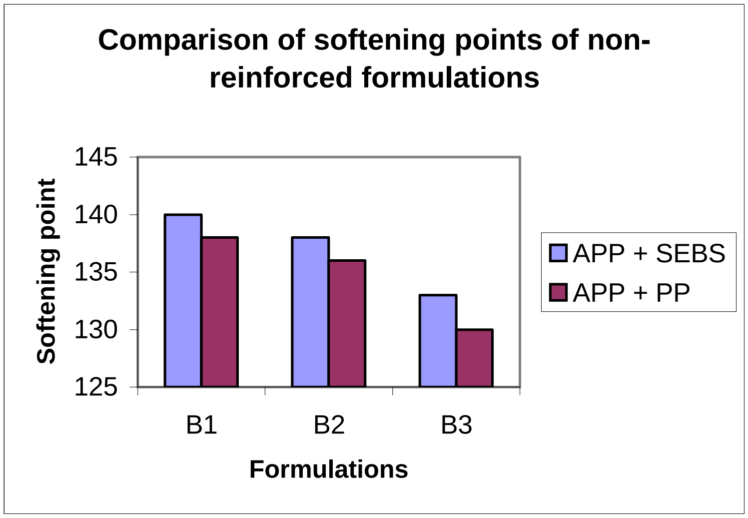


Fig: 19(a): softening points of APP-SEBS and APP - PPcombination

b) Penetration Point:

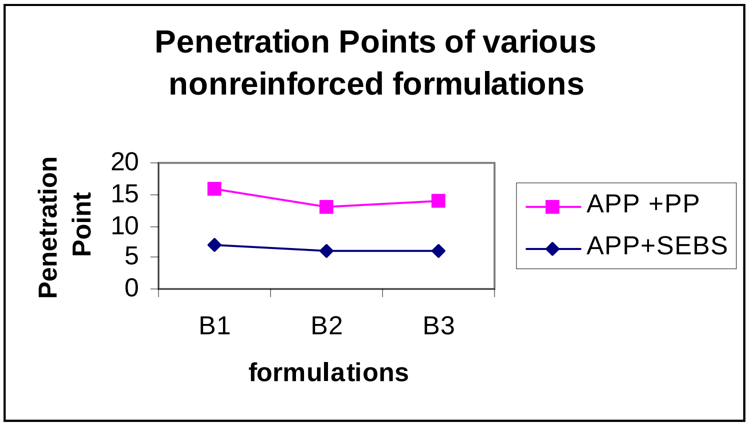
The table below shows the Penetration point of different Non reinforced formulations. Penetration point gives the measure of how much soft a material is so that a needle of specified dimensions penetrates into it.

Polymers as modifiers have a property to improve the stiffness of the bitumen which it lacks initially. The improvement in the penetration point upto certain % may be due to the good dispersion of modifier particles. The polymer forms the physical network with the bitumen and improves its properties.

The bar-graphs show the comparison of Penetration points of non-reinforced formulations and it is seen that with increasing modifier ratios there is significant decrease in Penetration point.

S.No.	*Code*	*Penetration Point(mm)*
1	*B1*	*7*
2	*B2*	*6*
3	*B3*	*6*
4	*B4*	*9*
5	*B5*	*7*
6	*B6*	*8*

Table 15(b)


Penetration Points of various nonreinforced formulations
Penetration Point
20
15
10
5
0
B1
B2
B3
formulations
APP +PP
APP+SEBS

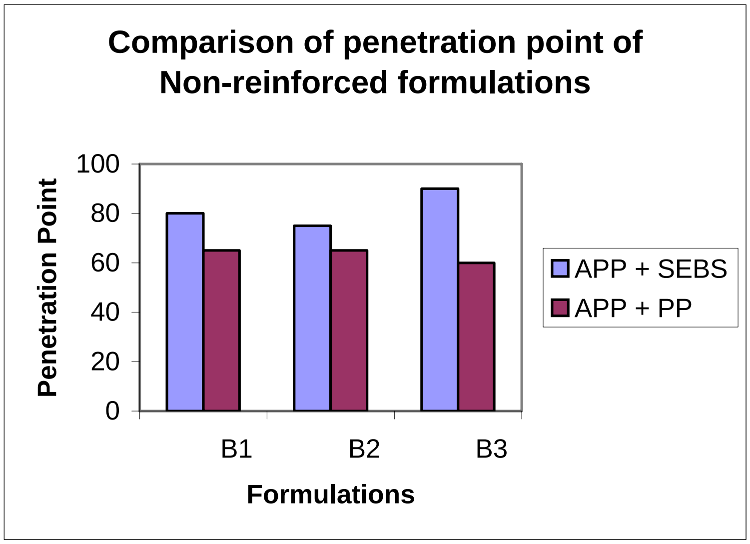

Comparison of penetration point of Non-reinforced formulations
Penetration Point
100
80
60
40
20
0
B1
B2
B3
Formulations
APP + SEBS
APP + PP

Fig.19(b)

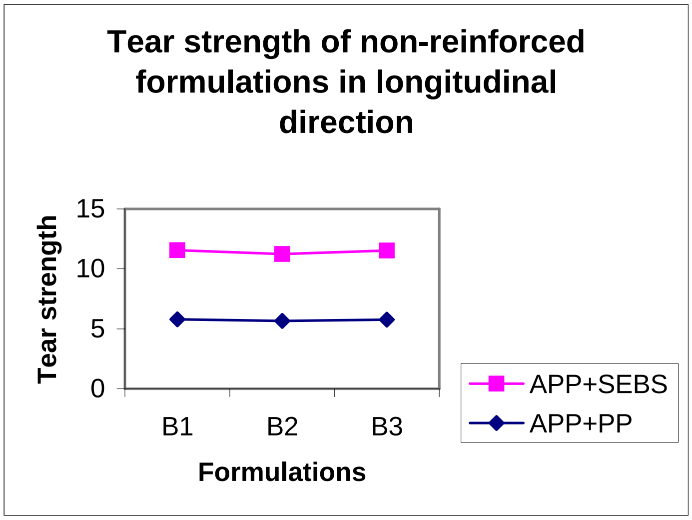
c)Tear Strength :*The table below shows the Tear Strength of different formulations*

As we know bitumen itself has no strength so it is seen that as the content of polymer is added sufficiently there is formed a tridimensional network which forms a physical interlocking of bitumen and polymer .APP – SEBS and APP- PP , these combinations have shown remarkable effect on bitumen and improved the physical properties of the bitumen.

- *As the percentage of modifiers is increased the mechanical properties enhances gradually.*
- *Tear strength is higher in one direction this is because of the molecular alignment*

S.No.	*Code*	*Direction*	*Tear strength KN/m*
1	*B1*	Longitudinal	5.79
2	*B2*	Longitudinal	5.65
3	*B3*	Longitudinal	5.77
4	*B4*	Longitudinal	5.77
5	*B5*	Longitudinal	5.60
6	*B6*	Longitudinal	5.75
7	*B1*	Transverse	4.75
8	*B2*	Transverse	4.6
9	*B3*	Transverse	4.72
10	*B4*	Transverse	4.71
11	*B5*	Transverse	4.55
12	*B6*	Transverse	4.7

Table 15©


Tear strength of non-reinforced formulations in longitudinal direction
Tear strength
15
10
5
0
B1
B2
B3
Formulations
APP+SEBS
APP+PP

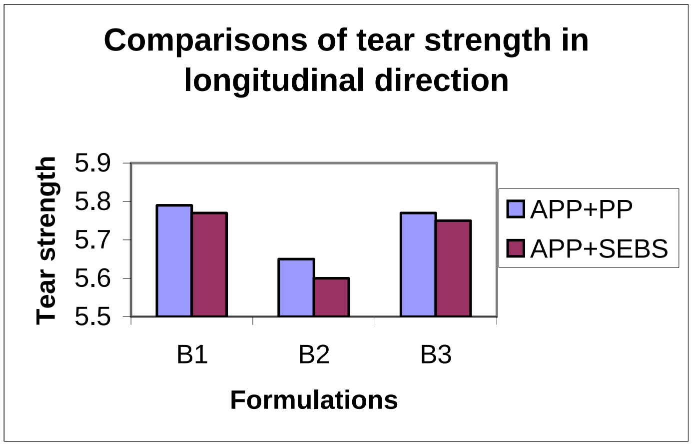
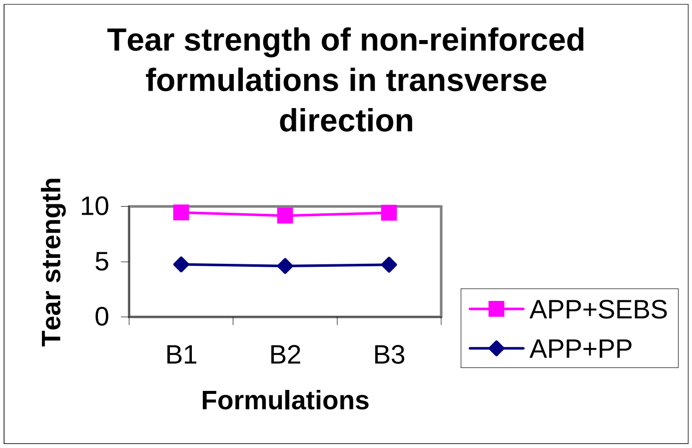

Comparisons of tear strength in longitudinal direction
Tear strength
5.9
5.8
5.7
5.6
5.5
B1
B2
B3
Formulations
APP+PP
APP+SEBS

Fig.19©


Tear strength of non-reinforced formulations in transverse direction
Tear strength
10
5
0
B1
B2
B3
Formulations
APP+SEBS
APP+PP

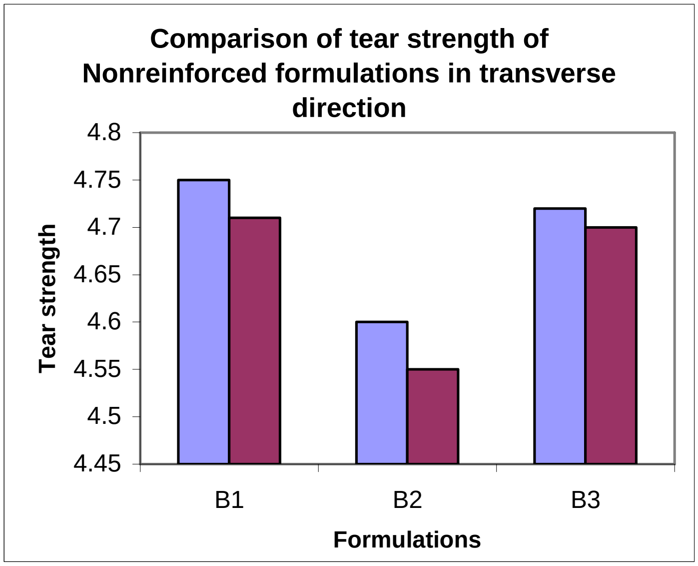
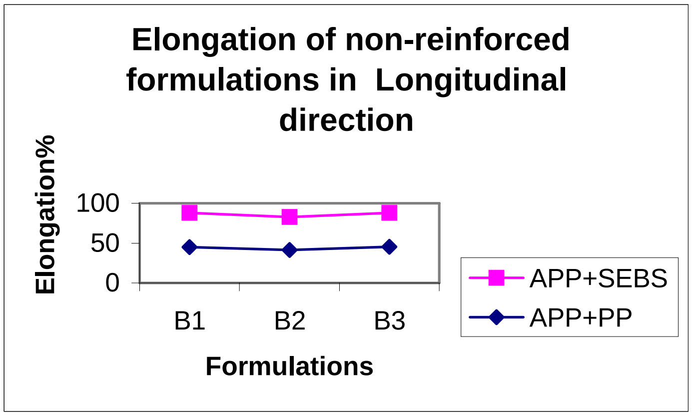

Comparison of tear strength of Nonreinforced formulations in transverse direction
4.8
4.75
4.7
4.65
4.6
4.55
4.5
4.45
Tear strength
B1
B2
B3
Formulations

Fig 19(d)

d)Tensile Strength. *The table below shows the Tensile strength of different formulations in longitudinal direction .*

S.No.	*Code*	*Direction*	*Elongation %*	*Tensile strength N/25mm*
1	*B1*	*Longitudinal*	*44.84*	*6.59*
2	*B2*	*Longitudinal*	*41.36*	*5.65*
3	*B3*	*Longitudinal*	*45.56*	*6.86*
4	*B4*	*Longitudinal*	*43.19*	*5.77*
5	*B5*	*Longitudinal*	*41.29*	*5.6*
6	*B6*	*Longitudinal*	*42.25*	*5.75*
7	*B1*	*Transverse*	*51.81*	*4.86*
8	*B2*	*Transverse*	*50.12*	*4.6*
9	*B3*	*Transverse*	*53.14*	*4.95*
10	*B4*	*Transverse*	*48.96*	*4.71*
11	*B5*	*Transverse*	*47.98*	*4.55*
12	*B6*	*Transverse*	*47.13*	*4.7*

Table 15(d)


Elongation of non-reinforced formulations in Longitudinal direction
Elongation%
100
50
0
B1
B2
B3
Formulations
APP+SEBS
APP+PP

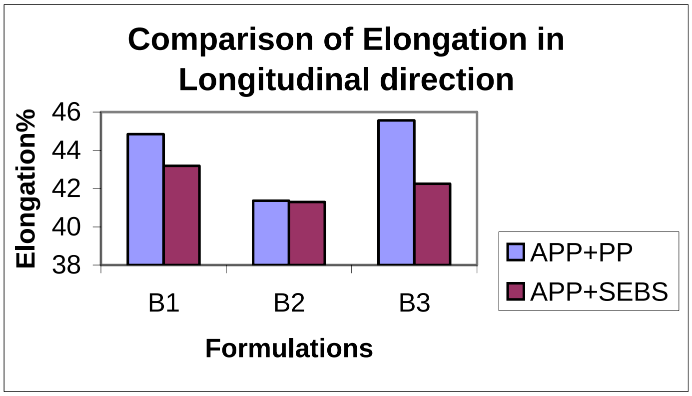
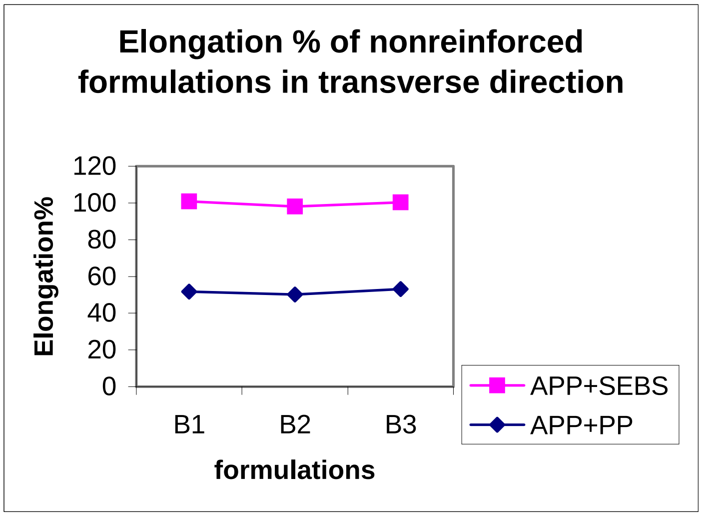

Comparison of Elongation in Longitudinal direction
Elongation%
46
44
42
40
38
B1
B2
B3
Formulations
APP+PP
APP+SEBS

Fig 19(e)


Elongation % of nonreinforced formulations in transverse direction
Elongation%
120
100
80
60
40
20
0
B1
B2
B3
formulations
APP+SEBS
APP+PP

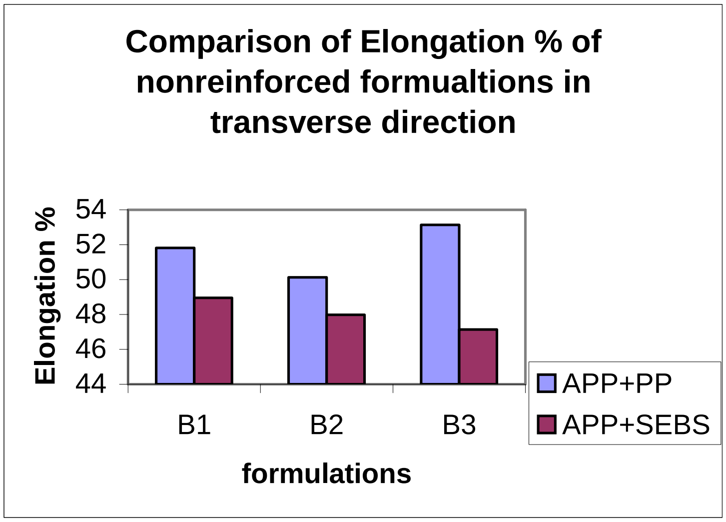
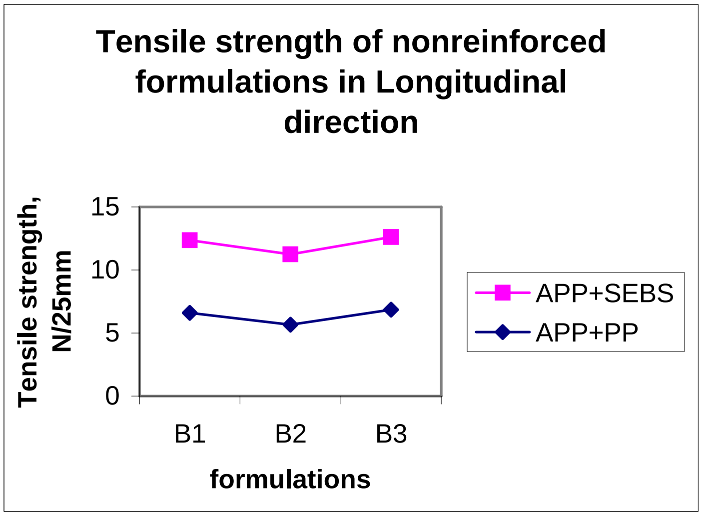

Comparison of Elongation % of nonreinforced formualtions in transverse direction
Elongation %
54
52
50
48
46
44
B1
B2
B3
formulations
APP+PP
APP+SEBS

Fig 19(f)


Tensile strength of nonreinforced formulations in Longitudinal direction
Tensile strength, N/25mm
15
10
5
0
B1
B2
B3
formulations
APP+SEBS
APP+PP

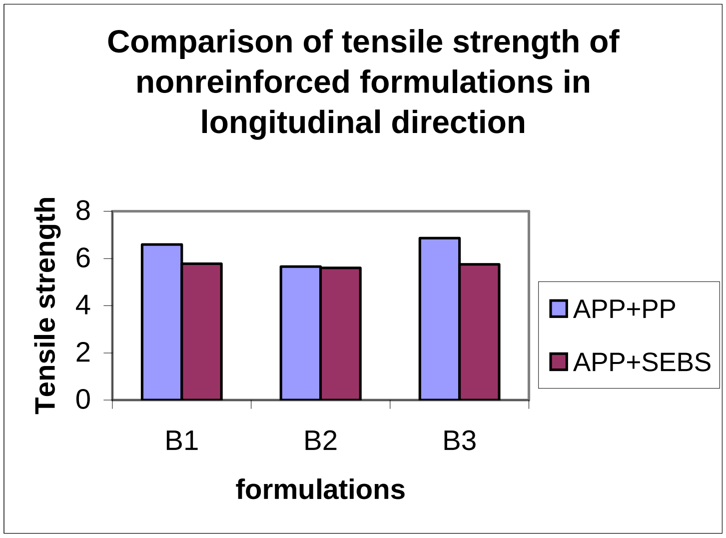
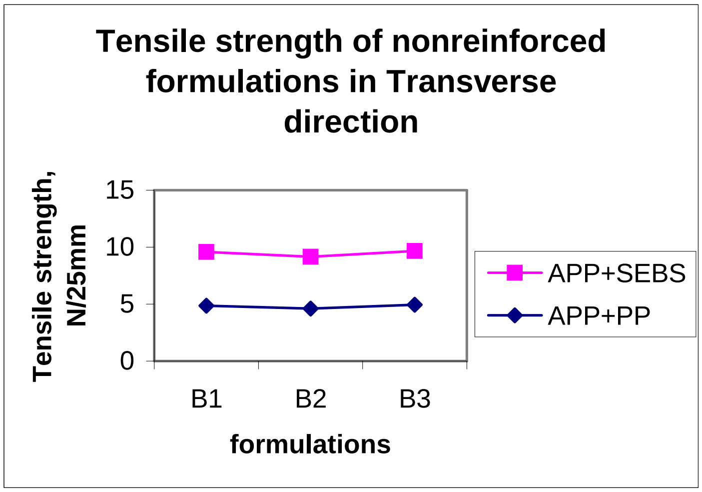

Comparison of tensile strength of nonreinforced formulations in longitudinal direction
Tensile strength
8
6
4
2
0
B1
B2
B3
formulations
APP+PP
APP+SEBS

Fig 19(g)


Tensile strength of nonreinforced formulations in Transverse direction
Tensile strength, N/25mm
15
10
5
0
B1
B2
B3
formulations
APP+SEBS
APP+PP

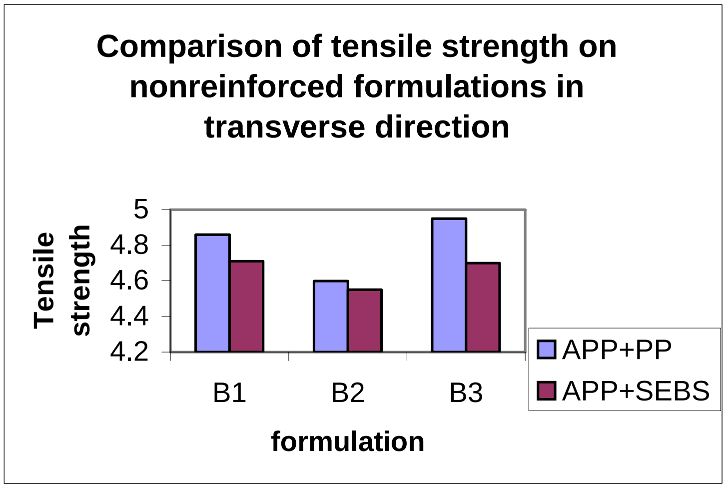

Comparison of tensile strength on nonreinforced formulations in transverse direction
Tensile strength
5
4.8
4.6
4.4
4.2
B1
B2
B3
formulation
APP+PP
APP+SEBS

Fig19(h)

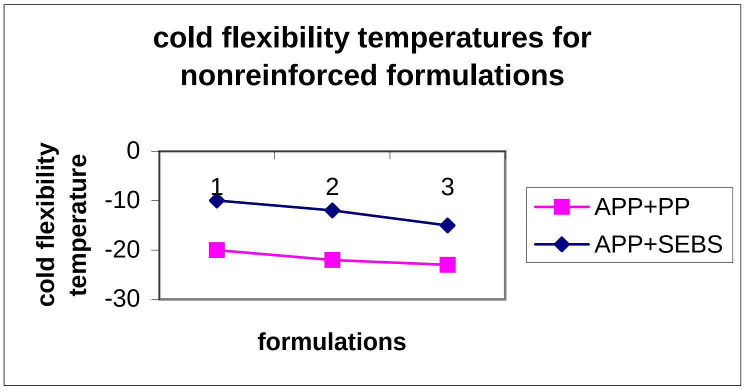
e) Cold Flexibility

The table reveals the cold flexibility temperatures of all the formulations increasing with the increase in the modifiers ratio. This is an important property so that the modified membrane could withstand low temperatures without any effect.

A combination of both the modifiers in the final blend can be used to improve certain mechanical properties. This provides properties to the final polymer such as improved low temperature performance.

S.No.	*Code*	*Cold Flexibility, ° C*
4	*B1*	*-10*
5	*B2*	*-12*
6	*B3*	*-15*
7	*B4*	*-10*
8	*B5*	*-10*
9	*B6*	*-8*

Table 15(e)


cold flexibility temperatures for nonreinforced formulations
cold flexibility temperature
0
-10
-20
-30
1
2
3
formulations
APP+PP
APP+SEBS

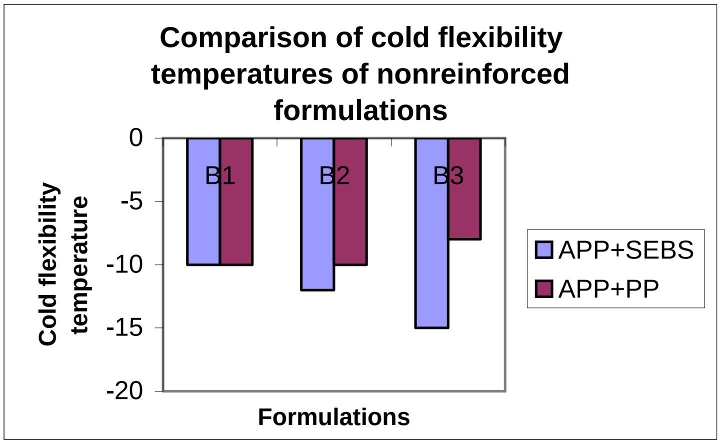

Comparison of cold flexibility temperatures of nonreinforced formulations
Cold flexibility temperature
0
-5
-10
-15
-20
B1
B2
B3
Formulations
APP+SEBS
APP+PP

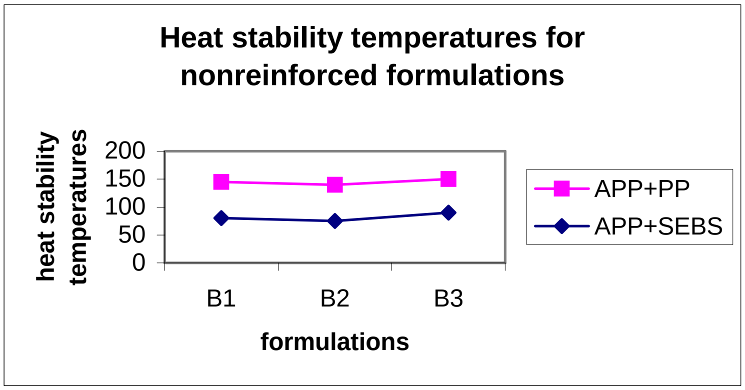
Fig 19(i)

f)Heat Aging: *The table below reveals the heat stability temperatures of various formulations*

The rise in Heat stability temperature of different formulations reveal that bitumen which initially because of no strength cannot withstand higher temperatures .when modified with polymers shows tremendous withstandanding capacity at higher temperatures.

S.No.	*Code*	*Heat Aging℃*
1	*B1*	*80*
2	*B2*	*75*
3	*B3*	*90*
4	*B4*	*65*
8	*B5*	*65*
9	*B6*	*60*

Table 15(f)


Heat stability temperatures for nonreinforced formulations
heat stability temperatures
200
150
100
50
0
B1
B2
B3
formulations
APP+PP
APP+SEBS

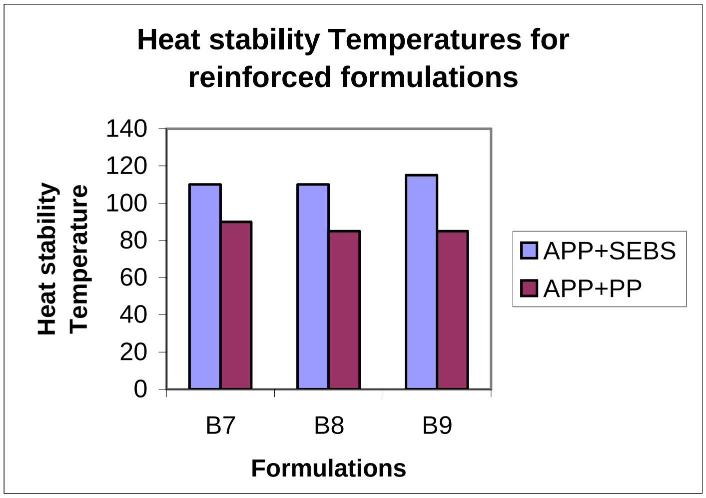

Heat stability Temperatures for reinforced formulations
Heat stability Temperature
140
120
100
80
60
40
20
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig. 19(j)

3.3) REINFORCEMENT OF OPTIMIZED COMBINATIONS:

Reinforcement is an important aspect for modified bitumen membranes.The polymer modifies the rheology of the bitumen by improving its physical and mechanical properties ,as the modified bitumen membranes has to serve various purposes ,it has to withstand various weather factors it is important that the membrane should have high strength to be easily handled , transported and installed.

So for these purposes the modified bitumen sheet was reinforced with glass fiber mat which enhances its physical properties tremendously.

Here the non reinforced combination which were earliar made were further modified with glass fiber reinforcement, their properties were studied and evaluated.

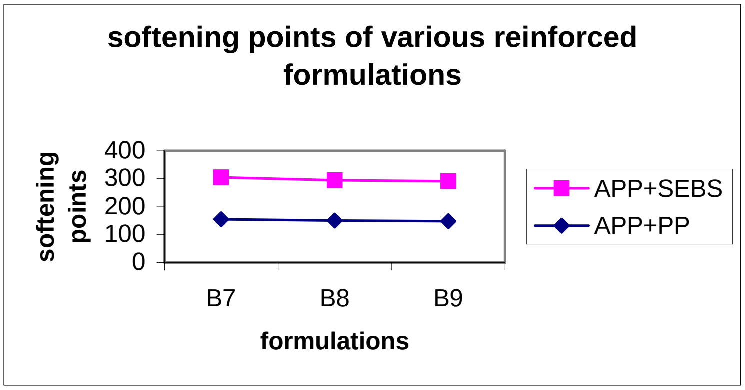
Reinforced formulations of Bitumen –(APP +SEBS) and Bitumen –(APP+PP) :

a)Softening Point:

The bar-graphs show the comparison of softening points of reinforced and formulations and it is seen that with increasing modifier ratios and reinforcement there is tremendous increase in softening point

S.No.	*Code*	*Softening Point ◦c*
1	*B7*	*155*
2	*B8*	*150*
3	*B9*	*148*
4	*B10*	*150*
5	*B11*	*145*
6	*B12*	*143*

Table 16(a)


softening points of various reinforced formulations
softening points
400
300
200
100
0
B7
B8
B9
formulations
APP+SEBS
APP+PP

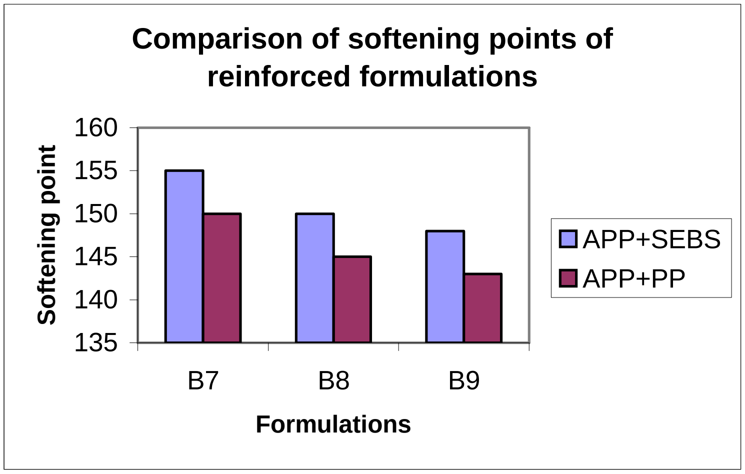

Comparison of softening points of reinforced formulations
Softening point
160
155
150
145
140
135
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig.20(a)

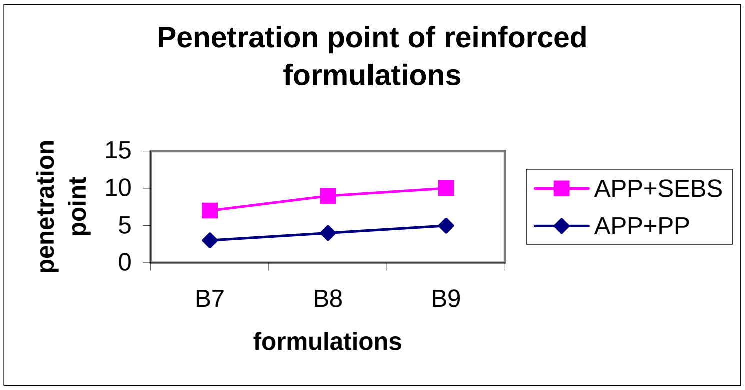
b) Penetration Point

The table below shows the Penetration point of different formulations

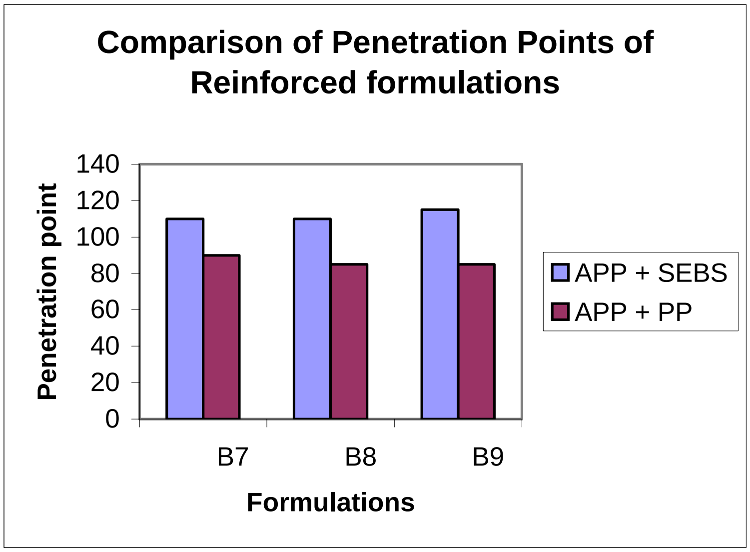
The bar-graphs show the comparison of Penetration points of reinforced formulations and it is seen that with increasing modifier ratios and reinforcement there is tremendous increase in Penetration point.

S.No.	*Code*	*Penetration Point(mm)*
1	*B7*	*3*
2	*B8*	*4*
3	*B9*	*5*
4	*B10*	*4*
5	*B11*	*5*
6	*B12*	*5*

Table 16(b)



Penetration point of reinforced formulations
penetration point
15
10
5
0
B7
B8
B9
formulations
APP+SEBS
APP+PP



Comparison of Penetration Points of Reinforced formulations
Penetration point
140
120
100
80
60
40
20
0
B7
B8
B9
Formulations
APP + SEBS
APP + PP

Fig .20(b)

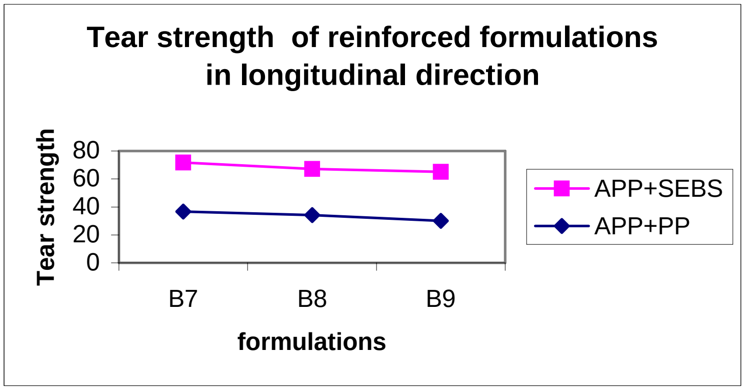
c)Tear Strength

The table below shows the Tear Strength of different formulations in longitudinal direction .

The bar-graphs show the comparison of Tear strength of reinforced and non-reinforced formulations and it is seen that with increasing modifier ratios and reinforcement there is tremendous increase in Tear strength

S.No.	*Code*	*Direction*	*Tear strength N/25mm*
1	*B7*	Longitudinal	36.75
2	*B8*	Longitudinal	34.15
3	*B9*	Longitudinal	30.14
4	*B10*	Longitudinal	35.04
5	*B11*	Longitudinal	33.12
6	*B12*	Longitudinal	34.98
7	*B7*	Transverse	27.16
8	*B8*	Transverse	25.16
9	*B9*	Transverse	22.45
10	*B10*	Transverse	26.18
11	*B11*	Transverse	23.75
12	*B12*	Transverse	25.1

Table 16©


Tear strength of reinforced formulations in longitudinal direction
Tear strength
80
60
40
20
0
B7
B8
B9
formulations
APP+SEBS
APP+PP

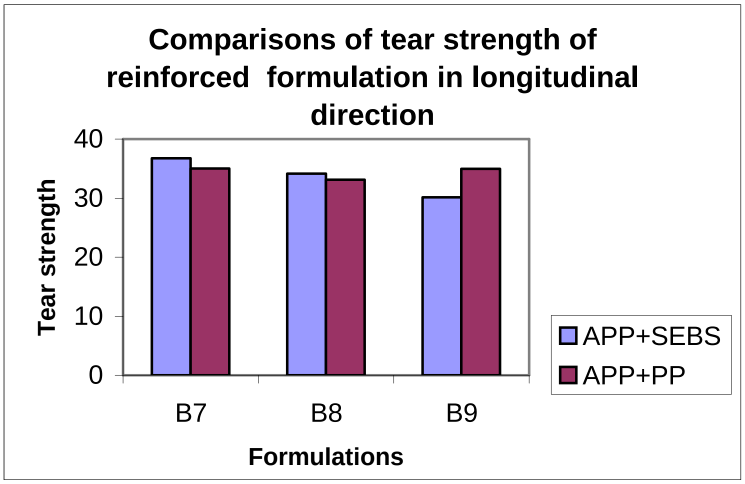
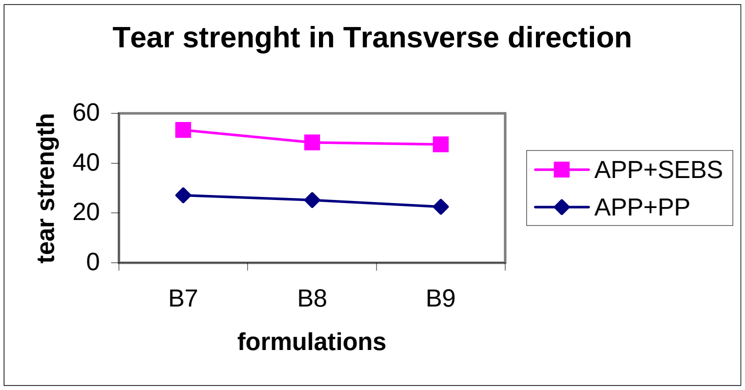

Comparisons of tear strength of reinforced formulation in longitudinal direction
Tear strength
40
30
20
10
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig.20©


Tear strenght in Transverse direction
tear strength
60
40
20
0
B7
B8
B9
formulations
APP+SEBS
APP+PP

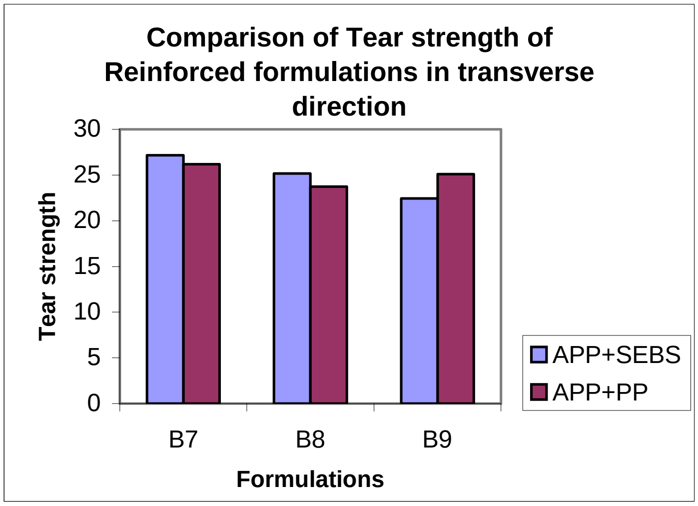

Comparison of Tear strength of Reinforced formulations in transverse direction
Tear strength
30
25
20
15
10
5
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig.20(d)

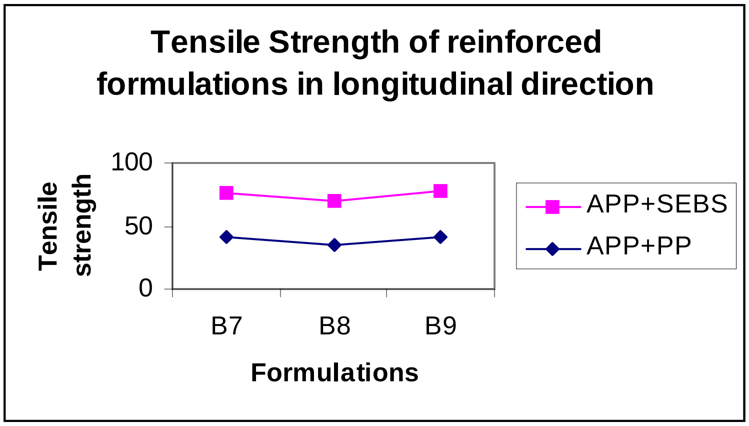
d)Tensile Strength

The table below shows the Tensile strength of different formulations in longitudinal direction .

The bar-graphs show the comparison of Heat stability Temperatures of reinforced and formulations and it is seen that with increasing modifier ratios and reinforcement there is tremendous increase in tensile strength.

S.No.	*Code*	*Direction*	*Elongation %*	*Tensile strength N/25mm*
1	*B7*	Longitudinal	45.01	40.56
2	*B8*	Longitudinal	43.25	35.15
3	*B9*	Longitudinal	47.98	41.04
4	*B10*	Longitudinal	43.25	35.12
5	*B11*	Longitudinal	42.59	33.98
6	*B12*	Longitudinal	41.59	37.12
10	*B7*	Transverse	52.01	29.15
11	*B8*	Transverse	51.18	26.16
12	*B9*	Transverse	53.24	30.18
13	*B10*	Transverse	48.56	25.75
14	*B11*	Transverse	48.23	25.1
15	*B12*	Transverse	47.56	26.15

Table 16(d)


Tensile Strength of reinforced formulations in longitudinal direction
Tensile strength
100
50
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

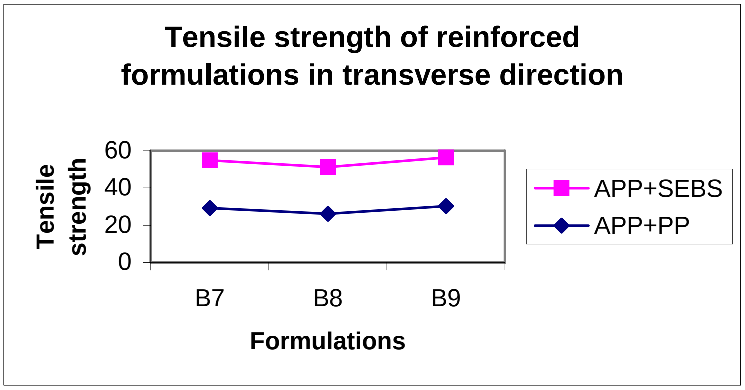
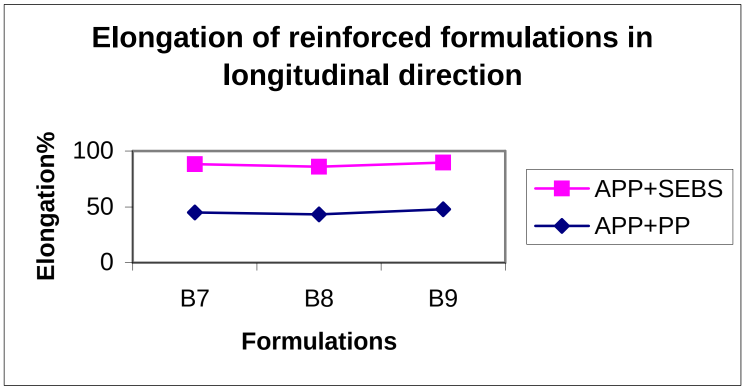

Tensile strength of reinforced formulations in transverse direction
Tensile strength
60
40
20
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig.20(e)


Elongation of reinforced formulations in longitudinal direction
Elongation%
100
50
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

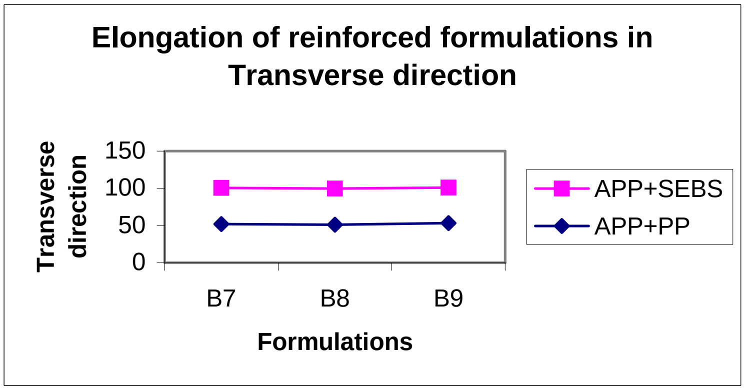
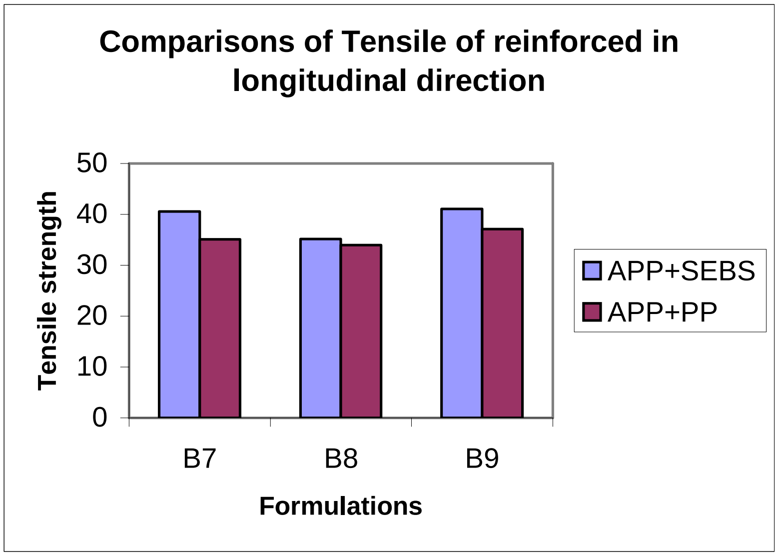

Elongation of reinforced formulations in Transverse direction
Transverse direction
150
100
50
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig.20(f)


Comparisons of Tensile of reinforced in longitudinal direction
Tensile strength
50
40
30
20
10
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

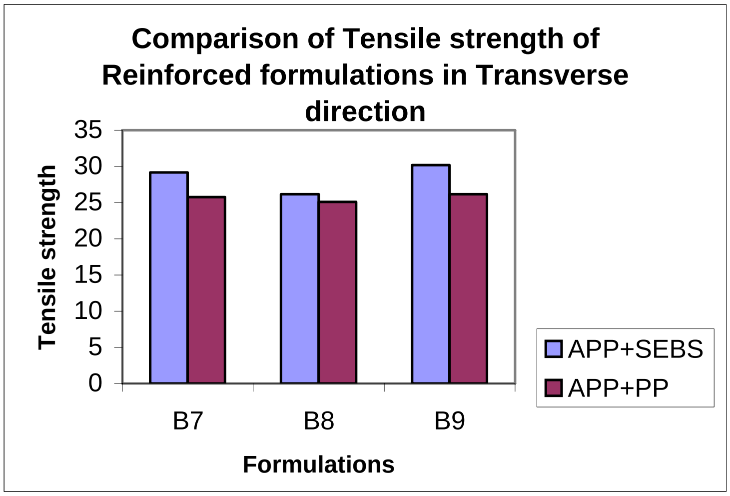
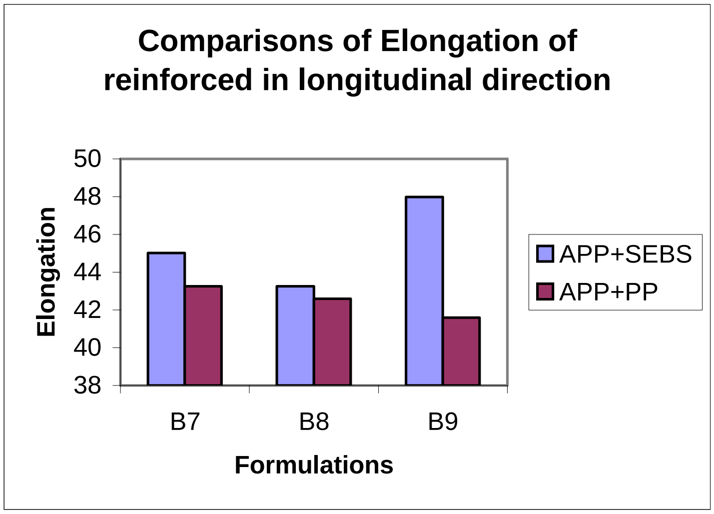

Comparison of Tensile strength of Reinforced formulations in Transverse direction
Tensile strength
35
30
25
20
15
10
5
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig.20(g)


Comparisons of Elongation of reinforced in longitudinal direction
Elongation
50
48
46
44
42
40
38
B7
B8
B9
Formulations
APP+SEBS
APP+PP

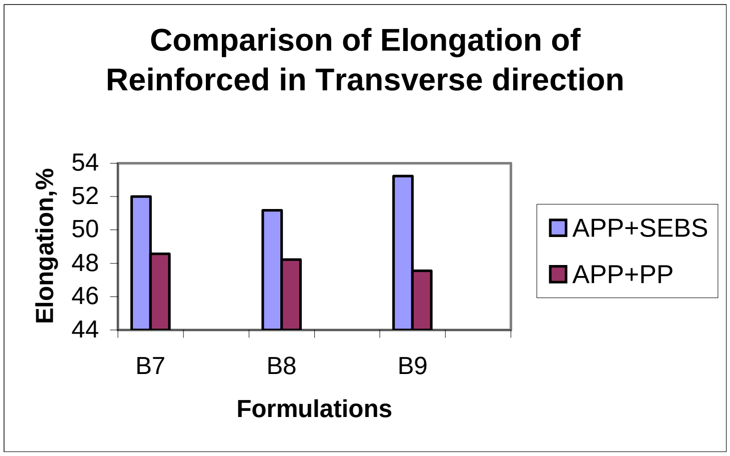

Comparison of Elongation of Reinforced in Transverse direction
Elongation,%
54
52
50
48
46
44
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig.20(h)

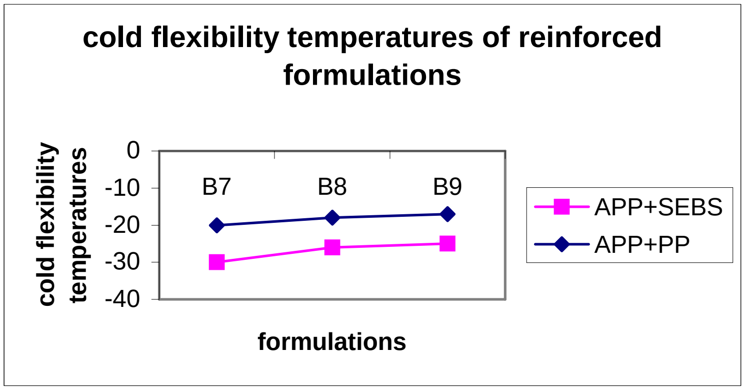
e) Cold Flexibility

The table below shows cold flexibility temperatures of formulations:

The bar-graphs show the comparison of cold flexibility temperatures of reinforced and formulations and it is seen that with increasing modifier ratios and reinforcement there is tremendous increase in cold flexibility temperature

S.No.	*Code*	*Cold Flexibility, ° C*
1	*B7*	*-20*
2	*B8*	*-18*
3	*B9*	*-17*
4	*B10*	*-10*
5	*B11*	*-8*
6	*B12*	*-8*

Table 16(e)


cold flexibility temperatures of reinforced formulations
cold flexibility temperatures
0
-10
-20
-30
-40
B7
B8
B9
formulations
APP+SEBS
APP+PP

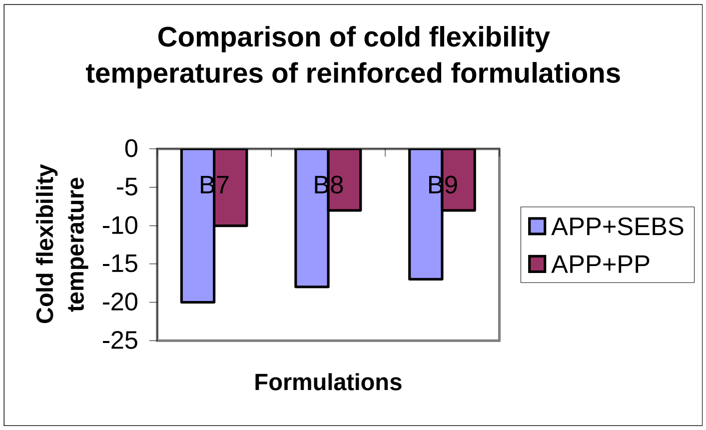

Comparison of cold flexibility temperatures of reinforced formulations
Cold flexibility temperature
0
-5
-10
-15
-20
-25
B7
B8
B9
Formulations
APP+SEBS
APP+PP

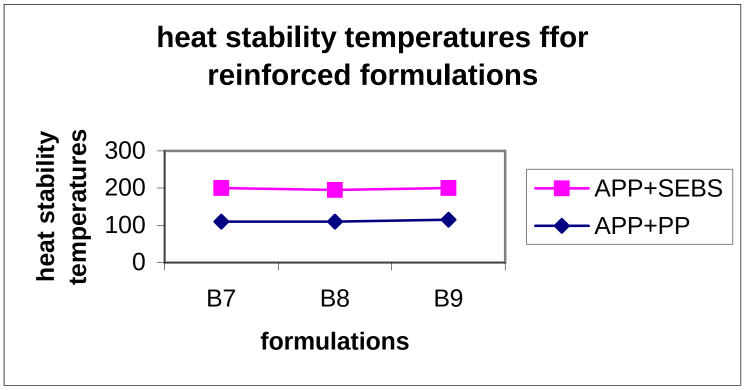
Fig.20(i)

***f)* Heat Aging:** *The table below reveals the heat stability temperatures of various formulations*

The bar-graphs show the comparison of Heat stability Temperatures of reinforced and formulations and it is seen that with increasing modifier ratios and reinforcement there is tremendous increase in Heat stability.

S.No.	*Code*	*Heat Aging°C*
1	*B7*	*110*
2	*B8*	*110*
3	*B9*	*115*
4	*B10*	*90*
5	*B11*	*85*
6	*B12*	*85*

Table 16(f)


heat stability temperatures ffor reinforced formulations
heat stability temperatures
300
200
100
0
B7
B8
B9
formulations
APP+SEBS
APP+PP

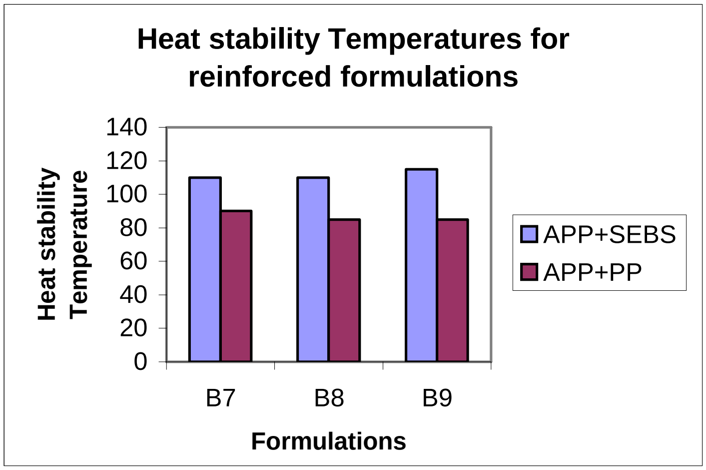

Heat stability Temperatures for reinforced formulations
Heat stability Temperature
140
120
100
80
60
40
20
0
B7
B8
B9
Formulations
APP+SEBS
APP+PP

Fig .20(j)

CONCLUSION AND FUTURE PROSPECTS

This study was to analyze the effect of various polymeric modifiers on paving grade Bitumen and to evaluate various characteristics of the membrane made from bitumen modified with these polymers. The improvement in properties of paving grade membrane is evaluated by studying softening point and penetration point. The membrane made out of this modified bitumen is evaluated by studying performance properties like tensile strength, elongation, tear strength, heat stability and cold flexibility. From the results obtained following conclusions can be drawn

- *20 % polymer content in the formulation was found to be more suitable for modification on the basis of improved softening point, lower penetration point and consideration of economical factors*

- *Among various polymeric modifiers used the combination of APP- SEBS polymers in the ratio 10:10 was found to be the best. This combination was chosen for fabricating a commercially competent membrane using glass mat reinforcement.*

- *The glass fiber reinforcement improved physical and mechanical properties.*

- *The study shows that the paving grade bitumen can be used to make bituminous membranes for roofing application by modifying with common polymeric modifiers.*

This study about modification of paving grade bitumen for water proof roofing application requires further consideration in several aspects. The future scope of this project includes the commercialization of the economical process for the manufacture of roofing membranes using paving grade bitumen, the study about other important parameters like water impermeability, resistance to environmental factors etc., and utilization of recyclable polymeric materials for modification.