EFFECT OF POLYMER ADDITIVES ON THE PHYSICAL PROPERTIES OF BITUMEN BASED COMPOSITES

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ABSTRACT

EFFECT OF POLYMER ADDITIVES ON THE PHYSICAL PROPERTIES OF BITUMEN BASED COMPOSITES

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Polymer modified bitumen is a binder obtained by the incorporation of various types of polymers in bitumen using mechanical mixing or chemical reactions. There are several factors affecting the properties of polymer modified bituminous composites such as; chemical composition of bitumen, kind of polymer and filler, compatibility of bitumen and polymer, amount of bitumen, polymer and filler, particle size of filler and process conditions.

The main objective of this study is to determine the effects of polymer type and concentration on mechanical, thermal, properties and morphologies of bitumen based composites. It was also aimed to determine the effect of process temperature on mechanical and thermal properties of bituminous composites.

Bituminous composites were prepared by using Brabender Plastic Coder, PLV 151. Mixing was made at two different temperatures (150 ºC and 180 ºC) at 60 rpm for 20 minutes.

Three different kinds of polymer and four different polymer concentrations were used to understand the effect of polymer type and polymer concentration on bituminous composites properties. Low density polyethylene (LDPE), styrene-butadiene-styrene copolymer (SBS) and ethylene-vinyl-acetate (EVA) were chosen as polymer. The compositions were adjusted as the polymer volumes were equal to 5%, 10%, 20% and 50% of bitumen volume.

According to the test results, addition of polymer increases the mechanical properties, reduces the melt flow index and thermal conductivity values of bituminous composites. Morphological analysis results show that, fibrillation occurs at tensile fractured surfaces of composites which contain LDPE and EVA when the polymer concentration reaches 20% of bitumen volume.

Keywords: Bitumen, bituminous composites, fibrillation, mixing, thermal conductivity

ÖZ

POLİMER KATKI MADDELERİNİN BİTÜM BAZLI KOMPOZİTLERİN FİZİKSEL ÖZELLİKLERİNE ETKİSİ

Doğan, Mehmet
Yüksek Lisans, Polimer Bilimi ve Teknolojisi Bölümü
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Polimer modifiye bitüm, mekanik karıştırma veya kimyasal reaksiyon kullanılarak polimerin bitüm ile karıştırılması ile elde edilen bir bağlayıcıdır. Bitümün kimyasal yapısı, polimerin ve dolgu maddesinin cinsi, bitüm ile polimerin uyumluluğu, bitüm, polimer ve dolgu maddesi miktarı, dolgu maddesinin parçacık boyutu ve işlem koşulları gibi birçok faktör polimer modifiye bitüm bazlı kompozitlerin özelliklerini etkiler.

Bu çalışmanın temel amacı, polimer tipinin ve konsantrasyonun bitüm bazlı kompozitlerin.mekanik, termal özelliklerine ve morfolojisine olan etkilerini belirlemektir. Ayrıca, işlem sıcaklığının bitümlü kompozitlerin mekanik ve ısıl iletkenlik özellikleri üzerine olan etkilerinin belirlenmesi de amaçlanmıştır.

Bitüm bazlı kompozitler Brabender Plastic Coder, PLV 151 kullanılarak hazırlanmıştır. Karıştırma işlemi iki farklı sıcaklıkta (150 ºC, 180 ºC) 60 tur/dakika'da 20 dakika boyunca yapılmıştır.

Polimer cinsinin ve polimer konsantrasyonun bitüm bazlı kompositlerin üzerine etkisini anlamak için üç farklı cins polimer ve dört farklı polimer konsantrasyonu kullanılmıştır. Polimer olarak alçak yoğunluklu polietilen (AYPE), stiren-bütadiyen-stiren kopolimer (SBS) ve etilen-vinil-asetat (EVA) seçilmiştir. Bileşimler polimer hacmi bitüm hacminin %5, %10, %20 ve %50'si olarak ayarlanmıştır.

Test sonuçlarına göre, polimer eklenmesi bitüm bazlı kompozitlerin mekanik özelliklerini artırmış, erime akış indisi ve ısıl iletkenlik değerlerini düşürmüştür. Morfolojik analiz sonuçları AYPE ve EVA içeren kompozitlerde polimer hacmi bitüm hacminin %20' sine ulaştığında kopma yüzeylerinde fibrilasyon meydana geldiğini göstermiştir.

Anahtar Kelimeler: Bitüm, bitüm bazlı kompozit, fibrillasyon, ısıl iletkenlik, karıştırma

To my family

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INTRODUCTION

Bitumen, which remains after vacuum distillation of crude oil, is a complex mixture of organic and inorganic compounds. Such compounds maybe separated into asphaltenes and maltenes. Asphaltenes are defined as the black-colored fraction of bitumen that is insoluble in n-heptane. Maltenes, composed of saturated compounds, aromatic compounds and resins, are soluble in n-heptane [1].

Bitumen binder is readily adhesive, highly waterproof, and durable making it a valuable engineering material. Bitumen has uses that range from the construction of the pavements of roads with an aggregate to waterproofing membrane in roofing and structural applications.

Bitumen binder is a thermoplastic liquid which behaves as an elastic solid at low service temperatures or during rapid loading. At high temperatures or during slow loading, it behaves as a viscous liquid. This classical dichotomy creates a need to improve the performance of an asphalt binder to minimize the stress cracking that occurs at low temperatures and plastic deformation at high temperatures [2].

Several additives are being used to increase the performance of asphalt binders. Polymers are most widely used additives in asphalt modification. Various types of polymers are used to change asphalt binders to achieve wider performance range. Many polymer modified asphalt binders tend to behave more as a polymer rather than bitumen [2].

In this study, polymer based bituminous composites, used as isolation material, were prepared from bitumen, filler ($CaCO_3$) and polymer. Low density polyethylene, styrene butadiene styrene copolymer and ethylene vinyl acetate were used as polymer. Mechanical, thermal, melt flow index values and morphologies of bituminous composites were examined.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Bitumen

The term bitumen is used by European and Eastern countries, whereas the term asphalt is used by Americans. The sources of bitumen can be classified into two categories. First bitumen is derivated from petroleum crude oil, second category includes the natural asphalt deposits [3].

Bitumen is a viscoelastic substance which behaves as an elastic solid at low temperatures or during rapid loading. At high temperatures or slow loading, it behaves as a viscous liquid. This classical dichotomy creates a need to improve the performance of bitumen to minimize the stress cracking that occurs at low temperatures and plastic deformation at high temperatures [2].

2.1.1 Definition of Bitumen

The term bitumen consists of a wide variety of reddish brown to black materials of semisolid, viscous to brittle character that can exist in nature with no mineral impurity or with mineral matter contents that exceed 50% by weight [4].

The American Society for Testing and Materials (ASTM) defines bitumen as a generic class of amorphous, dark colored, cementitous substances, natural or manufactured composed principally of high molecular mass hydrocarbons, soluble in carbon disulfide [5].

2.1.2 Chemical Composition of Bitumen

Knowledge of bitumen chemistry has progressed rapidly as more sophisticated methods of analysis have been developed. There are a lot of techniques such as solvent fractionation, thermal diffusion, sulfuric acid precipitation, adsorption and elution or by a combination of these procedures used for determining the composition of bitumen. The study of these fractions has been made by most available methods including infrared and ultraviolet spectrometry, x-ray analysis and electron-microscope techniques [6].

Bitumen is a mixture of hydrocarbons and compounds of a predominantly hydrocarbon character, varying both chemically and molecular size. These hydrocarbon components change from the nonpolar aliphatic wax compounds to highly polar condensed aromatics. Carbon and hydrogen compose approximately 90-95% of bitumen. The rest of the bitumen consists of heteroatoms such as nitrogen, oxygen and sulfur [6].

The knowledge of bitumen chemistry is largely based on separation by means of organic solvents into groups of similar properties. For asphaltic bitumens, Marcusson [7] gives the following groups of compounds whose nomenclature is generally accepted. Carboids represent the part of the asphaltic bitumen which is insoluble in carbon disulfide. Carbenes are soluble in carbon disulfide but insoluble in carbon tetrachloride. Both of them are present in bitumen in small quantities. Asphaltenes are obtained after freeing asphaltic bitumens from carbenes and carboids by precipitation with light petroleum naphtha of 86-88°C. They are highly aromatic and contain condensed rings. Asphaltic resins are amorphous solids of reddish to dark brown color and are soluble in light petroleum naphtha as well as in the solvents for asphaltenes. Their chemical structure is similar to that of asphaltenes. Oily constituents represent the remainder of asphaltic bitumens. They appear as fluorescent oils, and their viscosity varies not only with the source of the asphaltic bitumen but also with the method of processing. They contain various types of hydrocarbons and can be further separated into aromatic, cycloparaffinic, and aliphatic fractions [7].

2.1.3 Microstructure of Bitumen

Asphalt is a highly complex residue of crude oil which most technologists consider to be a natural colloid composed of two phases, dispersed and continuous. The dispersed phase asphaltenes can be described as high molecular weight, semi-polymeric, aliphatic/aromatic complexes which are present in asphalt as either discrete, uniformly dispersed particles, or flocculated or agglomerated electrostatically-bound clusters, or mixtures of both the discrete and flocculated forms. The continuous phase, alternately referred to as the petrolene, malthene or oils and resins phase, have been the subject of some effort to analytically separate and characterize individual components [8].

The microstructure of bitumen is generally understood as multi phase colloidal system. Bitumen classified into two categories sol-type bitumen and gel-type bitumen according to microstructure. In practice most bitumens are somewhere between these two states. A schematic representation of these two states is shown in Figure 2.1 [9].

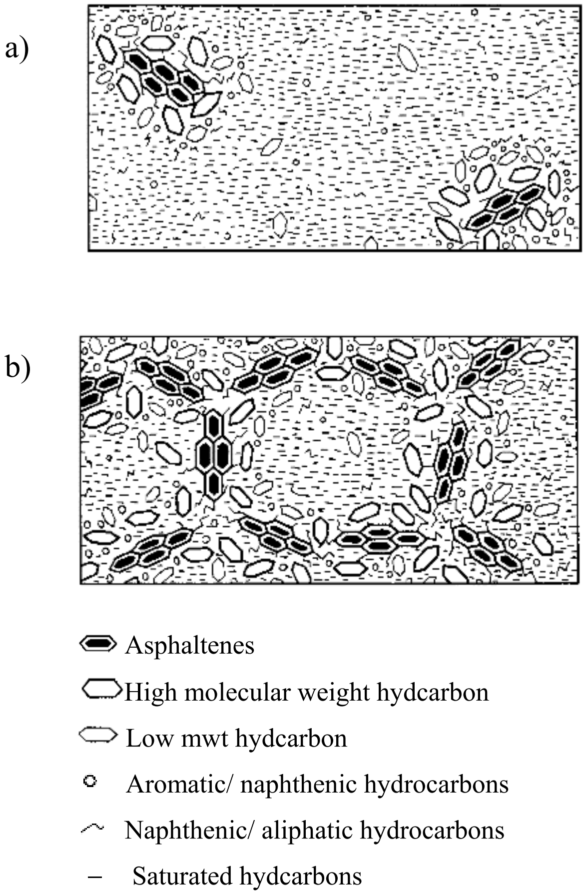


Figure 2.1 A schematic representation of a) sol-type bitumen, b) gel-type of bitumen [9].

In sol-type bitumens, asphaltene bitumens well dispersed within maltene continuum. In gel-type bitumen, the asphaltene micelles are not well dispersed and form large agglomerations. The degree of dispersion asphaltenes is controlled by the relative amounts of resins, aromatics and saturated oils. As the ratio of aromatics increases, the dispersion of asphaltenes increases because the aromatics form stabilizing layer around the asphaltene micelles. The saturate oils have little solvent power in relation to the asphaltenes, so that as the saturate fraction increases, there is a great tendency for the asphaltenes to aggregate to form gel structure. However a high ratio of saturates tends to reduce viscosity because of their low molecular weight [9].

2.1.4 Uses of Bitumen

Bitumen, which has thermoplastic nature, water resistance and adhesion toward most other substances, is a primary engineering material. There are over one hundred different industrial applications or products in which bitumen is used. Almost every home, building or traffic area uses bitumen in different form. Bitumen has uses that range from the construction of the pavements of roads with an aggregate to waterproofing membrane in roofing and structural applications. Bitumen serves primarily as a binder in asphalt compacted mixtures which in turn are widely used in many types of road, street, runway and parking area applications. The other uses of bitumen are paints and coatings, paper, rubber products, electrical cables and other products of electrical industry [3].

2.2 Polymer

2.2.1 Properties of Low Density Polyethylene Resin

Low density polyethylene (LDPE) commonly is made by polymerizing ethylene at high pressure to form polyethylene molecules. The structure of LDPE is shown in Figure 2.2.

$$-(CH_2-CH_2)_n-$$

Figure 2.2 Structure of low density polyethylene

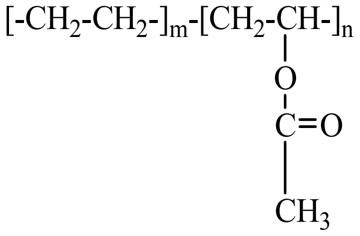
LDPE is a highly branched long- chain thermoplastic polymer having density of 0,915-0,925 g/cm^3 and molecular weight up to 4×10^6. The thermal properties of LDPE include a melting range with a peak melting point of 106-112° C. The glass transition temperature, Tg, of LDPE is well below room temperature (around -120), accounting for the polymer’s soft and flexible nature [10].

The molten state mechanical properties of LDPE are affected mostly by molecular weight (mw) and molecular weight distribution. The solid phase mechanical properties of LDPE are influenced mostly by mw and density and somewhat by molecular weight distribution. The optical properties of LDPE are affected by mw and density. High mw molecules produce a rough, low gloss surface, higher density polyethylene contains more or larger crystalline areas scatter light and cause hazy appearance [10].

LDPE has a good balance of mechanical and optical properties with easy processibility and low cost. It can be fabricated by many different methods for a broad range of applications making it one of the highest volume plastics in world. LDPE film applications include bread bags, shrink wrap, sandwich bags and garment bags. Substrates extrusion-coated with LDPE are used for milk and chemical storage. Injection molded items include housewires, can lids, toys and pails. Other important uses for LDPE include wire and cable jacketing, carpet backing [10].

2.2.2 Properties of Ethylene Vinyl Acetate Resin

Ethylene vinyl acetate (EVA) copolymers are the products of LDPE technology and normally sold in pelletized form, approximately spherical in shape and about 1/8 inch. in diameter. The molecule structure of EVA resins is represented in Figure 2.3.



$[-CH_2-CH_2-]_m-[CH_2-CH(-O-C(=O)-CH_3)-]_n$

Figure 2.3 Structure of ethylene vinyl acetate

Incorporation of vinyl acetate in the ethylene polymerization process produces a copolymer with lower crystallinity than conventional ethylene homopolymer. EVA copolymers are thermoplastic materials consisting of ethylene chain incorporating 5 to 50 % vinyl acetate (VA), in general. Their properties are governed by the percentage content of VA and the melt index. The VA content controls the resin crystallinity and flexibility. Lower crystallinity resins have lower melting points and heat seal temperatures, along with reduced stiffness, tensile strength and hardness. EVAs have improved clarity, low temperature flexibility, stress-crack resistance, and impact strength but poorer high temperature properties than LDPE. Chemical resistance is similar to that of LDPE, with somewhat better resistance to oil and grease for EVA resins with a higher VA content [10].

EVA copolymers are used in a variety of molding, compounding, and extrusion applications. Some typical end uses include flexible hose and tubing, footwear components, toys and athletic goods, extruded gaskets, molded automotive parts. EVA copolymers with a low VA content are used in film; the presence of 2-7 % VA enhances such desirable film properties as toughness and optical clarity. Higher comonomer content resins (18-40%) are used as wax-coating tougheners and in hot melt adhesives [10].

2.2.3 Properties of Styrene- Butadiene- Styrene Triblock Copolymer

The triblock copolymer, styrene-butadiene-styrene (SBS), is commercially important because of its physical characteristics. At ambient temperature, SBS is physically indistinguishable from conventional vulcanized elastomers, but chemically consists of individual chains with a complete absence of covalent crosslinks between the polymer chains. The molecular structure of SBS is shown in Figure 2.4.

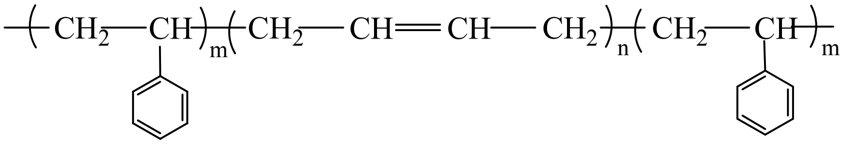


Figure 2.4 Molecular structure of SBS

The SBS triblock thermoplastic elastomer has the following physical characteristics; high extensibility, elastic recovery, high resilience, sharp rise in elastic modulus at low temperature, not affected by water, alcohol, or diluted acids, soluble in ketones, esters and hydrocarbons.[11].

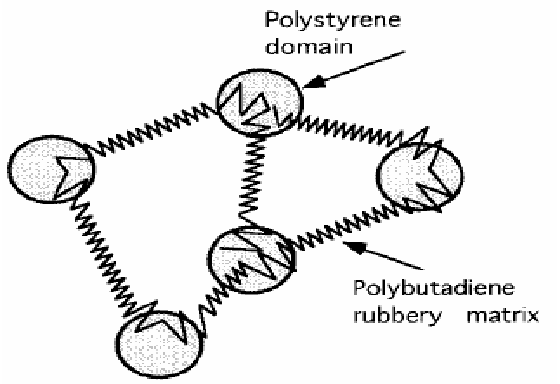


Figure 2.5 Structure of thermoplastic SBS showing polystyrene end block domains [12].

The morphology of SBS is that the molecules of the thermoplastic elastomer terminate with hard, glass like end-blocks, which are incompatible with the rubbery mid-blocks. SBS molecules are combined in the solid phase; a two phase structure is formed by the clustering of endblocks. The plastic-endblocks phase regions, called domain, are shown in sphere like form. It consists of multiple aggregates of polystyrene segments, referred to as domains. Each individual block copolymer molecule has its ends in polystyrene domains and its center segment in the continuous polybutadiene phase. These domains act as crosslinks between the ends of the rubber chains, serving to lock in place the rubber chains and their inherent entanglement. An idealized and simplified representation of this is shown in Figure 2.5 [11].

A variety of adhesives, coatings, films, extrusions, and molded articles made from SBS can be obtained using many techniques, such as solution casting, extrusion, and injection molding. SBS can be compounded with other materials such as inorganic filler, petroleum oils, asphalts and reactive monomers to develop the desired properties. SBS could be used as an asphalt binder on overlay design. The SBS binders posses a high softening temperature, which would reduce the sensitivity for rutting and corrugation and provide a reasonable penetration value to minimize the chances of cracking [11].

2.2.4 The Aim of Using Polymers with Bitumen

Many types of polymers are typically used in bitumen modification in different forms such as plastics, elastomers and reclaimed rubbers. Elastomers such as styrene-butadiene- styrene copolymer (SBS), styrene-butadiene rubber (SBR) and natural rubber can be used with bitumen. SBS is used as an elastomer in this study. A plastic such as polyethylene (PE), polypropylene (PP), polystyrene and ethylene vinyl acetate (EVA) are used with bitumen. EVA and low density polyethylene (LDPE) are used as thermoplastics [2].

Mixing polymers into bitumen has important consequences on the engineering properties of bituminous materials. The extent of modification and the improvements in the performance characteristics depend on bitumen nature, polymer chemical nature, its dosage and chemical compatibility, molecular weight, particle size, as well as blending process conditions such as type of mixing/dispersing device, time and temperature play important role in determining the modified asphalt properties [13].

Bitumen modification by polymers improves its mechanical properties, increases the viscosity, allows an expansion of temperature range of service and improves the deformational stability and durability of bitumen [1].

Elastomer modification of bituminous materials is manifest in the following ways; softening temperature is increased, cold flow is reduced, change in penetration with temperature is reduced, brittleness temperature is lowered, elastic recovery is imparted, resistance to deformation under stress is increased markedly, ductility is increased, particularly at low temperatures [7]**.**

2.2.5 Interaction between Bitumen and Polymer

The morphology of polymer modified bitumen is the result of the mutual effect of polymer and bitumen, consequently is influenced by bitumen composition, polymer nature and ratio [14]**.**

Most polymers are insoluble to some degree, in the bitumen matrix, resulting eventually in gross separation of both phases. These phases may become a continuous phase or a dispersed one depending on polymer nature, concentration and its ability to swell with maltene molecules [13]**.** Bitumen phase is artificially enriched in asphaltenes by a physical distillation of the lighter species from the original bitumen because polymer is swelled by the maltenes. This is the case of many elastomers and thermoplastics such as EVA, SBS, PE etc. [1].

In general at low polymer content, the small polymer spheres swollen by bitumen compatible fractions are spread homogeneously in a continuous bitumen phase. By increasing polymer content, a continuous polymer phase may be obtained. The minimum percentage of polymer to ensure the formation of its continuous phase depends to a great extent on the base bitumen, the polymer itself and its ability to swell with maltene molecules [1]**.** Polymer stabilization can be achieved by mechanical dispersion of the modifier, swollen by compatible components in the maltene fraction. It is well known that the polymer may dissolve and/or disperse into maltenic medium enhancing the mechanical properties of mixtures [14]**.**

Polyolefins are produced from olefinic monomers, the resulting homopolymers have nonpolar, non aromatic nature. The typical range for their solubility parameter is 15.6-17.4 MPa$^{1/2}$. This low solubility parameter reflects its incompatibility with an asphalt dispersion medium which is polar and aromatic. Polyolefins can also be copolymerized as either block or random copolymers such as SBS, EVA. The solubility parameter can be modified by the addition of a more polar comonomer yielding a more compatible system [2]. High molecular weight polymers have profound effects on the properties of bitumen. As the molecular weight of polymers increases, their compatibility with bitumen sharply decreases [15].

LDPE, because of its highly saturated aliphatic nature, tends to be insoluble in asphalt even at high temperatures and will form two separate phases. Moreover, it has the lowest solubility parameter of the polyolefins. So it is unlikely to absorb significant amounts of oils from the asphalt dispersion medium and will not disturb the delicate equilibrium that exists between the various components in the asphalt binder [2]. The blend of the bitumen thus lowers the extent of crystallization of the polymer by retaining a proportion within the amorphous bitumen-rich phase and it lowers the melting point of the crystalline regions within the polymer-rich phase by making the crystallites smaller [16].

A schematic representation of the structure of PE-asphalt suspension is illustrated in Figure 2.6. Polymer particles behave as physically active fillers that interact with the asphalt medium by absorption and adsorption mechanisms. This results in the penetration of asphalt into PE particles. PE absorbs the maltene phase of bitumen so that a swollen forms around the PE. The low molecular weight species of PE dissolves in the maltene phase. After the bitumen is washed out, there are a lot of hollows seen on polymer particles [15].

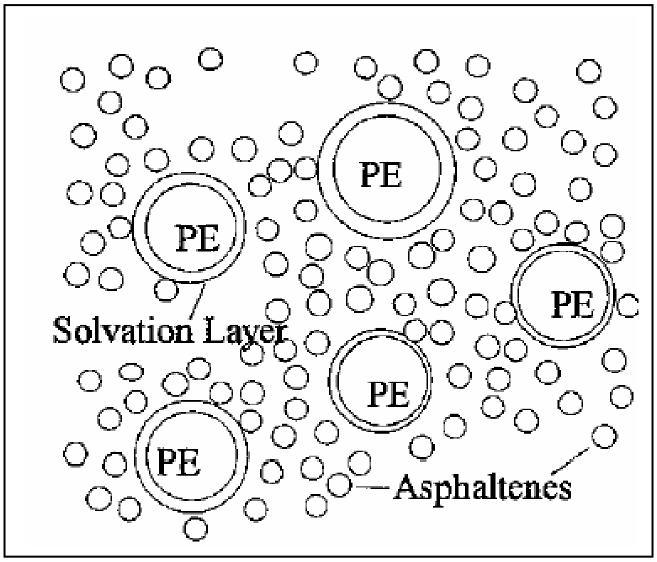


Figure. 2.6 Schematic Representation of PE Particles in Asphalt Medium [15]

Synthetic elastomers, SBS and styrene-butadiene-rubber (SBR), are common and very effective polymer modifiers. SBS have two phase morphology, showing spherical domains formed by the polystyrene blocks within a matrix of polybutadiene. SBS modified bitumens show two phase morphology at microscopic level. The modified bitumens with low SBS content exhibit a continuous bitumen phase in which the polymer particles are dispersed. On the other hand, the modified bitumens with a high SBS content exhibit a polymeric continuous phase in which bitumen globules are dispersed [17]**.** SBS-modified asphalt increases in apparent volume due to swelling with malten incorporated from asphalt when SBS is mixed with asphalt. The butadiene phase of the polymer absorbs the lighter ends of the asphalt and swells as much as nine times its original volume. The butadiene phase is cross-linked by the styrene to form a continuous network throughout the asphalt when cooled and significantly changes the physical properties of the asphalt [18].As shown in Figure 2.7 [12].

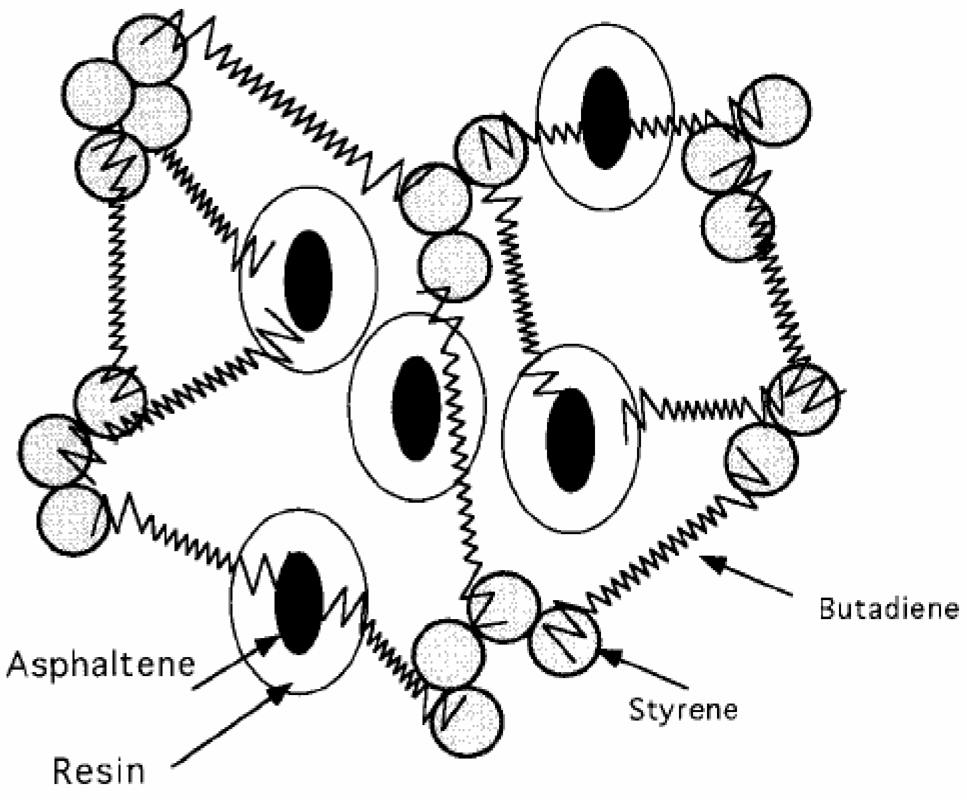


Figure 2.7 The SBS interacts with the asphaltene micelles forming a three-dimensional network if the SBS content is sufficiently high [12].

EVA is also used as polymeric modifier in bituminous materials. Vinyl acetate content of EVA affects the modification of bitumen. At low polymer content, small polymer droplets swollen by bitumen light fractions appear in a continuous bitumen phase. By increasing the polymer concentration, continuous polymer phase appear [1].

2.3 Fillers

A mineral filler is an inorganic additive which, when mixed with a bitumen, retains its original size and shape, does not react with the bitumen and does not assume colloidal properties in the filler-bitumen mixture [7]. The scientific evaluation of pulverized minerals involves first a consideration of their primary properties, such as particle size, size distribution, particle shape and surface configuration or texture and then the relation of these to the secondary properties of the powder, namely surface area, packing of the particles and void content and average void size in the compacted powder [19].

Many types of fillers have been used in bitumen composites such as silica, limestone, basalt, green stone, granite, fly ash, mica, oyster shells and asbestos. Almost every available pulverized stone has been used in bituminous composites because fillers are usually obtained from the nearest local source. It is apparent that most of the readily available mineral fillers and fibers may be used in one or more types of bituminous compositions [7].

2.3.1 Properties of Fillers

Fillers must be inert. They should not react with bitumens and must not decompose when mixed with them. Fillers must be physically sound. They should not crack or crumble during mixing or in service. A filler must be insoluble in water. A filler must be nonhygroscopic. Extensive use of bitumens as water proofing dictates that fillers should not absorb water into waterproofing material. A filler must be opaque. This requirement applies only to fillers used in products exposed to weather [7].

2.3.2 Effects of Fillers

Fillers have a bonus value; those most commonly used are less expensive than the bitumens to which they added. Fillers increase impact resistance, shear, and compressive strength; reduce brittleness, impede or control deformation and sag; increase viscosity and alter flow properties. The softening point of bituminous compositions is increased by addition of filler. The relationship between softening point and filler content is linear up to about 40-50% weight concentration for conventional fillers. Fillers decrease bitumen penetration (the penetration decrease-filler content relationship is similar to that of the softening point increase for fine fillers). Many types of fillers improve the weathering durability of bitumens. The resistance of bituminous compositions to deformation may be improved and regulated by addition of fillers. Fillers increase viscosity and lower the viscosity temperature sensitivity of bitumens. The rheological nature of bitumen is not changed by small concentrations of fillers. The viscosity increase is related to filler content up to about 40-50 % weight concentration of filler. Impact resistance is improved by fillers. Asbestos fiber and fillers of flat particle shape are far more effective than conventional powdered minerals [7].

2.3.3 Interaction Among Filler, Bitumen and Polymer

The interaction among filler, bitumen and polymer depends on composition of bitumen, type of filler and polymer, their ratios in composite. The maltene fraction of the bitumen swells the polymer. Large polymer particles could have a negative effect on the adhesion of bitumen and aggregates. Small polymer particles can remain in between the film of bitumen and reinforce the composite [15]. A schematic representation of the polymer, bitumen, and aggregates in an asphalt concrete mix can be represented as in Figure 2.8. [16].

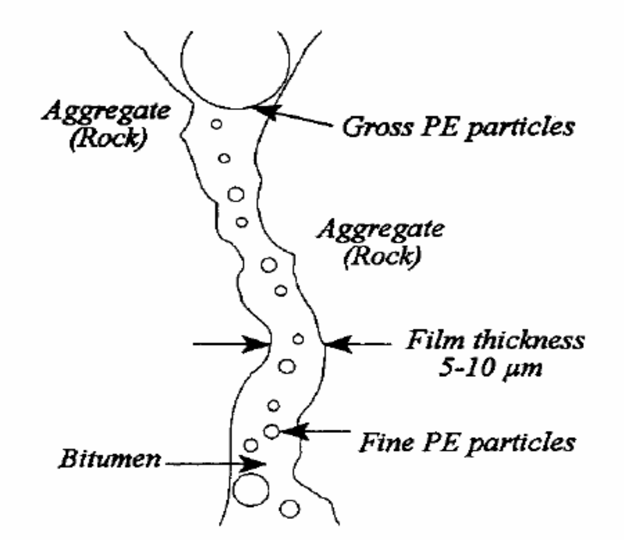


Figure 2.8 A schematic representation of the polymer, bitumen and aggregates in an bitumen concrete mix [16].

Calcium carbonate ($CaCO_3$) is used in this study. The polarity of the polymer affects the interaction between $CaCO_3$ and polymer. PE and SBS have no significant affinity to $CaCO_3$ but EVA seems to have an affinity to $CaCO_3$. The phenomena with the EVA film around or close to the surface of the aggregates can be explained by the polarity of the different components in the asphalt mixture. The EVA phase will surround the aggregates. EVA film is seen a few milimeter from the aggregate; it is a possibility that a part of the polar asphaltenes surrounds the aggregate [20].

2.3.4 Calcium Carbonate

$CaCO_3$ is the most common deposit formed in sedimentary rocks. Natural $CaCO_3$, used as filler in plastics, is produced from chalk, limestone or marble found in the upper layers of the Earth's crust. $CaCO_3$ is abundant, largely inert, low cost, white filler. The primary function of calcium carbonate as a filler is to lower costs, while having moderate effects on mechanical properties [21].

2.4 Mixing

Mixing involves dispersion of stabilizers, pigments and other additives into polymer, exclusion of air and volatiles, transformation of solid polymer feed stock into melt and achieving a fluid state which is uniform in composition, temperature and deformation history [22].

There are two basic stages in mixing: dispersing additives in the polymer and achieving a uniform and shapeable state. The final degree of mixing may be achieved in one operation but more commonly there are two or more separate operations. There are two common types of mixers used such as the intensive mixer and the two- roll mill [22].

2.4.1 The Banbury Intensive Mixer

The registered trade name Banbury is used to describe similar types of lobed, counter rotating; two roll intensive mixers from different manufacturers as a matter of tradition. The schematic representation of Banbury mixer is shown in Figure 2.9 [23].

The intensive mixer consists of a robust casing defining two connecting cylindrical cavities side by side, within which two rotors counter rotate. There is only a small clearance between the tips of the rotors and the casing. Ingredients are fed through an aperture in the top of the chamber; this aperture can be closed to apply pressure to the contents of the full chamber to ensure contact between polymer and mixer. The rotating blades moving past the stationary casing induce drag flow of the polymer and other ingredients: there is a high degree of shear in the clearance between the blade tips and the casing and much less shear elsewhere, resulting in high intensive mixing action. Rotor blades typically have the shape of a broken spiral with the blade tip at say 40º to the rotor axis, one blade being left handed and the other right-handed. The mixture is therefore pumped along the axis of the rotors as well as becoming circumferentially and radially mixed by interaction of the blades [24].

There are a lot of advantages of the batch internal mixer. It accepts feed stock in various forms, has intensive mixing action, has a well-defined residence time and a wide range of mixing procedure can be used. Some disadvantages of the batch internal mixer are: it is not a self-wiping mixing device, batch to batch variations can affect product quality, it is difficult to achieve fine process control. It can not handle high-temperature engineering plastics [22].

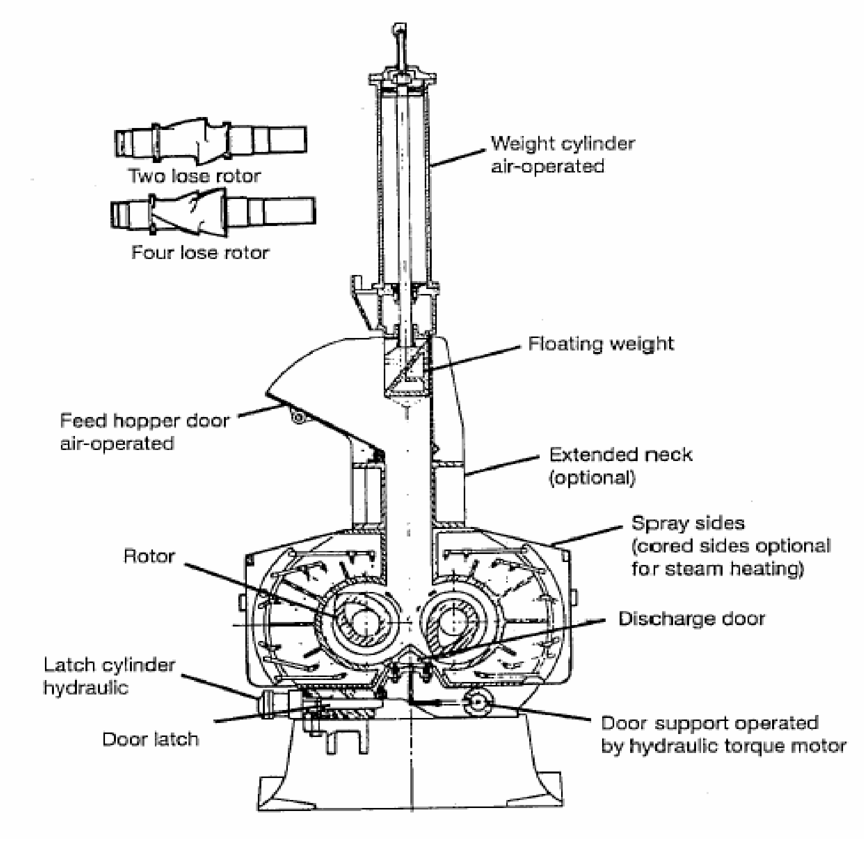


Figure 2.9 Cross section of a Banbury mixer [25].

2.5 Characterization

2.5.1 Mechanical Test

The mechanical properties, among all the properties of plastic materials, are often the most important properties because virtually all service conditions and the majority of end-use applications involve some degree of mechanical loading. The material selection for a variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength [25].

2.5.1.1 Tensile Test

Tensile tests are performed in order to measure the force required to break a specimen and the extent to which the specimen elongates to that breaking point. The test is applied according to standardized testing method. Standard test method for tensile properties (ASTM D638M-91a) employs samples of a specified shape, typically a dog-bone, as depicted in Figure 3.1 [26].

The tensile testing machine of a constant- rate- of crosshead movement is used. It has a fixed or essentially stationary member carrying one grip, and a moveable member carrying a second grip. The ends of the specimen are clamped into these grips of the testing machine and the grips are separated by the application of a known force. Since the specimen is pulled up, it elongates or breaks when the load applied is higher than the load which the specimen can resist. Tensile test provides a stress-strain diagram, which is used to determine the tensile modulus. A typical stress strain curve is shown in Figure 2.10 [25]

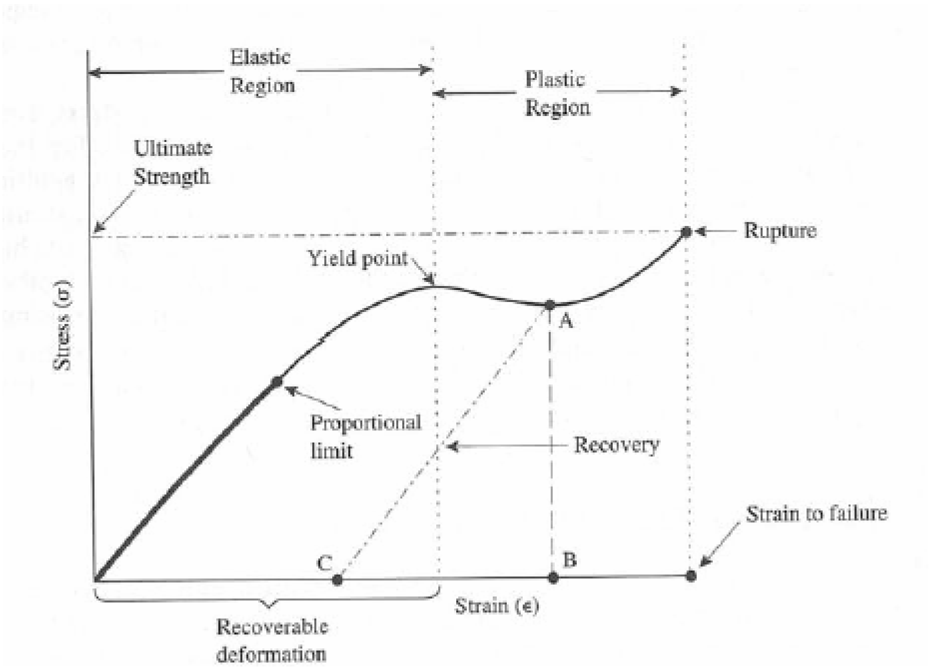


Figure 2.10 Stress-strain behavior over the entire strain range for a typical polymeric material [27]

Stress-strain test gives information related with the modulus, the strength of the material, toughness which is an indication of the energy that a material can absorb before breaking [28].

2.5.2 Flow Characteristics

2.5.2.1 Melt Flow Index (MFI)

The melt index, more appropriately known as melt flow rate test, measures the rate of extrusion of a thermoplastic material through an orifice of specific length and diameter under prescribed conditions of temperature and load. This test is primarily used as a means of measuring the uniformity of flow of the material [25].

The melt index apparatus is preheated to a specified temperature. The material is loaded into the cylinder from the top and a specified weight is placed on a piston. The material is allowed to flow through the die. The initial extrudate is discarded because it may contain some air bubbles and contaminants. Depending upon the material or its flow rate, cuts for the test are taken at different time intervals. The extrudate is weighed and melt index values are calculated in grams per 10 minutes [25].

2.5.3 Morphological Analysis

2.5.3.1 Scanning Electron Microscopy (SEM)

SEM is particularly well suited for examining the top topography of polymer surfaces because of the large depth of field that is possible. SEM is a microscope that uses electrons instead of light to form an image. At comparable magnifications, the depth of field capacity is approximately 300 times greater than that of a conventional optical microscope. The resolution of SEM is approximately 3 nm, which is two orders of magnitude greater than the optical microscope. But the surface can be monitored as black and white images which can be fitted to x-ray instrument and elemental analysis can be made. The images can be used to make accurate conclusion about the morphology of the polymer systems.

In scanning electron microscopy, a fine beam of electrons is scanned across the surface of an opaque specimen to which a light conducting film (gold, platinum, silver) has been applied by high vacuum evaporation. Polymer samples can be mounted on metal stubs for SEM examination by using conductive cement. This can simply be clear nail varnish containing graphite powder. Non conductive polymer samples must be super-coated with gold to reduce the incidence of charging, which is due to high negative charges accumulating on the sample surface; these cause bright spots on the image [29].

2.5.4 Thermal Analysis

2.5.4.1 Thermal Conductivity

Thermal conductivity and diffusivity are discussed together because they differ only in that the former is descriptive of equilibrium or steady state conditions and the latter describes nonequilibrium or transient conditions. Under steady state conditions, the amount of heat transferred is a function of the temperature difference across the material. For transient conditions, however, the amount of the heat the material can store as internal energy must also be considered [30].

Thermal conductivity is defined as the rate at which heat is transferred by conduction through a unit cross sectional area of material when temperature gradient exists perpendicular to the area. The coefficient of thermal conductivity is expressed as the quantity of heat passes through a unit cube of the substance in a given unit of time when the difference in temperature of the two faces is 1 ºC. The quantity of heat flow depends upon the thermal conductivity of the material and upon the distance that the heat must flow. This relationship is expressed as:

$$Q = K / X$$

where Q is the quantity of heat flow, K is the thermal conductivity, X is the distance the heat must flow [25].

Thermal conductivity is also related to the specific heat capacity C_p .This relationship expressed as: $\alpha = k / C_p . \rho$

where α is thermal diffusivity, k is the thermal conductivity, C_p is the heat capacity and ρ is the density.

In dielectric solids and liquids, which include most polymers, heat is conducted by the interactions of thermal vibrations of molecules and their component atoms. The transmission of heat is favored by the presence of ordered crystalline lattices and covalently bonded atoms. Thus graphite, quartz and diamond are good thermal conductors, while less ordered forms of quartz such as glass have lower thermal conductivities. Most polymeric materials have K values between 10^{-1} and 10^{0} W/m K.

In comparison with the amorphous polymers, crystalline polymers are characterized by a more ordered, denser structure which yields a higher thermal conductivity. The difference between amorphous and crystalline polymers with respect to heat conduction may be characterized as a lower resistance to intermolecular transfer in crystalline polymer. Thermal conductivity of polymers depends on a lot of parameter such as temperature, molecular weight and orientation. Thermal conductivity of polymer changes by temperature, as temperature increases, it increases. Polymers may be superior thermal insulating materials at very low temperature. Thermal conductivity should increase as the square root of the weight average molecular weight and become independent of molecular weight at high molecular weights. When a polymer is oriented by stretching or by cold drawing the anisotropy of structure is reflected in a corresponding anisotropy in properties. Polymers show an increase in conductivity parallel to stretching with a decrease normal to the stretch direction [31].

Hot wire method was used in this study in order to find the thermal conductivity of the samples. In typical hot wire method, a wire embedded in the material being investigated. The wire is heated up with a constant power source and the thermal conductivity can be derived from the transient temperature response of the wire. A schematic representation of hot wire method is shown in Figure 2.11. This method is used extensively for high precision measurements on liquids and gases. Powders, granular systems and solid materials have also been successfully investigated using the hot-wire method.

During experiment, the hot wire is heated with an electrical power source. The wire simultaneously serves as a heating element and a temperature sensor. The hot wire temperature is calculated from the increase of temperature dependent electrical resistance of the wire. Thermal conductivity is determined by evaluating the temperature rise in the hot wire, which depends on the thermal conductivity of sample surrounding it [32].

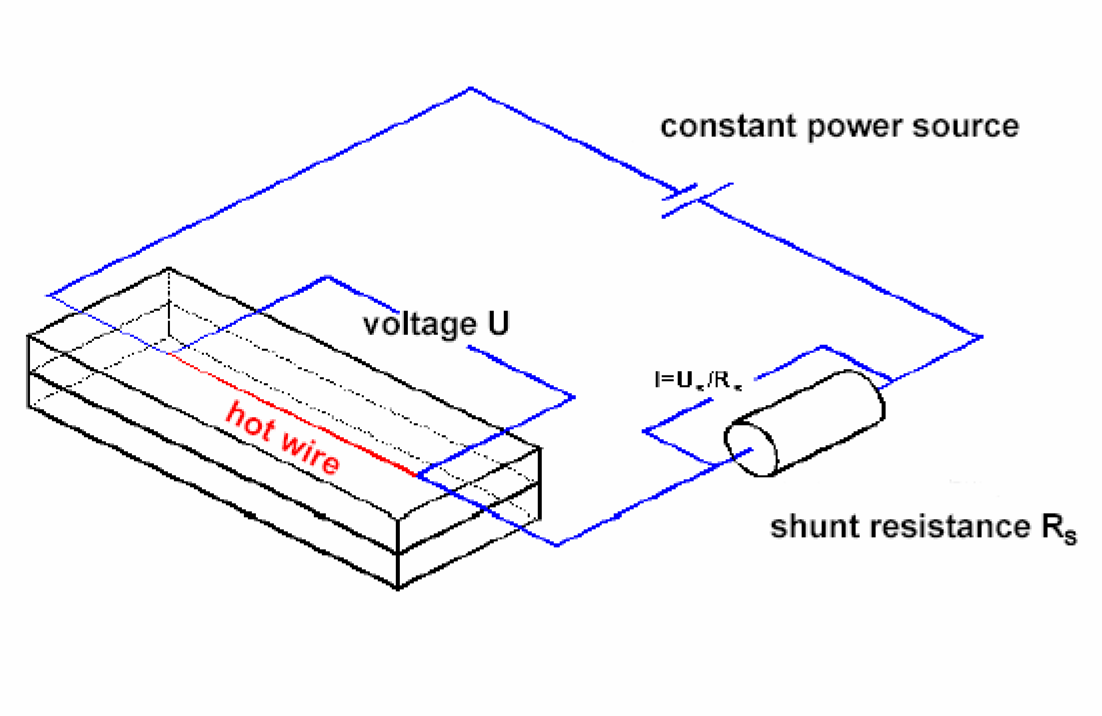


Figure 2.11 The configuration in generalized hot wire method [32].

2.6 Previous Studies

Xiaohu Lu et.al. [14] prepared polymer modified bitumens by blending bitumens with different thermoplastic polymers (SBS, SEBS, EVA, EBA). The fundamental properties, morphology, rheology and ageing of modified binders were studied. It was concluded that morphology and the rheological properties of the modified binders were influenced by characteristics and content of the polymer and nature of the bitumen.

A. Perez-Lepe et.al. [13] investigated the influence of processing variables exert on the rheological properties of polymer-modified bitumens. They used two penetration grade bitumen, 60/70 and 50/120, as base binder. HDPE, LDPE, EPDM were used as polymer. They concluded that a rotor stator mixer device enhanced the rheological properties of binders prepared with HDPE, LDPE, EPDM and their blends as compared to a stirred tank device.

Xiaohu Lu et. al. [33] studied the rheological properties of SBS copolymer modified bitumens.. The modified binders were prepared using a laboratory mixer. They studied rheological properties of the modified binders by using dynamic mechanical analysis. It was found that the addition of SBS polymer increased the binder elasticity at high temperatures and improved the binder flexibility at low temperatures.

Ulf Isacson et. al. [34] used two fillers; hydrated lime and calcium carbonate. The effect of fillers on the isothermal low temperature hardening was evaluated with the aid of physical hardening index. Burger model is used in order to understand the viscoelastic nature of the bitumens and bitumen-filler mixtures.

Pedro Partal et. al. [35] studied the modification of petroleum bitumen with four different types of waste polymers (EVA, EVA/LDPE blend, crumb tire rubber and ABS). Optical microscopy, modulated calorimetry and a set of different rheological tests were developed in order to characterize the modified bitumens. It was concluded that bitumen had significant increase in the elastic modulus and viscosity.

Gordon D. Airey et. al. [36] investigated the morphological, thermal and fundamental rheological characteristics of EVA modified bitumens. The morphologies, thermal properties and rheological characteristics of the EVA modified bitumens have been analyzed by using fluorescent microscopy, differential scanning calorimeter and dynamic mechanical analysis. EVA polymer modification increases binder stiffness and elasticity at high service temperature and low loading frequencies with the degree of modification being a function of bitumen source, bitumen-polymer compatibility and polymer concentration.

A.H. Fawcett et.al. [16] prepared blends of a 100 penetration grade bitumen with four different PE.having up to 29% of polymer by weight by using a Z-blade mixer at more than 160 ºC. The blends were studied by fluorescence optical microscopy, differential scanning calorimetry and dynamic mechanical thermal analysis. Optical measurements indicated the presence of bitumen rich and polymer rich phases. It is concluded that the presence of bitumen lowered the melting point of the crystallites and extent of crystallinity was reduced.

Ali Ekber Yousefi [37] studied the effects of the structural parameters of PE on its dispersion in bitumen and the performance of the resulting polymer modified bitumens was studied. It is concluded that the performance of bitumen at high temperatures increased as the MFI decreased. At low temperature the performance of bitumen decreased as the MFI of PE decreased.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Bitumen

In this study, 50/70 penetration grade and 20/30 penetration grade bitumen was used. Both of them were purchased from TUPRAS A.S. Some selected properties of these bitumens are shown in Tables 3.1 and 3.2.

Table 3.1. Properties of 50/70 penetration grade bitumen used in the study.

PROPERTY	ASTM	UNIT	VALUE
Penetration at 25 ^{0}C, 100 g, 5 sec	D 5	x 0.1 mm	50/70
Softening Point (ring and ball method)	D 36	^{0}C	46-54
Solubility	D 2042	wt %	99

Table 3.2. Properties of 20/30 penetration grade bitumen used in the study.

PROPERTY	**ASTM**	**UNIT**	**VALUE**
Penetration at 25 ^{0}C, 100 g, 5 sec	D 5	x 0.1 mm	20/30
Softening Point (ring and ball method)	D 36	^{0}C	57-67
Solubility (dicholoroethane)	D 2042	wt %	98
Ductility at 25 ^{0}C, 5 cm/min	D113	cm	15

3.1.2 Polymers

Low density polyethylene (LDPE), styrene butadiene styrene block copolymer (SBS) and ethylene vinyl acetate (EVA) were used. LDPE G03-5 was supplied by PETKIM A.S. SBS was obtained from Elastron Kimya A.S. EVA Alcudia® PA-461 was supplied by Alcudia. Some selected properties of these polymers are shown in Table 3.3, 3.4 and 3.5, respectively.

Table 3.3. Properties of LDPE used in the study

PROPERTY	**ASTM**	**UNIT**	**VALUE**
Melt Flow Rate (MFR)(2160 g, 190°C)	ASTM D-1238	g/10 min	0.2-0.4
Density, 23°C	ASTM D-1505	g/cm^3	0.919-0.923

Table 3.4. Properties of SBS used in this study

PROPERTY	ASTM	UNIT	VALUE
Hardness	ASTM D-2240	Shore A	70 ± 2
Density	ASTM D-792	g/cm^3	1.03 ± 0.02
Tensile strength at break	ASTM D-412	kgf/cm^2	65 ± 7
Elongation at break	ASTM D-412	%	750 ± 100
Tear resistance	ASTM D-624	N/mm	50

Table 3.5. Properties of EVA used in this study

PROPERTY	UNIT	VALUE
Melting point	°C	59 - 64
Density @ 23°C	kg/m3	956
Vinyl Acetate content	%	33
Melt Flow Rate (190°C,2.16kg)	g/10 min	45

3.1.3 Calcium Carbonate ($CaCO_3$)

$CaCO_3$ used in this study was supplied from OMYA Madencilik A.Ş. The trade name of this product is OMYACARB 3 EXTRA- GZ. The chemical composition of this product is 98.5 % $CaCO_3$, 1.5 % $MgCO_3$, 0.05 % Fe_2O_3. The average particle size is 5 μm. The pH value is 9.5. The density of product is 2.7 g/cm^3.

3.2 Experimental Parameters

3.2.1 Polymer Type and Ratio

Three different types of polymer at four different concentrations were used in this study. LDPE, EVA, SBS were used as polymers in order to analyze the nature of polymer on physical properties of bituminous composites. Four different concentrations were used for realizing the effect of polymer quantity on physical properties of bituminous composites. The compositions were adjusted as the polymer volumes are equal to 5%, 10%, 20% and 50% of bitumen volume. All compositions with regard to polymer type and ratio are shown in Table 3.6.

Table 3.6. Compositions with regard to polymer type and ratio.

Polymer	**Bitumen 20/30**	**Bitumen 50/70**	**$CaCO_3$**	**LDPE**	**EVA**	**SBS**
PE (5%)	23.23	23.23	51.22	2.31	-	-
PE(10%)	22.20	22.20	51.13	4.46	-	-
PE(20%)	20.43	20.43	50.98	8.17	-	-
PE(50%)	16.45	16.45	50.64	16.47	-	-
SBS(5%)	23.23	23.23	51.20	-	-	2.35
SBS(10%)	22.23	22.23	51.09	-	-	4.45
SBS(20%)	20.46	20.46	50.90	-	-	8.18
SBS(50%)	16.48	16.48	50.47	-	-	16.57
EVA(5%)	23.19	23.19	51.24	-	2.39	-
EVA(10%)	22.13	22.13	51.18	-	4.47	-
EVA(20%)	20.40	20.40	51.07	-	8.13	-
EVA(50%)	16.37	16.37	50.81	-	16.45	-

3.2.2 Filler Concentration

Three different filler concentrations were used in order to see the effect of filler concentration on mechanical properties and melt flow index (MFI) of composites.For EVA 20% composition which contains %74 filler, the filler ratio reduced to 64% and5 4% by weight. The compositions are shown in Table 3.7.

Table 3.7 Compositions related to the effect of filler (v/v)

	Bitumen 20/30	**Bitumen 50/70**	**$CaCO_3$**	**EVA**
EVA(20%)	20.40	20.40	51.07	8.13
EVA(20%)	21.86	21.86	47.54	8.75
EVA(20%)	23.61	23.61	43.33	9.45

3.2.3 Temperature

Two different process temperatures were chosen for analyzing the effect of temperature on physical properties of bituminous composites. The compositions shown in table 3.8 were mixed at two different temperatures 150 °C and 180 °C.

Table 3.8 Compositions investigated for the effect of temperature

	Bitumen 20/30	**Bitumen 50/70**	**$CaCO_3$**	**LDPE**	**EVA**	**SBS**
PE (5%)	23.23	23.23	51.22	2.32	-	-
PE(10%)	22.20	22.20	51.13	4.46	-	-
PE(20%)	20.43	20.43	50.98	8.17	-	-
SBS(5%)	23.23	23.23	51.20	-	-	2.35
SBS(10%)	22.23	22.23	51.10	-	-	4.45
SBS(20%)	20.46	20.46	50.90	-	-	8.18
EVA(5%)	23.19	23.19	51.24	-	2.39	-
EVA(10%)	22.13	22.13	51.18	-	4.47	-
EVA(20%)	20.40	20.40	51.07	-	8.13	-

3.3 Sample Preparation

3.3.1 Mixing

Bitumen, filler, polymer blends were prepared by using Brabender Plastic Coder, PLV 151. Bitumen was added then polymer was added. They mixed for five minutes then filler was added. Experiments were carried out at 60 rpm by mixing the materials for 20 minutes.

3.3.2 Compression Molding

The prepared blends at Brabender Plastic Coder were molded by compressing molding at 150°C. Molded blends were cooled at room temperature.

3.4 Characterization Experiments

3.4.1 Tensile Tests

All mechanical tests were carried out at room temperature. Five samples were tested and average results with standard deviations were reported for each type of composite. Tensile tests were performed on dog bone shaped molded samples. The shape and dimensions of the specimens are given in Figure 3.1 and Table 3.9 respectively. The crosshead speed was 10 cm/min. Tensile tests were performed according to ASTM D 638-M 91a [26] by using a Lloyd LS computer controlled tensile machine.

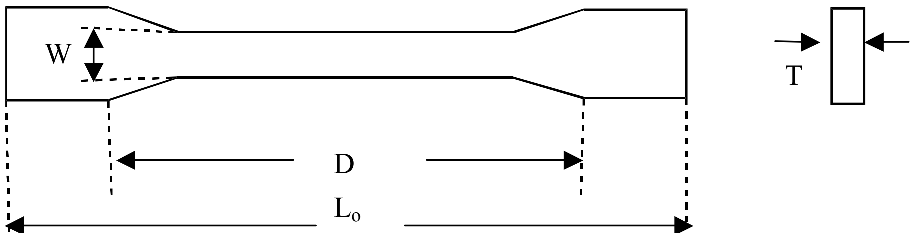


Figure 3.1 ASTM Tensile test specimen

Table 3.9 Dimensions of tensile test specimen

Symbol	**Specimen Dimensions (mm)**
W, Width of narrow section	12.3
D, Distance between grips	93
L_0, Total length of specimen	140
T, Thickness of specimen	3

3.4.2 Melt Flow Index (MFI) Measurements

The measurements were done according to ASTM D 1238 by using Coesfield Material Test, Meltfixer LT. The measurements were carried out at two different temperatures 150 °C and 180 °C with a load of 2.16 kg. The weight of sample passing through the die in 10 min, defined as melt index, was determined for all compositions. The results were recorded as grams/10 min.

3.4.3 Density Measurements

Density measurements were done by using electronic densimeter MD-3005 manufactured by Alfa Nirage Co. Ltd.

3.4.4 Thermal Conductivity

Thermal conductivity tests were performed according to hot wire test method (ASTM C 177, TS 4360-1, EN 993-14) at Turkish Standards Institution (TSE). Figure 3.2 shows Thermal Conductivity Test Equipment that was used for this study. Results were recorded as W/mK. Thermal Conductivity tests are carried out on hot pressed composite rectangular specimens that have dimensions of 15 cm×7 cm×1 cm.

Figure 3.2 Thermal Conductivity Test Equipment (TSE) [38].

3.4.5 Scanning Electron Microscopy (SEM) Analysis

A low voltage SEM (JEOL JSM-6400) was used to analyze the tensile fracture surfaces of the composites to observe the effects of polymer type and concentration on the morphologies of the composites. Fractured surfaces were coated with gold provide conductive surfaces.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Morphological Analysis

SEM analysis, have been performed in order to characterize the morphology of tensile fractured surfaces of bituminous composites. SEM images of these samples are presented with magnifications of x500 and x2500 to provide a more detailed observation.

Figure 4.1 shows the tensile fractured surfaces of bituminous composites which contains no polymer at magnifications of x500 and x2500. It is seen that bitumen surrounds the $CaCO_3$ and forms the continuous phase.

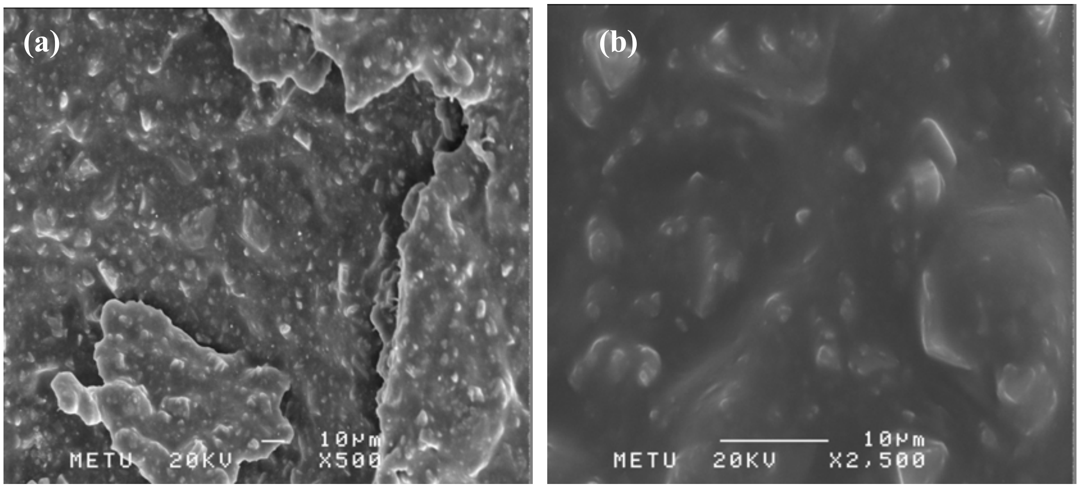


Figure 4.1 SEM micrographs of bituminous composite which contains no polymer (a) x500, (b) x2500.

Figure 4.2 shows the tensile fractured surfaces of bituminous composites containing volume wise 5%, 20%, 50% LDPE. No significant morphological difference is observed between the composite which does not contain polymer and the composite which contains 5% LDPE, the small polymer spheres swollen by compatible bitumen fractions are spread homogeneously in a continuous bitumen phase at low polymer content. The morphology of the tensile fractured surfaces changes when the polymer percentage reaches the 20% of the bitumen volume. As the polymer ratio increases, large polymer domains are formed. Plastic deformation and fibrillation of LDPE can also be observed. As LDPE ratio increases to 50%, more fibrillation occurs.

Figure 4.3 shows the tensile fractured surfaces of bituminous composites containing 5%, 20%, 50% SBS. As seen in SEM micrographs, when the amount of SBS increases, the filler ($CaCO_3$) becomes more visible compared to LDPE. This may be due to swelling of SBS with maltene portions of bitumen. The butadiene phase of the polymer absorbs the lighter ends of the asphalt and swells as much as nine times its original volume [18]. This may weaken the interaction between filler and bitumen. No plastic deformation or fibrillation is observed with SBS.

Figure 4.4 shows the tensile fractured surfaces of bituminous composites containing 5%, 20%, 50% EVA. According to SEM micrographs, when the ratio of EVA reaches 50%, plastic deformation and fibrillation is seen. EVA has affinity to $CaCO_3$ as seen SEM micrograph of 50% EVA containing bituminous composite at 2500 magnification. The reason of this affinity is the polarity of EVA. The EVA used in this study containing 33 % acetate groups. $CaCO_3$ has polar character so, EVA adheres to the surface of $CaCO_3$.

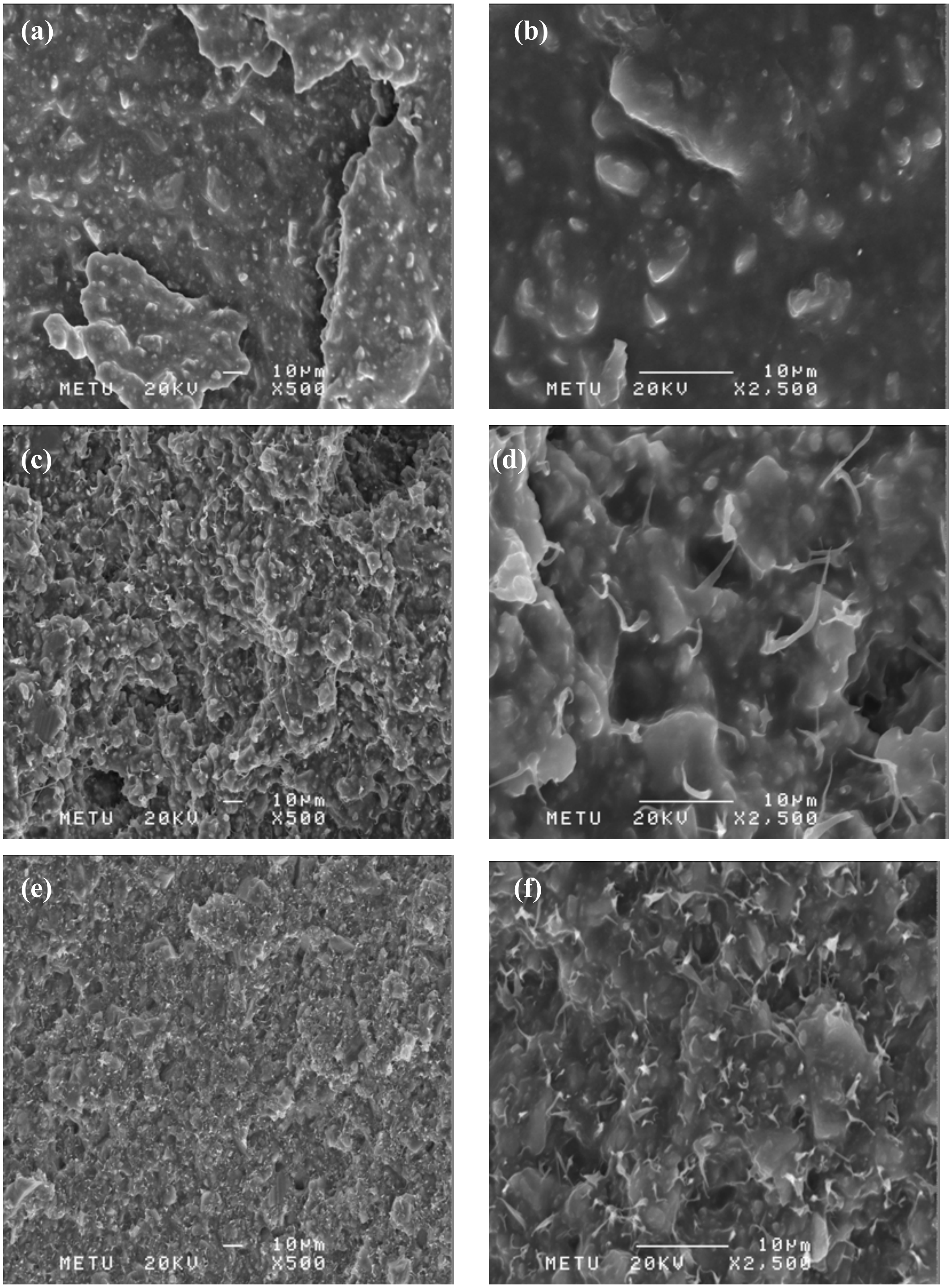


Figure 4.2 SEM micrographs of bituminous composites containing LDPE at two different magnification (a) 5 % x500, (b) 5% x2500; (c) 20 % x500, (d) 20 % x2500; (e) 50% x500, (f) 50 % x2500.

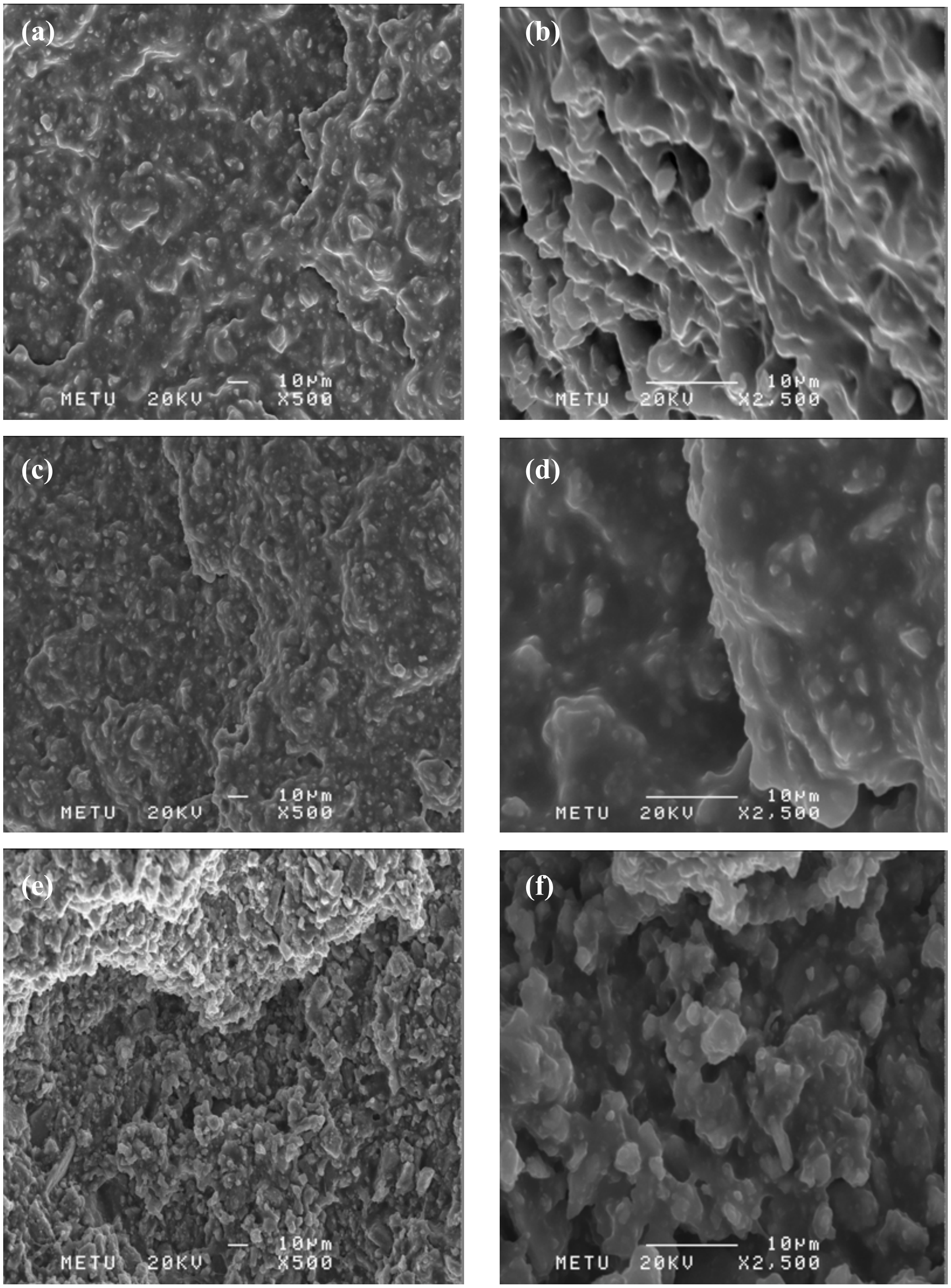


Figure 4.3 SEM micrographs of bituminous composites containing SBS at two different magnification (a) 5 % x500, (b) 5% x2500; (c) 20 % x500, (d) 20 % x2500; (e) 50% x500, (f) 50 % x2500

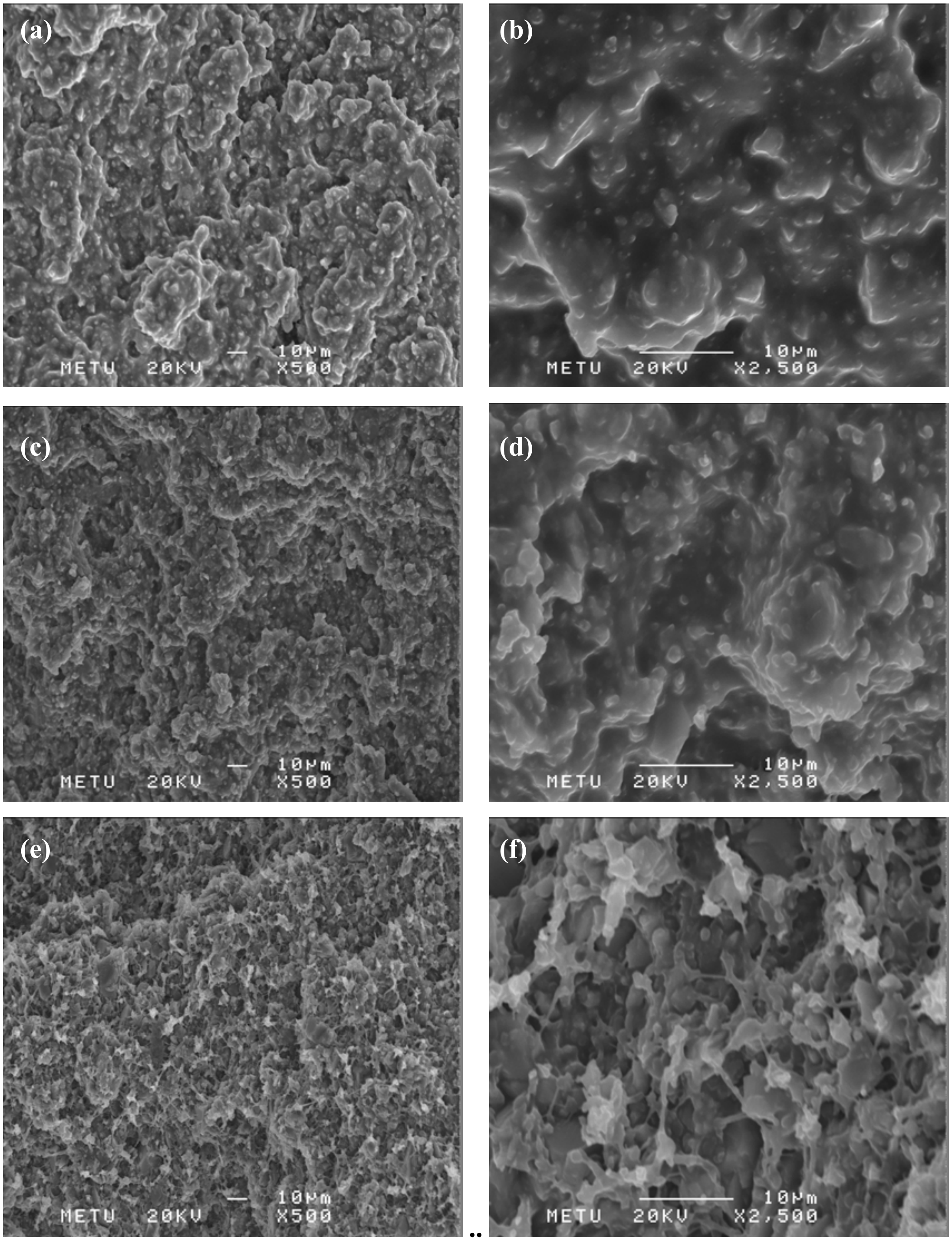


Figure 4.4 SEM micrographs of bituminous composites containing EVA at two different magnification (a) 5 % x500, (b) 5% x2500; (c) 20 % x500, (d) 20 % x2500; (e) 50% x500, (f) 50 % x2500

4.2 Mechanical Properties

In order to investigate the effects of the polymer type, concentration of polymer and filler and process temperature on the mechanical properties of the bituminous composites tensile test were performed. Stress-strain curves provide information about the response of the materials to applied stress during the tensile tests. Figure 4.5 represents the typical stress-strain curves of composites.

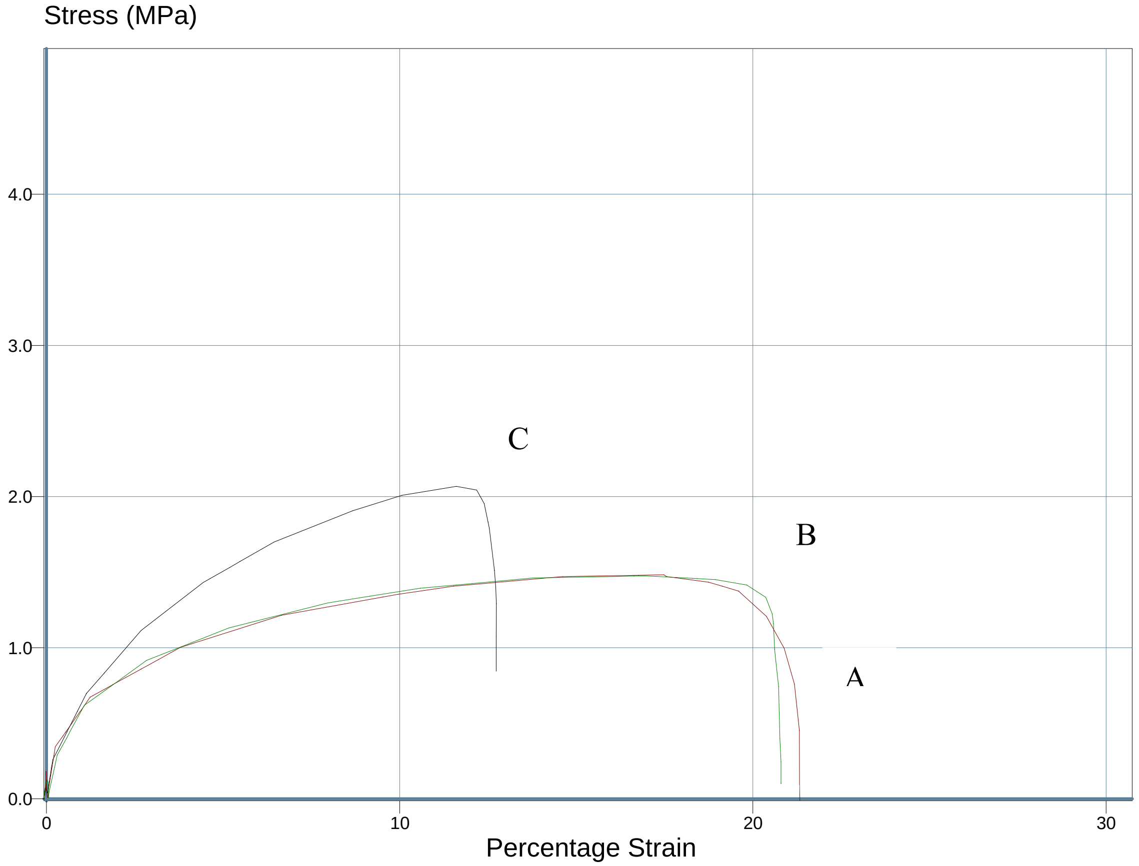


Figure 4.5 Stress- strain curves of composites which contain 5% polymer prepared at 150 ºC. A) 5% LDPE, B) 5% SBS, C) 5% EVA.

Figure 4.6 and 4.7 represent the effect of process temperature on tensile strength and percentage strain at break values. As it is seen from the Figure 4.6 and 4.7, the process temperature has no significant effect on the tensile strength and percentage strain at break values. The mixing process for preparing the modified bitumen exposes the bitumen to high temperature and air for an extended time, which leads to hardening of the bitumen because low molecular weight species of bitumen evaporates during mixing [17]. The bitumens used in this study have low penetration values so that they contains negible amount of low molecular weight species.The mixing time is 20 minute. It was concluded that the processing time is not long enough to allow the evaporation of the low molecular weight species of bitumen so that the effect of process temperature is not observed.

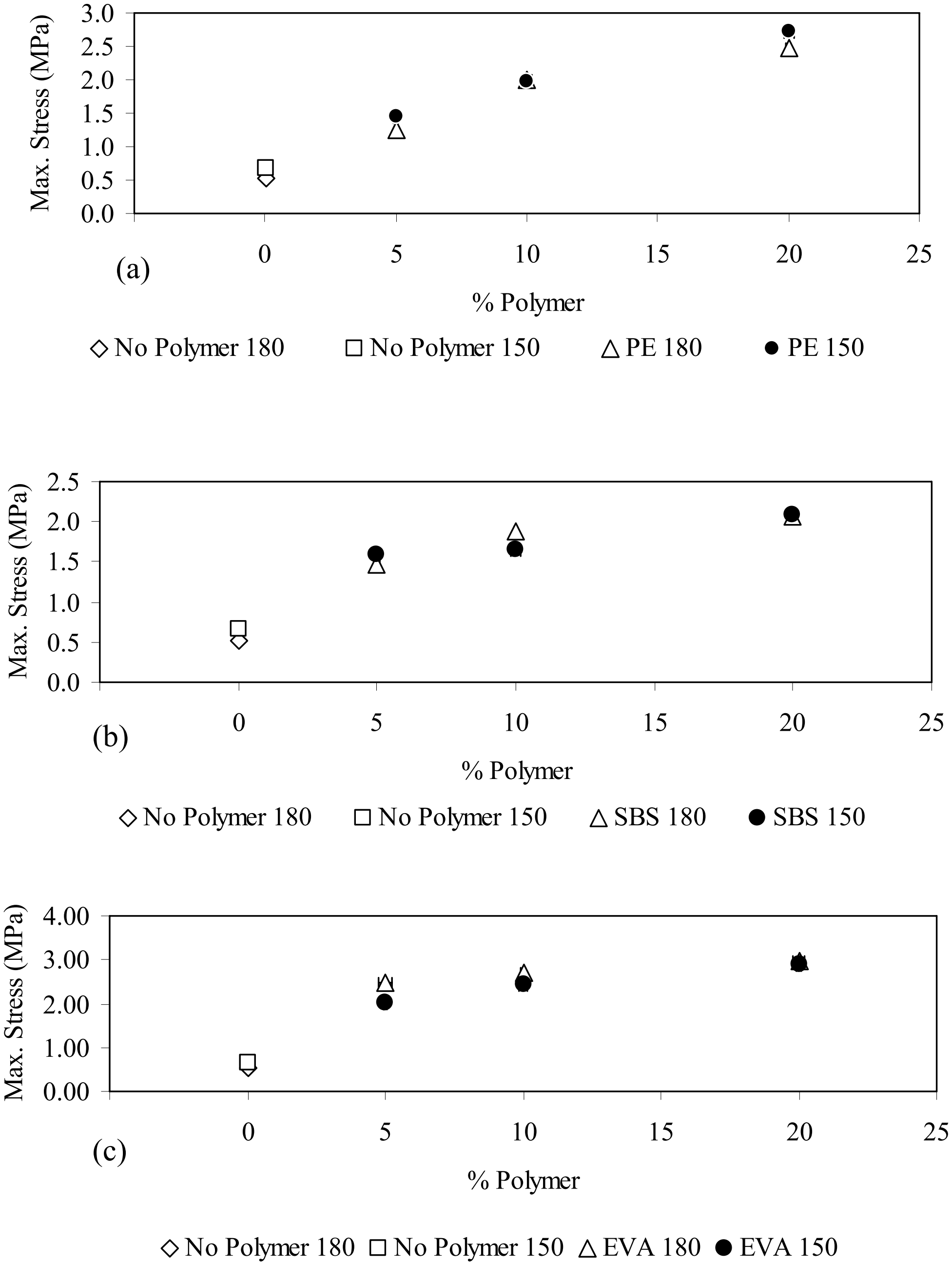


Figure 4.6 Effect of process temperature on tensile strength of bituminous composites, (a) for PE, (b) for EVA and (c) for SBS

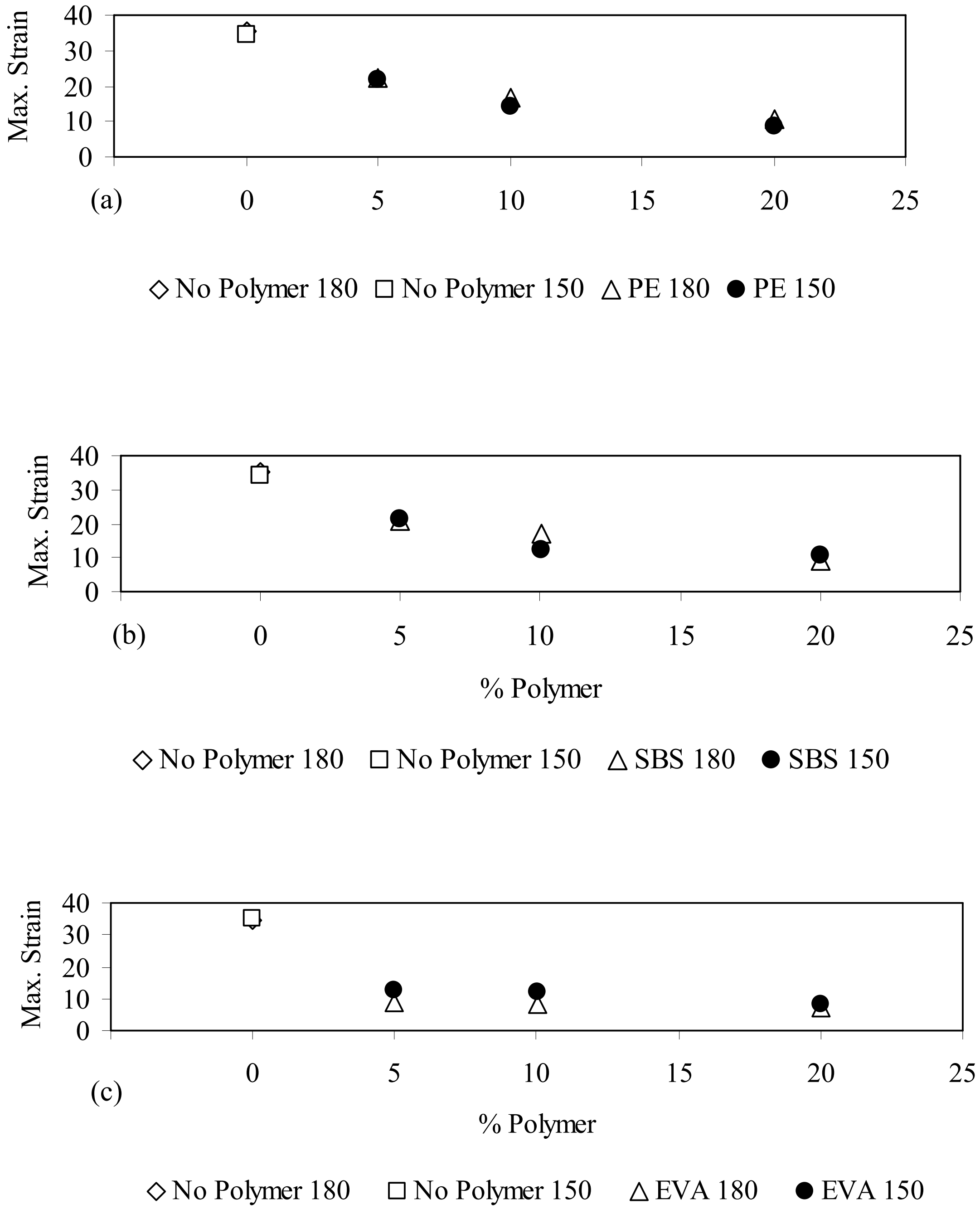


Figure 4.7 Effect of process temperature on percentage strain at break values of bituminous composites,(a) for PE, (b) for SBS and (c) for EVA.

Figure 4.8 and 4.9 represent the effect of polymer type and concentration on tensile strength and percentage strain at break values. According to these figures, addition of polymer increases the tensile strength and reduces the percentage strain regardless of polymer type. There is a slight increase at tensile strength of SBS when the polymer concentration increases but the increase at tensile strength is higher for EVA and much higher for LDPE. According to SEM analysis, fibril formation occurs during the tensile test for LDPE and EVA containing bituminous composites. The 4-fold increase in the maximum tensile strength at equal volume fractions of bitumen and LDPE is interesting. This may be due to the formation of bi-continuous bitumen and LDPE phases which then can make use of the superior mechanical properties of LDPE. The other two polymers SBS and EVA almost exhibit a gradual increase in tensile strength as polymer volume fraction increases. At low polymer volume fraction EVA has about %30 higher tensile strength than the other polymers. This finding is also significant, because, polymers are mostly used at low volume fractions in applications of bituminous compounds.

Figure 4.10 represent the effect of polymer type and concentration on Young Modulus values of bituminous composites. Young modulus of bituminous composites increases as the polymer concentration increases. Again EVA has the highest Young’s modulus value for low (5%, 10%) volume percentages of the polymer. The SEM micrographs show that there is good adhesion between EVA and the filler resulting in better mechanical properties. One can say that at relatively low volume fractions EVA and at high volume fractions LDPE improves the mechanical properties of the bituminous composites.

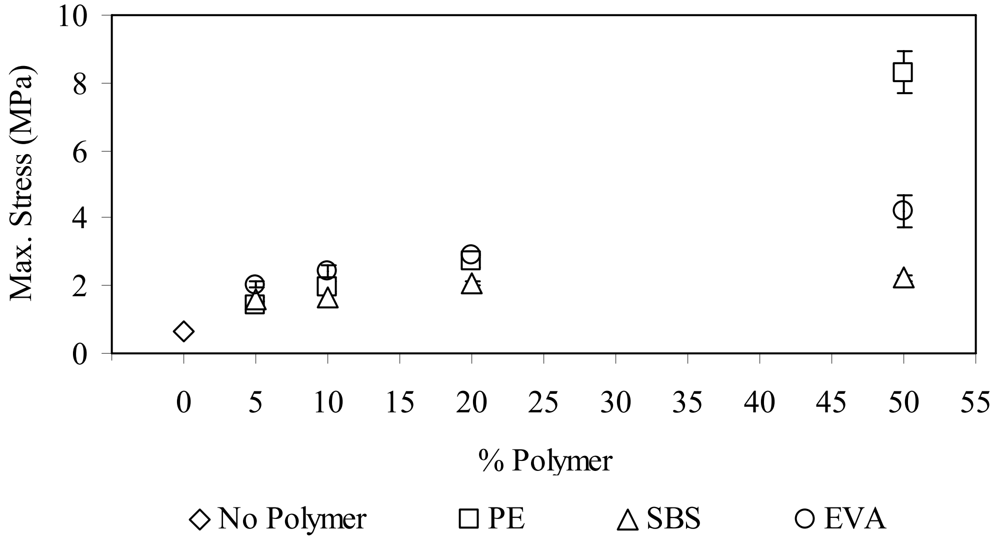


Figure 4.8 Effect of polymer type and concentration on tensile strength of bituminous composites

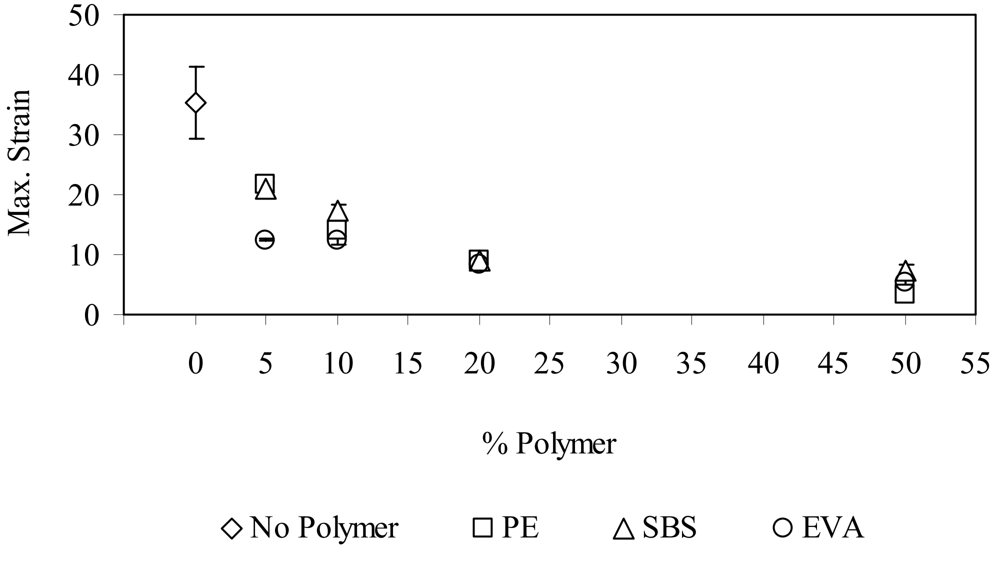


Figure 4.9 Effect of polymer type and concentration on percentage strain at break values of bituminous composites.

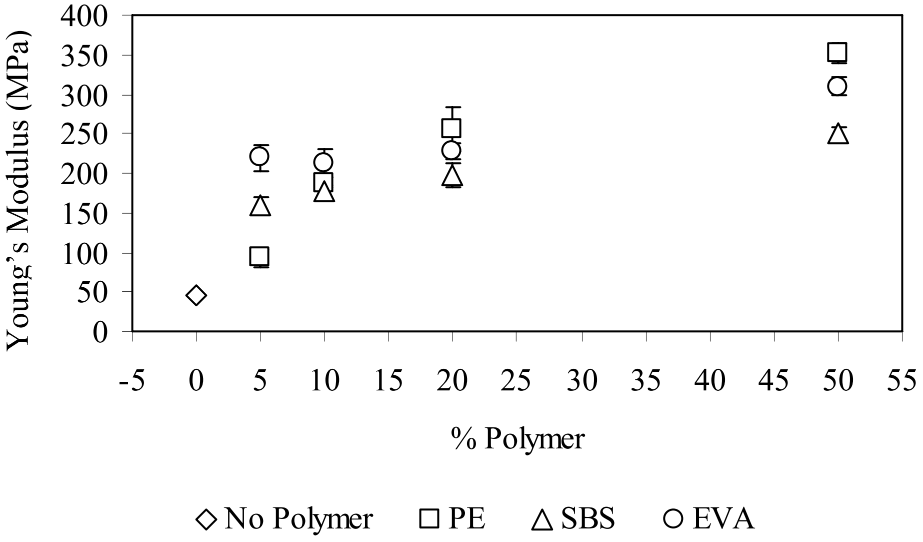


Figure 4.10 Effect of polymer type and concentration on Young modulus values of bituminous composites.

Figures 4.11, 4.12 and 4.13 represent the effect of filler concentration on tensile strength, percentage strain at break values and modulus values of bituminous composites with 20% (v/v) EVA. According to these figures, as the $CaCO_3$ concentration decreases, tensile strength, modulus values of the bituminous material decrease and percentage strain at break values increase as expected. According to rule of mixtures, adding rigid powder fillers raise the modulus and tensile strength of the composite and reduce the elongation at break [39].

In the SEM micrographs of 54% and 74% $CaCO_3$ (w/w) containing compositions no apparent difference is observed. The filler particles in both cases are well dispersed (Fig. 4.14).

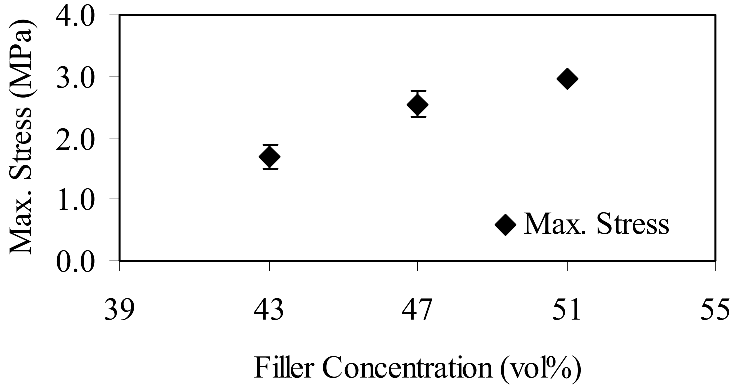


Figure 4.11 Effect of filler concentration on tensile strength of bituminous composites

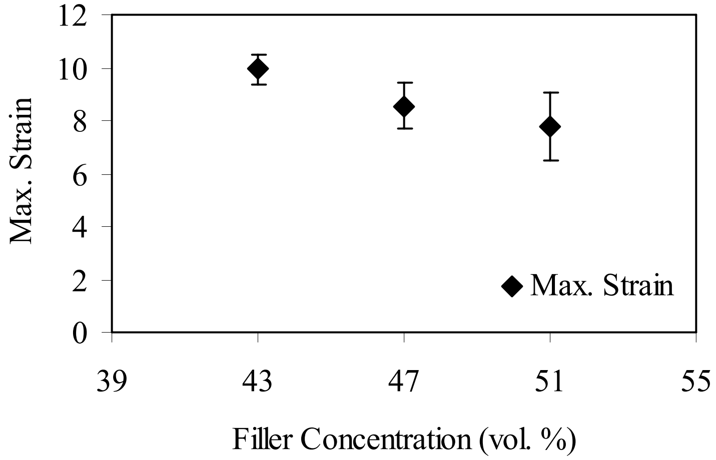


Figure 4.12 Effect of filler concentration on percentage strain at break values of bituminous composites.

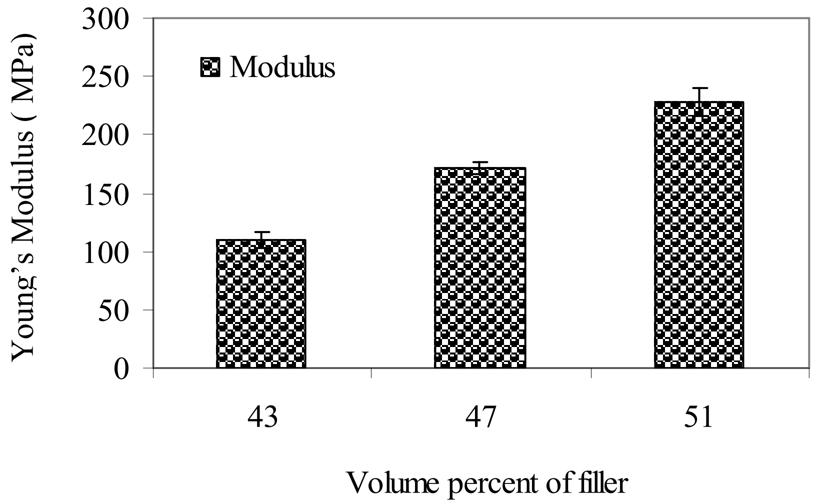


Figure 4.13 Effect of filler concentration on Young modulus values of bituminous composites.

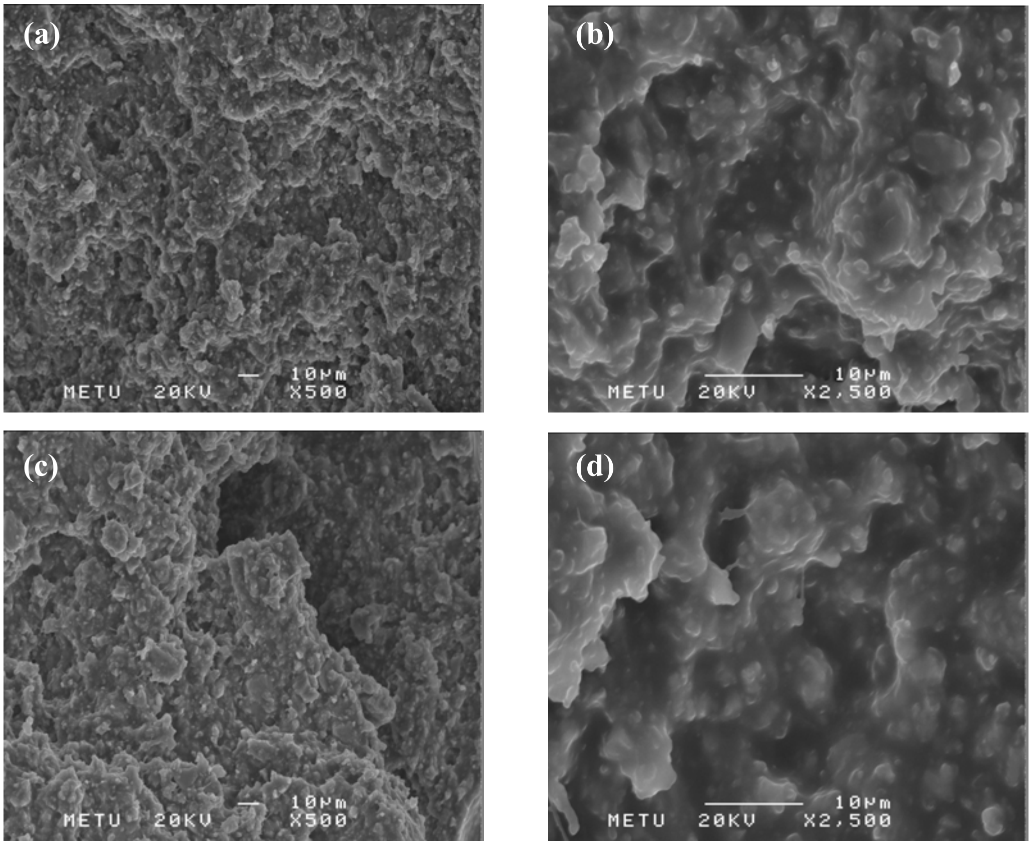


Figure 4.14 SEM micrographs of bituminous composites containing two different percentage fillers at two different magnifications (a) 51% x500, (b) 51% x2500; (c) 43% x500, (d) 43% x2500

4.3 Flow Characteristics

Melt flow index (MFI) determinations were performed in order to investigate the flow behavior of the samples, which is inversely related to melt viscosity. The test was carried out under a specified load of 2.16 kg and two specified temperature of 150 °C and 180 °C.

Figure 4.15 and Table 4.1 represent the effect of polymer type and concentration on melt flow index values of bituminous composites. As seen from the figure 4.14 and

Table 4.1, addition an amount of polymer deducted from bitumen percentage reduces the MFI value of bituminous composite. Melt flow index decreases as polymer amount increases. Polymers with higher melt viscosity than bitumen as expected decreases the MFI values of the composite. MFI values are important in order to determine the processing parameters of the composite in industrial applications where extrusion of the material is the preferred processing method. Among the three polymers investigated EVA gives a gradual and slow decrease in MFI values. The most probable reason is the polar nature of EVA which tends to have a stronger interaction with the filler $CaCO_3$. The EVA-filler interaction may have stabilizing effect in terms of viscosity changes.

Table 4.1 MFI values of bituminous composites

SAMPLE	**150 ºC**	**180 ºC**
NOPOLYMER	110	490
PE(%5)	83.1	366
PE(%10)	26.3	149
PE(%20)	11.4	49
PE(%50)	0.05	0.25
SBS(%5)	49.2	335
SBS(%10)	16.3	120
SBS(%20)	4.5	28.6
SBS (%50)	0.06	0.6
EVA(%5)	82.6	145
EVA(%10)	59.4	138
EVA(%20)	17.5	73
EVA(%50)	0.51	7.6

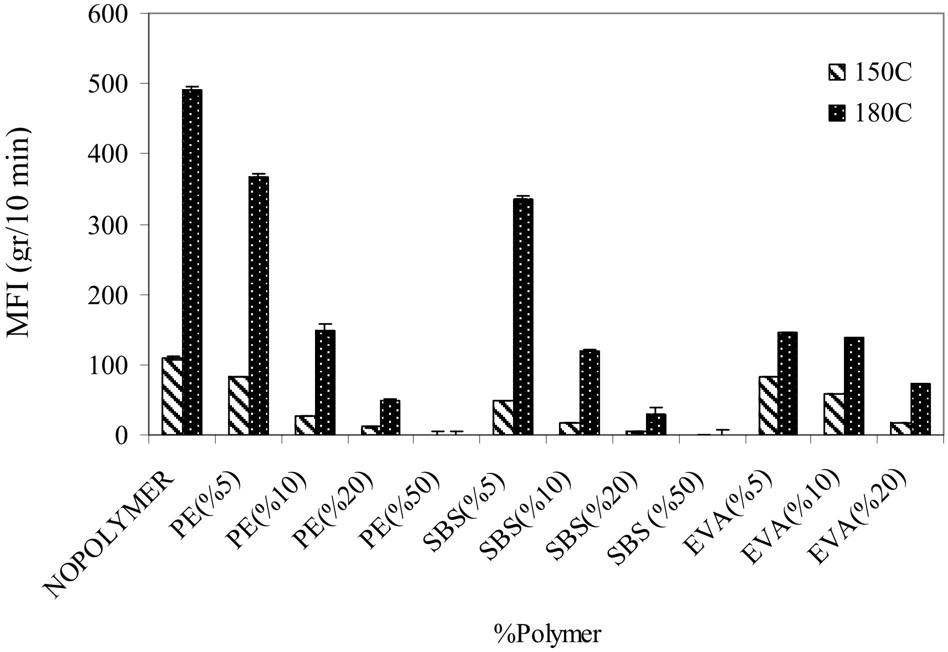


Figure 4.15 Effect of polymer type and concentration on melt flow index values of bituminous composites.

4.4 Density Measurements

Voids and air bubles are a problem in viscous composites. In order to estimate the magnitude of pores density measurements are performed.

Theoretical density is calculated from the composition of samples. Density of $CaCO_3$ is taken 2.7 gr/cm^3, bitumen as 1 gr/cm^3. Densities of LDPE, EVA and SBS were taken as 0.92 g/cm^3, 0.956 gr/cm^3 and 1.01 g/cm^3 respectively.

Porosity is calculated from the theoretical and measured density values. Percent porosity is equal to theoretical density minus density measured divided by theoretical density multiply by 100. The calculations give approximate values for void formation during composite preparation, because of the swelling of the polymer with low molecular weight portions of the bitumen phase. In any case during compression molding of the composites, despite measures taken to reduce air entrapment a small amount of air does get entrapped in the structure. Vacuum bagging techniques, which are expensive processes not applicable to bituminous composites, can be used to reduce void formation.

Table 4.2 Density of samples prepared at 150 ºC.

	Theoretical Density (g/cm^3)	**Density Measured (g/cm3)**	**Porosity (%)**
NO POLYMER	1.87	1.85	1.28
%5 (PE)	1.87	1.83	1.98
%10 (PE)	1.87	1.83	2.20
%20 (PE)	1.86	1.80	3.33
%50 (PE)	1.85	1.83	0.98
%5 (SBS)	1.87	1.85	0.72
%10 (SBS)	1.86	1.83	1.64
%20 (SBS)	1.86	1.83	1.51
%50 (SBS)	1.84	1.83	0.38
%5 (EVA)	1.87	1.82	2.84
%10 (EVA)	1.87	1.82	2.63
%20 (EVA)	1.86	1.84	1.42
%50 (EVA)	1.85	1.82	1.83

Table 4.3 Density of samples prepared at 180 ºC.

	Theoretical Density (g/cm^3)	**Density Measured (g/cm^3)**	**Porosity (%)**
NO POLYMER	1.87	1.84	1.68
%5 (PE)	1.87	1.87	0.05
%10 (PE)	1.87	1.82	2.36
%20 (PE)	1.86	1.8	3.23
%5 (SBS)	1.87	1.80	3.80
%10 (SBS)	1.86	1.83	2.09
%20 (SBS)	1.86	1.86	0.00
%5 (EVA)	1.87	1.87	0.03
%10 (EVA)	1.87	1.85	1.04
%20 (EVA)	1.86	1.83	2.04

4.5 Thermal Conductivity

The thermal conductivity values of the specimens are given in Table 4.2. The addition of polymers in general reduces the thermal conductivities. For bitumen, $CaCO_3$, LDPE, SBS are used in composites, thermal conductivities of these substances are 0.17 W/mK, 1.26-1.33 W/mK, 0.35 W/mK, 0.15-0.16 W/mK respectively. Heat capacities of these substances are 0.19 kcal/kg^{o}C, 0.2 kcal/kg^{o}C, 0.55 cal/g.C, 0.45-0.5 cal / g/C. No data for EVA is found.

It should be noticed that as polymer volume fraction increases there is a corresponding decrease in the volume fraction of bitumen. Overall heat conduction values of composites are less than that of $CaCO_3$, but, larger than the conductivities of bitumen and the polymers. The filler $CaCO_3$ occupies more than half of the composite volume, so it has animportant effect in the measured thermal conductivity values. It is interesting to observe a decreasing tendency in conductivity as polymer volume fraction increases inspite of polymers which in general have higher conductivity values than the bitumen itself. One possible explanation is that at the volume fractions used the polymer phase is discontinous and forms a non-connected dispersed phase. Their contribution to conductivity is therefore reduced. $CaCO_3$ on the other hand is over 50 volume percentage and might be forming a continuous path through aggregation of $CaCO_3$ powder.

On the other hand by polymer addition volume fraction of bitumen is reduced. At the same time as a consequence of reduced volume fraction cross-section area of bitumen in the sample is also reduced. So, heat is forced to flow through a reduced cross sectional area which can result in low thermal conductivities. The explanation gives above is highly simplified but capture the main features of the heat flux data observed in Table 4.4.

In terms of the effect of polymer type on thermal conductivities, EVA seems to be more effective than the other two polymers investigated. Here, again the polar nature of EVA which can isolate $CaCO_3$ particles from each other may be the operating mechanism.

Table 4.4 Thermal conductivity of the bituminous composites prepared at two different temperatures.

Sample	**Thermal Conductivity (W/m.K) 150 ºC**	**Thermal Conductivity (W/m.K) 180 ºC**
No Polymer	1.02	1.04
%5 (PE)	0.89	1.00
%10 (PE)	0.81	0.85
%20 (PE)	0.81	0.79
%5 (SBS)	0.80	0.88
%10 (SBS)	0.74	0.82
%20 (SBS)	0.81	0.76
%5 (EVA)	0.77	0.80
%10 (EVA)	0.76	0.77
%20 (EVA)	0.76	0.79

CHAPTER 5

CONCLUSIONS

In the preparation of bituminous composites, it was observed that the process temperature has no significant effect on the tensile strength and percentage strain at break values. In this study mixing time was kept constant as 20 minutes. It was concluded that the processing time was either not long enough to allow the evaporation of the low molecular weight species of bitumenor evaporation was already completed at 150 ºC so that the effect of process temperature was not observed.

The addition of polymer of all types investigated increases the tensile strength and reduces percentage strain at break values of the samples. There is a small increase at tensile strength of the composites which contains SBS when the polymer concentration increases but there are higher increases at tensile strengths for EVA and much higher for LDPE. Young modulus of bituminous composites increases as the polymer concentration increases but at low volume fractions EVA produces stronger composites due to larger interaction with the filler $CaCO_3$ compared to other polymers. The very high tensile strength value of LDPE at 50% volume percentage is thought to result from the formation of bicontinuous morphology.

Melt flow index decreases as polymer amount increases. As the $CaCO_3$ concentration decreases, tensile strength, percentage strain at break values and modulus values of the bituminous material decrease as expected. Again $CaCO_3$ EVA interraction gives rise to a more gradual change in MFI values at both temperatures.

From SEM micrographs, as the polymer ratio increases for composites which contain LDPE or EVA, large polymer domains are formed. Plastic deformation and fibrillation of LDPE and EVA is observed. EVA has affinity to $CaCO_3$ as seen SEM micrograph of 50% EVA containing bituminous. There is no plastic deformation or fibrillation of polymer observed at the composites which contains SBS.

The thermal conductivities decrease as the polymer content of the composite increases. This effect is basically due to the formation of dispersed polymer phase which reduces the cross-sectional area of the bitumen phase. Among the polymers, EVA has the least thermal conductivity due to its polar nature and insulating capacity of the CaCO3 powder.

Samples which contain 20% LDPE , 10% and 20% EVA are suitable for using as isolation material. Thermal conductivity and the mechanical properties of the other samples get better by using different fillers such as mica, barite, kiesel guhr.

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