Chapter 13

Bitumen and Its Modifier for Use in Pavement Engineering

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Additional information is available at the end of the chapter

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Abstract

This chapter focuses on bitumen specifically. This chapter consists of several parts that can be mentioned, including the history of the appearance of bitumen and the types of constituent elements, as well as its mechanical properties and chemical structure and its thermal sensitivity. In all parts, the effects of bitumen on asphalt are discussed. In the following sections, the bitumen modification mechanism, polymer modifiers, and their behavior on the bitumen resistance to asphalt failures are also discussed. This chapter is very suitable for students and researchers interested in improving polymerization asphalt and bitumen and will help them to carry out research and concepts.

Keywords: bitumen, modify, asphalt, polymer

1. Introduction

Traffic loading and environmental factors are one of the most important destructive causes in asphalt pavement. Traffic loading leads to breakdowns such as rutting and fatigue cracks, and environmental factors such as temperature are the main cause of the refrigerant cracks. Traffic loading can cause tensile, compression, shear stresses, or a combination of them in different pavement points, depending on factors such as load size, contact surface, temperature, hardness, and pavement thickness.

Typically, the repetition of these stresses and strains leads to damage the pavement. Fatigue cracks are, in fact, fine cracks, which increase with the continuity of loading in the pavement system and ultimately expand into fatigue cracks. The accumulation of these cracks eventually disrupts the pavement. Therefore, the ability to predict the behavior of pavement against the phenomenon of fatigue is important. Since the fatigue phenomenon occurs more in the bitumen phase of the asphalt mixture [1], identifying the structure of the bitumen in the asphalt is very important to develop durability and life span.

1.1. History of bitumen and its reformation

The Sumerians, the Assyrians, and many earlier civilizations have used bitumen widely. The beginning of the modern bitumen industry can be attributed to 1712 when bituminous stones were discovered in France. At that time, the bitumen was simply distributed as the clod on the surface of the local roads, and under load traffic, they were rub and consolidated. This technique was quite successful, and shortly afterward, improvements were made in the form of powdering and warming the material before using. Then they, slamming and flattening the asphalt, tightened and consolidated the asphalt, known as compressed rock asphalt, and used on the streets of Europe. Such streets than earthy roads were more durable, healthier, and interesting. Their only drawback was that they were loose, volatile, and slippery during heavy traffic [2].

The first bitumen reformation dates back to 1843. In the 1930s, experimental bitumen refinement project experiments were carried out in Europe, and in the 1950s, the use of Neoprene Latex, as bitumen modifier in North America, was begun [3]. In 1963, the first experimental modified bitumen roads in France were made in order to understand the behavior of modified bitumen with various types of natural and synthetic rubbers [4].

In the late 1970s, Europe was better than the United States in the process of refining bitumen. One of its reasons was the requirement for European contractors to provide a guarantee for the durability and shelf life of the pavement, which would have reduced the costs of the lifespan of the road, even at the expense of increasing initial costs. The relatively high initial cost in performing refurbished asphalt had limited its consumption in the United States. In the mid-1980s, European technology introduced new polymers that increased the consumption of polymeric bitumen in the United States [3].

1.2. Bitumen sources

The bitumen used in the road construction industry is divided into two general categories:

1. Bitumen (mineral pitch)
2. Bitumen produced from distillation of crude oil (petroleum pitch)

1.2.1. Bitumen (natural pitch)

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

1.2.2. Petroleum pitch

Oil pitch is obtained from the refinery of crude oil in distillation towers. In fact, what remains at the bottom of the distillation tower above 380°C is pure oil pitch. Bitumen with different stiffness degrees for different road applications can be obtained by setting the temperature and pressure inside the distillation towers [5].

1.3. Chemical bitumen building

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

The chemical structure of bitumen is not fully known, and the chemical composition of the bitumen and its structure is heavily dependent on the initial crude oil from which it is derived and the processes applied for its production. Chemical compositions and crude oil structure are also very diverse. In this regard, considering the type of predominant hydrocarbons in crude oil, it can be divided into three groups of paraffins, asphaltenes, and naphthenes (**Table 1**).

As mentioned, the chemical structure of the pitches differs according to the location and source of the crude oil. The operation and production process in the refinery (such as aeration) also influence the chemical structure of bitumen.

Generally, the components constituting pitch include carbon, hydrogen, sulfur, oxygen, nitrogen, and some metallic elements found in very small percentage. The percentage of each element is given in **Table 2**.

Hydrocarbons	Paraffinic crude oil	Naftens crude oil	Asphaltenes crude oil
Paraffins	40	12	5
Naftens	48	75	15
Aromatics	10	10	20
Asphaltenes	2	3	60

Table 1. Chemical structure of different types of crude oil.

Elements	Percent
Carbon	82–88
Hydrogen	18–11
Sulfur	0–6
Oxygen	0–5/1
Nitrogen	0–1

Table 2. Bituminous ingredients.

1.3.1. Components of bitumen

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

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

1.3.1.1. Asphaltenes

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

Asphaltene rate in bitumen has many effects on rheological properties of bitumen. The higher the bitumen asphalt, the more the stiffness of the bitumen, and subsequently the degree of penetration would be less. In addition, it will result in a greater softening point and more penetration of bitumen.

1.3.1.2. Polar aromatics (resins)

These compounds are usually composed of carbon and hydrogen, which also contain a small amount of oxygen, nitrogen, and sulfur. The compounds are solid and semisolid and in dark brown color. They are anticoagulants for asphaltene, and the ratio of the resin to the asphaltenes may be as high as that from the sol[1] or gel[2] mode. The resins in bitumen have a molecular weight of 500–50,000. The adhesive properties of bitumen result from its resins.

[1] Mode (sol): in this case, the particles are dispersed uniformly and homogeneously in solution. The pitches obtained from the refinery are usually of this category.

[2] Mode (gel): in this case, colloidal pitch particles create a regular sponge-like network that propagates throughout the system. In this case, the system is semisolid, and this is where the material constituting the maltene in terms of chemical compositions has the most properties of oil or paraffin hydrocarbons.

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1.3.1.3. Oil aromatics

The aromatic oils are the least molecular weight ring compounds that contain aromatic or petroleum lateral chains and are an excellent anticoagulant for asphaltenes. The group, which consists of 40–60% bitumen, is a viscous liquid in dark brown color with an average molecular weight between 300 and 2000. The aromatics have polar carbon chains.

1.3.1.4. Saturated materials (paraffins)

Saturated compounds are composed of straight and branched chain aliphatic hydrocarbons with alkyl naphthenes and some aromatic alkyls. These compounds are often nonpolar and colorless viscose oils. The average molecular weight of these is similar to that of aromatics. The components of the saturated compositions include saturated waxy and non-wax[3] materials. Saturated compositions comprise 5–20% bitumen.

1.4. Mechanical and physical bitumen properties

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

1.4.1. Bitumen behavior

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

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

In ambient conditions, between very low cold temperatures and very high warm temperatures, i.e., the average temperature of bitumen, it has the behavior of viscous fluids and the

[3] Wax: part of the paraffins is crystalline. The method for determining the amount of bitumen wax is given in DIN 52015.

behavior of plastic solids simultaneously. Bitumen, in this case, has either viscous behavior or elastic behavior, depending on the temperature and loading time.

In environmental conditions, between high cold temperatures and high heat temperatures, i.e., the average temperature of bitumen, the behavior of viscous fluids, and the behavior of plastic solids are simultaneously obtained. In this case, bitumen has both viscous and elastic behaviors depending on the temperature and loading time.

1.4.1.1. Newtonian behavior of bitumen

When there is a linear relationship between shear stress applied to fluids and velocity gradient or shearing strain rate, they are called Newtonian fluids. Road bitumen often shows Newtonian behavior at high temperatures. **Figure 1** shows stress ratio with strain rat that is a feature of Newtonian materials.

Another condition required for a Newtonian material is that it does not show any elastic behavior. For that bitumen show elastic behavior at low temperatures; they cannot be classified as Newtonian materials, although they display Newtonian flow behavior (n = 1) [6].

1.4.1.2. Pseudo-plastic behavior and Bingham plastic

A type of behavior which results in shear thinning of fluid (decrease of viscosity with increase of stress or reduce of strength with increase of shear stress) is called pseudo-plastic. Fluid which shows solid behavior under stresses less than yield stress and shows fluid behavior under stresses more than yield stress; Bingham fluid and this behavior are said Bingham plastic that in this case (1 = n). Bitumen, which in the low temperatures and the low shear stresses (low shear velocities) have been tested, generally displays pseudo-plastic behavior or Bingham plastic behavior.

Figure 2 shows that the shear velocity in high stresses is increased faster that leads to reduce of viscosity. When (n < 1), the bitumen is sensitive to stress and acts as a pseudo-plastic material. Blown bitumen as roof coverings has a pseudo-plastic behavior. At low temperatures, often the material displays one special yield point, which is seen in Bingham plastic behavior

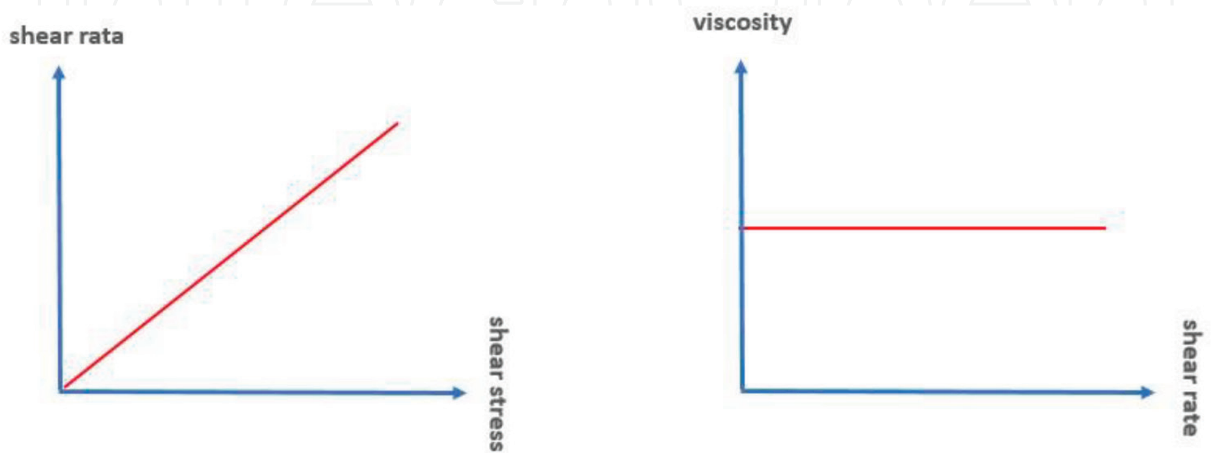

Figure 1. Newtonian behavior [6].

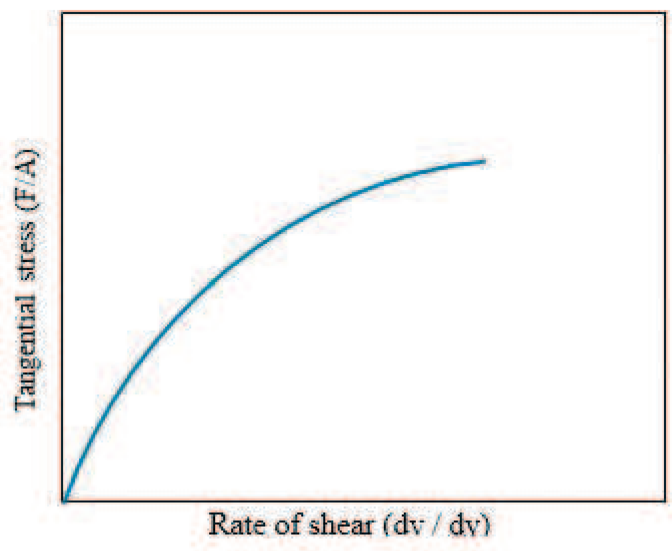

Figure 2. Pseudo-plastic behavior [7].

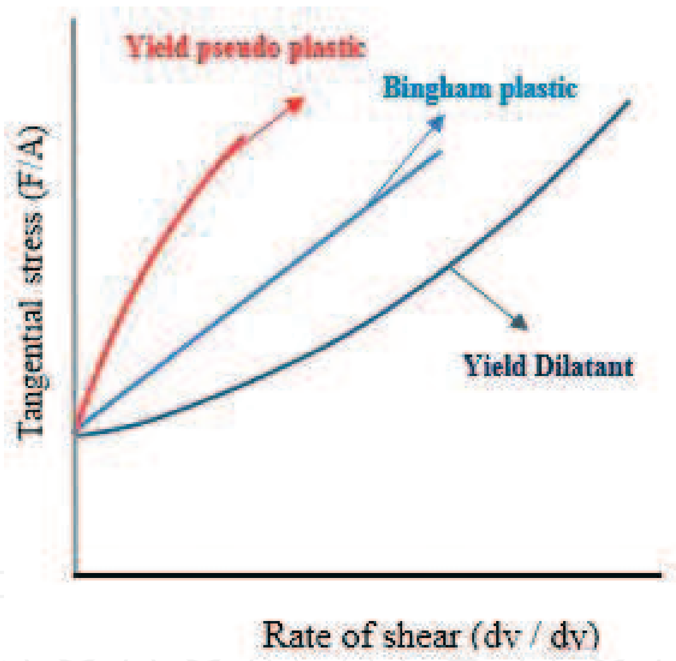

Figure 3. Bingham plastic behavior [7].

in **Figure 3**. All bitumen at very low temperatures display the behavior of a friable elastic solid with flow potential or very low creep. Usually bitumen is considered as glass solids at temperatures below the glass transition temperature (Tg)[27] [7].

1.4.2. Bitumen temperature susceptibility

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

1.4.3. Bitumen hardening

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

All abovementioned processes are dependent on environmental conditions, temperature, and thickness of bitumen lining on aggregates in asphalt mixtures. Bitumen hardening in asphalt occurs in two stages: one is short term and fast, and the other is long term and gradual. The hardening stage occurs in the short term with high speed and intensity over a short period during heating bitumen and mixing it with rocky materials at high temperatures. The second stage of hardening of the bitumen is gradually and slowly made during service. The results of the physical hardening of the bitumen reduce the degree of penetration, increase the softening point, reduce the plasticity, increase viscosity, decrease adhesion property, and increase the bitumen fragility property. The main factor in the hardening of bitumen is the changes, which occur in the chemical components of bitumen during heating the bitumen, mixing it with stone materials and at the time of service due to the abovementioned factors. In **Figures 2–4**, the rate of change in each of the chemical components of bitumen has been shown in each of the different stages of the pavement life. As it is seen in the figure, the amount of asphalt gradually increases, while the amount of resin and aromatic compounds decreases; as a result, at these stages, the aging index (the ratio of the viscosity of bitumen available to the initial bitumen) increases. The aging index in these shapes is the ratio of viscosity of bitumen extracted from samples to the initial bitumen at 25°C. Investigations show that the most changes in the bitumen viscosity occur during mixing and diffusing the mixture, and after that, the bitumen viscosity changes are insignificant in the period of the service. Regarding the chemical compositions of bitumen, asphalt is increased while mixing and density as shown in **Figure 4**, and this process continues in the period of the service. Resin and aromatics are decreased in the course of time. The tested samples have been gotten with a thickness of 3 mm more than the samples taken from the pavement.

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1.4.4. *Bitumen aging*

The gradual changes in the physical and chemical properties of oil bitumen have been accepted as a principle. Researchers believe in this field that the most important factor of these changes is the phenomenon of aging hardening that causes the appearance of various types of damages in the asphalt. Various and different processes interfere with the gradual changes or the bitumen hardening such as oxidation, photochemical reactions, sublimation of bitumen light weight and volatile materials, polymerization, carbonization, absorption of oils in bitumen by aggregates, chemical reactions between bituminous components and mineral compounds of rocky materials, and microbiological transformations. All of the processes mentioned are dependent in time, ambient temperature, heat, thickness, and membrane around aggregates. For example, the rate of oxidation, which is the most important factor of the hardening of the materials, which it doubles with an increase 10 at 100°C. Physical hardening is another factor of aging or usual hardening in bitumen. Physical hardening occurs when bitumen is at ambient temperature and is usually attributed to the rearrangement of bitumen molecules and slow crystallinity of waxes. Of course, physical hardening is reversible, and the initial viscosity of bitumen is obtained by heating. **Figure 5** shows the dependence of viscosity in temperature

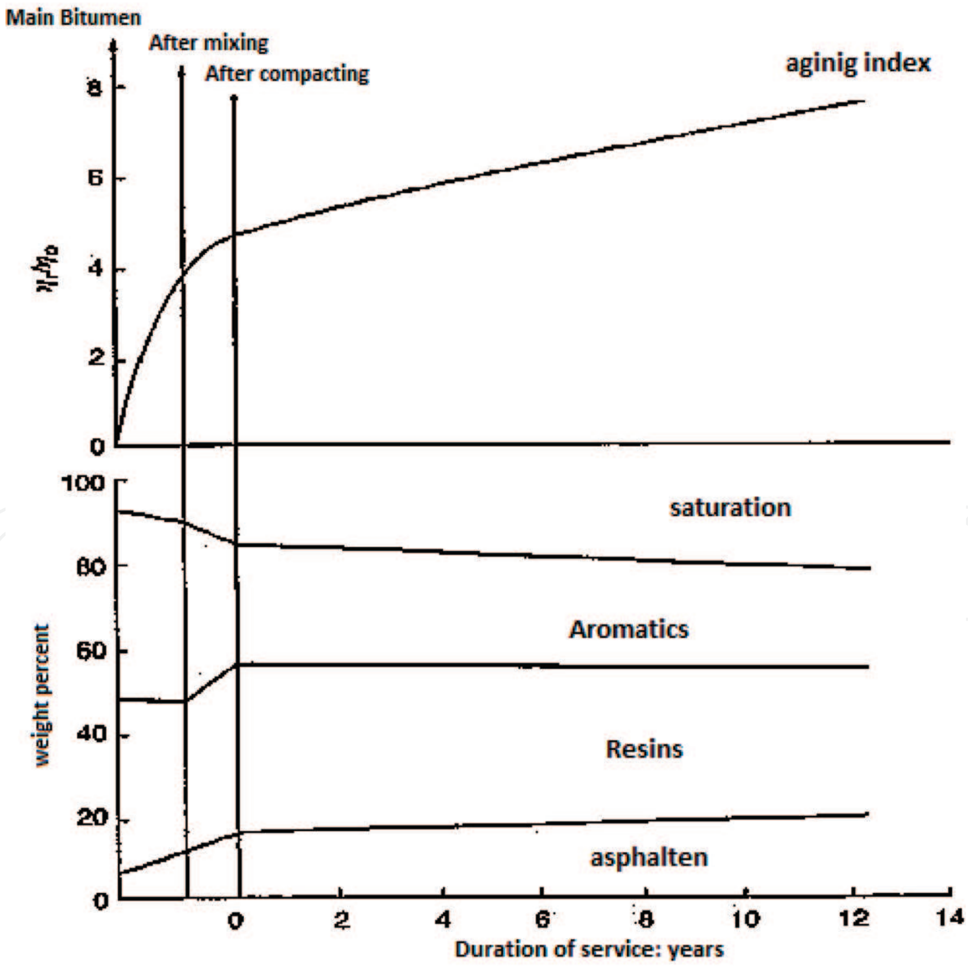

Figure 4. The changes of bitumen components during mixing, diffusing, compacting, and serving.

for two samples of bitumen. These two figures also show that all bitumen are not hardened equally or their physical and chemical properties do not change with the same rate.

High and long-term studies have been done on bitumen used in making the road in order to determine the chemical compositions of bitumen changed over time; the results of this research were definition of the aging index of bitumen:

$$\text{Aging index} = \eta_r/\eta_o \quad (1)$$

The aging index is calculated according to the ratio of the viscosity of bitumen recycled (η_r) to the viscosity of main bitumen (η_o) at a temperature of 25°C.

1.5. Bitumen modification

As mentioned before, there is a complex relation between bitumen chemical structure, bituminous colloid structure, and its physical and rheological properties. Any material which changes the chemical structure of bitumen consequently changes the properties of bitumen, and as a result, it can be a modifier [4].

Ideally, modified bitumen has more adhesion than pure bitumen and lower thermal sensitivity in the range of service temperatures and sufficient viscosity at execution temperature. In addition, its sensitivity to the time of loading is low, and its strength to plastic deformation, fatigue, and cryogenic cracks is high. Eventually, its properties after aging are good for execution and service [4].

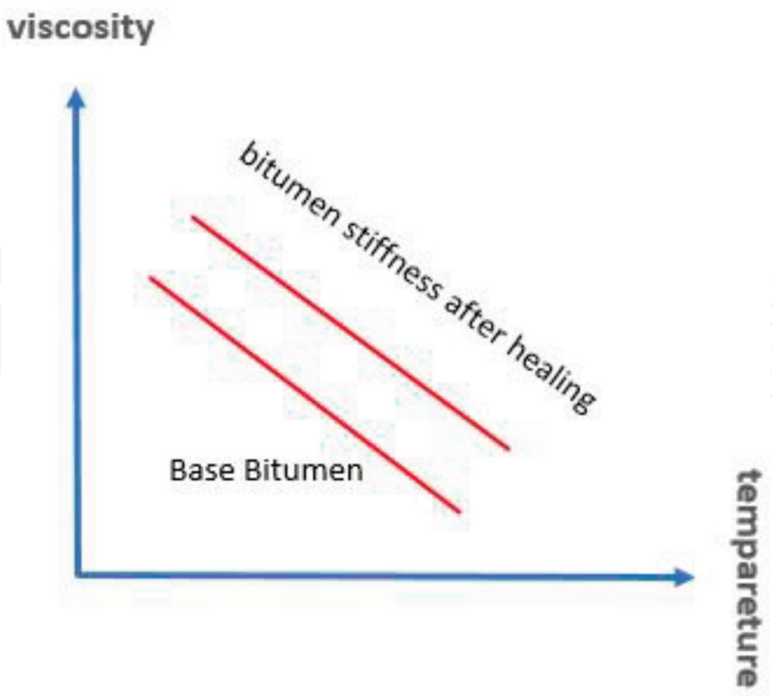

Figure 5. Dependence of viscosity in temperature for two bitumen samples.

Thermoplastic elastomers	Styrene butadiene diblock (SB)
	Styrene butadiene triblock/radial (SBS)
	Styrene isoprene (SIS)
	Styrene ethylbutylene styrene (SEBS)
	Styrene butadiene rubber latex (SBR)
	Polychloroprene latex
Plastomers	Ethylene vinyl acetate (EVA)
	Ethylene propylene diene monomer (EPDM)
	Polyisobutylene
	Polyethylene (low density and high density)

Table 3. Types of thermoplastic elastomers and common plastomers in rendering bitumen [12].

1.5.1. Bitumen modification by polymer

By adding polymers, the chain of small molecules is repeated, and as a result, the pavement performance improves. Polymer-modified bitumen increases strength against rutting and fatigue and cryogenic cracks and reduces damask and thermal sensitivity. So polymer-modified bitumen are used successfully in places with high stress such as intersections, airports, truck weighing areas, and race routes. The positive properties of polymeric bitumen include increase of elastic recovery, viscosity, softening point, adhesion, and flexibility [3].

Polymers used to accommodate bitumen are usually in three forms: thermoplastic elastomers, plastomers, and reactive polymers [8, 9]. Thermoplastic elastomers usually have more elasticity against pavement at low temperature, while reactive polymers and plastomers cause the hardening and strength to be increased against permanent deformations. It should be considered that reactive polymers react with bitumen due to the presence of operating groups and show greater compatibility than the other two polymers [8–11].

Experience shows that only a few polymers have desirable compatibility with bitumen. Industrial polymers used to modify bitumen are usually divided into two general categories:

- One of the most common types of plastomers is copolymer ethylene vinyl acetate (EVA) in which its category is determined according to the percentage of vinyl acetate and its molecular weight (determined in terms of the melting temperature) [4].
- One of the most common types of thermoplastic elastomers is copolymer styrene-block styrene-butadiene (SBS). These polymers are classified according to percentage of styrene, molecular weight, and structure (linear and radial) [4].

Types of elastomers and plastomers common in modifying bitumen are shown in **Table 3** [12].

The result of the mixing of bitumen with a polymer of thermoplastic elastomers at high temperature can be in three types:

- Heterogeneous mixture: in this type of mixture which is most likely, polymers and bitumen are incompatible and cause the separation of mixed components. This bitumen mixture does not have any proper properties for pavement application [4].
- Homogeneous mixture: this mixture is completely homogeneous to the molecular level in which bitumen and polymer are completely compatible. The oil in the bitumen completely resolves the polymer and eliminates any interaction at inter-micromolecular level. In such a situation, the bitumen is completely stable, and its properties change than the base bitumen quite low, in which the viscosity is increased. As a result, such a situation is not desirable [4].
- Micro-heterogeneous mixture: this mixture contains two distinct parts, which are simply locked and clamp together. Such a level of compatibility is desirable and improves the properties of bitumen. In this status, the polymer particles that are compatible absorb the oil-based phase of the bitumen, and they swell to create a polymer phase distinct from residual bitumen components (consisting of heavier components of bitumen such as oil, resin, and asphaltene) [4].

1.5.2. The mechanism of bituminous modification with a polymer

As described below, three general statuses can be defined for the mixing of bitumen and polymer:

- The first status—low polymer content (less than 4%). In this situation, the bitumen is the base phase, and the polymer phase is dispersed in it. In this status, in order to maintain the stability during the storage, the polymer should absorb a significant amount of light materials and volatile asphalt; thus in comparison to its initial volume, it swells five to ten times. When the polymer absorbs the bitumen oil, the asphaltene percentage in bitumen increases, so the adhesion and the elasticity of bitumen increase. At a high service temperature (about 60°C), the polymer phase hardness modulus is higher than the bitumen matrix modulus, which enhances the mechanical performance of bitumen at that temperature. At low temperatures, the polymer hardness modulus is less than bitumen, which results in a reduction in the brittleness of modified bitumen. Therefore, it can be concluded that the polymer dispersed in bitumen (discontinuous phase) improves the properties of bitumen at high and low temperatures. In this status, the properties of the base bitumen significantly affect the modified bitumen properties [4].
- The second status—the polymer content is about 5%: in this status, two-phase, continuous, and interconnected microstructures are created. Controlling such a system is often difficult, and there is a problem of instability in it. In this method, the micromorphology and the properties of bitumen are usually dependent on the bitumen temperature history. In this status, as the percentage of polymer increases, the softening point increases significantly [4].
- The third status—high polymer content (more than 7% if suitable bitumen and polymer are selected): in this status, the polymer is the dominant phase and forms a continuous matrix

in the system. In fact, this system is no longer bitumen, but it is a polymer plasticized with bitumen oil in which a heavy phase of bitumen is dispersed. The properties of such a thermoplastic adhesive material are essentially different from those of bitumen, and in fact, it has the polymer properties. In this status, the softening point, which in the previous states increased with the increase of the polymer content, is fixed and may experience a minor change with the increase of polymer content [4].

The microstructure of the polymeric bitumen is very important, and as described above, there is a close relationship between polymer bitumen microstructure and its physical properties. Studies have shown that in the same percentage of bitumen and base bitumen with the same grade but different sources, polymer bitumen can have a very different microstructure and properties, especially at low temperatures [4].

1.5.3. Polymer bitumen stability

Sustainability is one of the most important issues in polymer-modified bitumen. As this type of bitumen has two separate phases, it will be studied under Stokes' law. In other words, the speed of dispersion of particles (polymer particles in a bitumen matrix or bitumen in a polymer matrix) increases with the increase of the particle size, with an increase of the difference between the density of the two phases, and with the decrease of the viscosity of the continuous phase [4]. In order to increase the stability of polymer-modified bitumen, it is necessary to control the particle size by controlling the production process. Furthermore, by controlling the chemical structure of the base bitumen and the polymer-modified bitumen, it is possible to move toward the equilibrium of the density of the two phases. For example, the stability of EVA-modified bitumen is highly dependent on the percentage of asphaltene in the base bitumen. This process is shown in **Figure 6**. In this figure, by "sustainability" parameter, the amount of delamination is meant. When this parameter is zero, it means no delamination occurred [4].

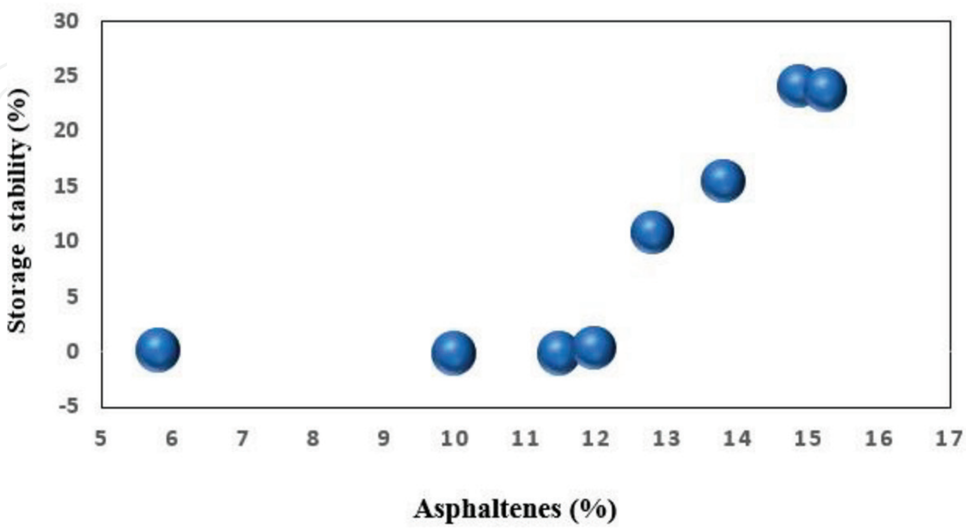

Figure 6. The effect of asphaltene content in the base bitumen on the stability of EVA polymer-modified bitumen [4].

1.5.4. Temperature history

A study in the LCPC laboratories in France showed that the formation of the continuous polymer phase in polymer-modified bitumen improves the properties of polymer bitumen, such as plasticity at low temperature. On the other hand, in polymer-modified bitumen, the plasticity of the continuous polymer phase is increased with the increase of the cooling rate in the laboratory. The polymer-modified bitumen, which was cooled at the same rate as the real conditions of the runtime (about 30°C/h), had a different structure. In this status, the bitumen had the continuous phase, and the polymer had a discontinuous and dispersed phase. This experiment showed that in the case of rapid cooling of the polymer-modified bitumen, the physical properties of polymer-modified bitumen decrease significantly so that the softening point dropped to 30°C [4].

1.6. Common polymers in bitumen modification

As shown in **Tables 2** and **3**, the different types of polymers are used in bitumen modification, each of which is different in terms of modification mechanism and properties. In this section, some of the most common polymers that are used in the modification of bitumen properties have been reviewed.

1.6.1. Styrene butadiene rubber (SBR)

SBR is a type of copolymer, in which styrene and butadiene monomers are irregularly bonded in a polymeric chain, based on their initial percentages. This copolymer has good strength due to the presence of thermoplastic styrene monomers between the layers of butadiene rubber monomers, which is why it is used extensively in the tire industry. Unfortunately, this rubber inflated in bitumen to a limited extent is not compatible with bitumen, so it cannot significantly improve the properties of bitumen [13–15].

1.6.2. Styrene butadiene styrene (SBS)

SBS is a block copolymer that increases the bitumen elasticity. This polymer is one of the most suitable bituminous modifying polymers in terms of improving the properties of bitumen, but it has some economic and technical limitations. However, after the rubber powder, SBS is the most widely used modifier in pavement [3]. The morphology of the SBS and bitumen mix may vary depending on the source of the base bitumen and the polymer. In one of the bitumen statuses, the phase is continuous, and the SBS particles are dispersed in bitumen. In the other statuses, the bitumen cells exist in the polymer as a continuous phase. In the third status (high polymer content), bitumen and polymer continuous phases interlock. In this status, a critical network is created between bitumen and polymer that increases the complex shear modulus of the mixture (G*) and thus increases the resistance to the rutting [3].

In super PIO experiments on bitumen containing 1–3% SBS, this modifier improved the high-temperature performance grade, but the intermediate-temperature performance grade remained relatively constant relative to the base bitumen. Performance tests at low temperatures by Bending Beam Rheometer (BBR) showed that this amount of SBS reduced the hardness range temperature, but due to a decrease in the creep rate (m-value), resulting in an increase in the creep rate temperature, the low temperature performance grade in these types of bitumen got worse [16]. Other research have shown that using a higher percentage SBS, it is possible to improve the low- and intermediate-temperature performance grades [17]. According to the definition of the BBR test, the hardness range temperature is a temperature at which the stiffness (bitumen hardness modulus) reaches 300 MPa and the temperature is the creep rate temperature range is a temperature at which the value of M-Value is less than 0.3.

The studies showed that in bitumen containing 5% of SBS, the property-controlling factor is the molecular weight of the polystyrene and polybutadiene blocks. On the other hand, for viscosity at 180°C, the molecular weight of polybutadiene is more effective than polystyrene. It was also observed in high-SBS-containing bitumen that the oil content of the bitumen has a determining effect on the degree of penetration and plasticity point of polymer-modified bitumen [4].

Mohammad et al. when studying samples taken from SBS-modified 8-year-old bitumen pavements in Louisiana observed hardening resulted from oxidation. The hardness of the samples at low and high temperatures was more than it was expected. By performing the test, they found that the effect of extraction and reduction of bitumen on the quality of bitumen containing SBS was very insignificant. The experiments showed that in asphalt recycling operation, increasing the percentage of reduced bitumen containing SBS increased rutting resistance, while it reduces fatigue-cracking resistance [18]. This behavior can be due to the increased hardness and brittleness of the aging bitumen containing SBS. Other findings from this study were the differences between the effect of natural aging and the effect of Pressure Aging Vessel (PAV) test on SBS-containing bitumen. Differential scanning calorimetry (DSC) analysis of bitumen showed that the aging process of bitumen tested with PAV reduces the number of paraffinic crystalline structures in bitumen, while natural aging in a sample extracted from the road increases the paraffinic crystalline structures of the bitumen, thereby in comparison with PAV tested bitumen, its hardness and brittleness increase [18].

1.6.3. Ethylene vinyl acetate (EVA)

Figure 7 shows that by increasing the percentage EVA, the degree of penetration decreases, and the softening point increases. This effect is more evident in EVA-containing less vinyl acetate (VA) [4]. In another study by Madela et al., it was found that in bitumen with a low percentage of EVA (bitumen matrix is dominant), the chemical structure of bitumen plays a determining role in the physical properties of polymer-modified bitumen. At high percentages of EVA (polymer matrix is dominant), it significantly reduces the effect of bitumen chemical structure [4].

1.6.4. Modification of bitumen with rubber powder (CRM)

The US Federal Highway Administration (FHWA) analyzed the life-cycle cost of the pavement, including rubber powder and other modifiers and showed that the use of rubber

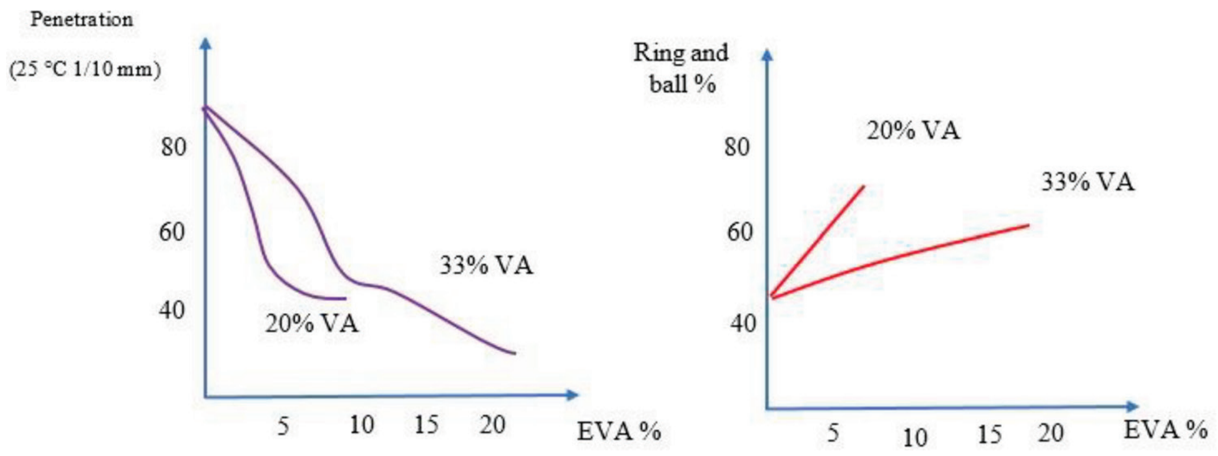

Figure 7. The effect of percentage changes of EVA in bitumen and vinyl acetate, on the degree of penetration and softening point of polymer-modified bitumen [18].

powder to modify bitumen is economical. In 1991, a US law was approved requiring the government from 1994 to use rubber powder (5%) in roads constructed with the support from the state budget. This amount should be increased to 20% by 1997. Of course, this law was later changed. Typically, rubber is made from the recycled tires. This reduces the space needed to burrow worn tires [3].

Modifying bitumen with natural rubber increases the resistance of asphalt mixture to rutting and improves its flexibility. On the other hand, it tends to be delaminated. Due to the higher molecular weight of rubber powder, this material is less compatible than bitumen. Another common problem with the use of natural rubber is the need for a higher temperature and a longer time to mix and disperse rubber in bitumen [3].

Although much research has been done about the nature of the reaction of rubber and bitumen particles, the exact mechanism of this operation is still unknown. According to the opinions of many researchers, after mixing melt pure bitumen with rubber powder, rubber powder's polymer chains absorb aromatic compounds of pure bitumen. Powdered rubber particles become soft and swollen that lead to an increase in the viscosity of the rubber-bitumen blend [19].

This swelling occurs because of the physical and chemical reaction of bitumen and particulates of rubber powder that the volume of powdered rubber particles rises two to three times the initial value. If the temperature or mixing time is high enough, the particles of the rubber are degraded and dispersed in the bitumen, and the polymeric chains are broken, which reduces the viscosity of the mixture. The swelling of powdered rubber particles and the particle breakdown of powdered rubber are two factors affecting the properties of rubber-bitumen mixtures [20].

Adding rubber powder to bitumen can increase one to three performance grades (PGs) above the operating temperature and reduce one to two performance grades to lower temperatures which is the lower temperature for the operating temperature of bitumen. Therefore, the operating temperature range of bitumen rises from both sides [21]. Other researchers also observed the same trend at high operating temperatures but did not see a change in the performance grade with the increase for rubber [22–24]. The lower limit in all cases was controlled by the value of the creep rate (m-value) which is obtained from the Bending Beam Rheometer (BBR) test. The increase in the upper limit was due to an increase in the value of the parameter $G^*/\text{Sin}\delta$ from the dynamic shear rheometer test (DSR) [22, 24]. Overall, according to the results of various studies, it can be concluded that the rubber powder improves the performance grade but in the low performance, the amount of improvement is highly dependent on the bitumen, and the results are different depending on the bitumen used.

DSR testing has shown that G^* is highly dependent on temperature, type of bitumen, and the percentage of rubber powdered. The effect of the rubber powder is more than other factors, while the particle size of the rubber does not affect it. In δ changes (phase angle), the aging index plays an important role than other factors. Factors such as temperature, loading frequency in the test, type of bitumen, and the percentage of plastic powder are also effective [25].

Researchers have found that adding rubber powder reduces hardness at low temperatures. Gopal showed that this event happens for the different sizes and percentages of the rubber powder, and for each compound, the size and the optimal percentage should be determined [22, 26]. The experiments, which were conducted by Bahia et al., showed that the effect of adding rubber powder is less effective in reducing the hardness at low temperatures in soft bitumen [23]. Due to the low rubber hardness at low temperatures (0–20°C), compared to bitumen hardness, its composition with bitumen reduces the hardness of the rubber bitumen [21].

1.6.5. Bitumen modification using polyphosphoric acid (PPA)

One of the modifiers of bitumen is the polyphosphoric acid, which is added to it independently or as a substitute for other modifiers in bitumen like SBS. Polyphosphoric acid acts like deflocculant of the bitumen phases, the charge of polar groups, using neutralization of the load of polar groups. This can be done by neutralizing the bases with acid or esterification [27].

One of the important issues that should be considered in the use of acids as the modifier of bitumen is reversibility of bitumen modification. The presence of lime, limestone, or anti-stripping agents can neutralize the acid added to bitumen. On the other hand, most of the acids, including PPA, are soluble in water and may be washed out by rain over time [28].

1.6.6. Bitumen modification using basalt fiber

Basalt fiber is a kind of fiber that is made of basalt stones, melting at a temperature of about 1500°C and converting into continuous fibers. Researchers have paid more attention to this fiber because of the following reasons:

- Its good performance in strength
- Its suitability for a wide range of temperature variations
- Its durability

In recent decades, basalt fibers have been used in the asphalt concrete as a highly efficient additive. Compared to two other common additions, for the arming of asphalt, namely, polyester fibers and lignin fibers, basalt fibers have a higher tensile strength and elastic modulus and a lower elongation rate [29]. Its resistance to high temperature and good chemical stability of the basalt fiber makes it an excellent additive for asphalt concrete [30].

Different researchers have carried out various experiments to evaluate the applicability of basalt fiber as a reinforcing material for structural concrete, and they have compared the efficiency of basalt fiber and glass fibers. Using the accelerated weathering test, they found that basalt fiber provides better resistance in comparison to glass fibers [31]. Basalt fibers (especially those used with Scoria) will not be dangerous to the environment, and basalt is not usable as a building material. This material is not new but can be used initially in construction with regard to mechanical and chemical properties. The base cost of basalt fibers depends on the quality and chemical compounds, and this fiber has various types and different chemical properties [33]. However basalt fiber has properties like high Marshall stability, stability against water, and stability against rutting; fewer studies have been conducted to analyze the application of basalt fibers [34–36]. Bitumen modification using basalt fiber has the potential to perform better at low and high temperatures and to increase fatigue life and reduce permanent changes [36, 37]. The use of fibers has a great influence on viscosity and mixed properties [38]. Zhao et al. added fiber basalt (with a diameter of 16 mm) to asphalt mix and using the Marshall Test and hardness with different percentages of fibers; they showed that adding 3% weight percent of basalt fibers improves it at lower temperatures [39]. The addition of basalt fiber to the asphalt mixture increases its dynamic modulus [40]. In order to increase the resistivity of the asphalt, Xiao et al. conducted different experiments, and they concluded that the basalt fibers with different lengths and values of resistance improve the crack resistance in asphalt [41].

Synthetic basalt increases the shear modulus, and the viscosity of the bitumen, as a result, increases its stiffness and decreases the difference in the phase angle. These factors have been improved in the bitumen foam synthesized with the basalt, more than bitumen modification using synthetic basalt.

In terms of molecular weight, the lower molecular weight of isocyanate used in the synthesis of basalt is the more effective synthetic basalt that is on increasing the shear modulus and reducing the phase difference angle.

Synthetic basalt is well adapted due to its chemical reaction with bitumen polar groups and the formation of new bonds in bitumen and stability in bitumen storage, which is achieved without any problem. The temperature of mixing the synthetic basalt and bitumen is 90°C, which is more favorable environmentally.

2. Conclusion

Bitumen is one of the main components of the asphalt mixture, which plays a major role in creating adhesion between the aggregates in relation to environmental factors such as temperature and traffic loading in the asphalt mixture.

Because the vast majority of asphalt failures are due to the weakness of the rheological and chemical properties and the thermal sensitivities of the bitumen in asphalt, over time, with the development in the materials science of road building. Moreover, the use of polymer modifiers could potentially improve the bitumen in the asphalt, which has led to improve the durability of asphalt against breakdowns due to rutting, permanent deformations in the high temperature, and the increasing fatigue life.

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References

[1] Bahia HU, Zhai H, Zeng M, Hu Y, Turner P. Development of binder specification parameters based on characterization of damage behavior. Journal of the Association of Asphalt Paving Technologists. 2001;**70**:442-470

[2] Bahramnejad Dariush, Riazi Mohammad Reza, Bahram Secretary, Nabibi Ali Ehsan. The possibility of mixing Iran's base beams with SBS family polymers and studying their physical-mechanical and rheological properties for road building applications [master's thesis]; 1372

[3] Yildirim Y. Polymer modified asphalt binders. Construction and Building Materials. 2007;**21**(1):66-72

[4] Brule B. Polymer-Modified Asphalt Cements Used in the Road Construction Industry: Basic Principles. Transportation Research Record 1535. Washington D.C.: TRB, National Research Council; 1997

[5] The Asphalt Handbook. 2nd ed. The Asphalt Institute; 1966. https://www.abebooks.com/servlet/BookDetailsPL?bi=147629682&searchurl=tn%3Dthe%2Basphalt%2Bhandbook%26sortby%3D17%26an%3Dthe%2Basphalt%2Binstitute&cm_sp=snippet-_-srp1-_-title9

[6] Navarro FJ, Partal P, Martínez-Boza F, Gallegos C. Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens. Fuel. 2004;**83**(14-15):2041-2049

[7] Aklonis JJ. Introduction to Polymer Viscoelasticity. Wiley Interscience; 2005. https://www.wiley.com/en-us/Introduction+to+Polymer+Viscoelasticity%2C+3rd+Edition-p-9780471740452

[8] Giovanni P, Jiri S, Zora V, Dario B, Ludovit Z. Rheology of asphalts modified with glycidylmethacrylate functionalized polymers. Journal of Colloid and Interface Science. 2004;**280**(2):366-373

[9] Navarro FJ, Partal P, García-Morales M, Martínez-Boza FJ, Gallegos C. Bitumen modification with a low-molecular-weight reactive isocyanate-terminated polymer. Fuel. 2007;**86**(15):2291-2299

[10] Becker Y, Müller AJ, Rodríguez Y. Use of rheological compatibility criteria to study SBS modified asphalts. Journal of Applied Polymer Science. 2003;**90**(7):1772-1782

[11] Iqbal MH, Hussein IA, Al-Abdul Wahhab HI, Amin HB. Rheological Investigation of the influence of acrylate polymers on the modification of asphalt. Journal of Applied Polymer Science. 2006;**102**(4):3446-3456

[12] Bahia HU, Hanson DH, Zeng M, Zhai H, Katri MA, Anderson RM. Characterization of Modified Asphalt Binders in Superpave Mix Design. NCHRP Report 459. Washington, D.C.: National Academy Press; 2001

[13] Whiteoak D, Read JM. The Shell Bitumen Handbook. London: Thomas Telford Services Ltd; 2003

[14] Mohammad S. Asphalt. Dehkhoda Publications; 1377

[15] Sengoz B, Topal A, Isikyakar G. Morphology and image analysis of polymer modified bitumens. Construction and Building Materials. 2009;**23**(5):1986-1992

[16] Aflaki S, Tabatabaee N. Proposals for modification of Iranian bitumen to meet the climatic requirements of Iran. Construction and Building Materials. 2009;**23**(6):2141-2150

[17] Ho S, Zanzotto L. The low temperature properties of conventional and modified asphalt binders evaluated by the failure energy and secant modulus from direct tension tests. Materials and Structures. 2005;**38**(1):137-143

[18] Mohammad LN, Negulescu II, Wu Z, Daranga C, Daly WH, Abadie C. Investigation of the use of recycled polymer modified asphalt binder in asphalt concrete pavements. Journal of the Association of Asphalt Paving Technologists. 2003;**72**:551-594

[19] Michael H. Design and construction of asphalt paving materials with crumb rubber modifier. Transportation Research Record. 1992;**1339**:1-8

[20] Abdolrahman MA, Carpenter SH. Mechanism of interaction of asphalt cement with crumb rubber modifier. Transportation Research Record. 1999;**1661**:106-113

[21] Troy K, Sebaaly PE, Epps JA. Evaluation systems for crumb rubber modified binders and mixtures. Transportation Research Record. 1996;**1530**:3-10

[22] Tabatabaee N, Tabatabaee HA, Sabouri MR, Teymourpour P. Evaluation of performance grading parameters for crumb rubber modified asphalt binders and mixtures. In: Proceedings of the 7th International RILEM Symposium on Advanced Testing and Characterization of Bituminous Materials, Rhodes, Greece. Vol. 1. 2009. pp. 597-606

[23] Bahia HU, Davies R, Martinez V. Recycling of Scrap Tires and Plastic Waste in Modification of Asphalt Binders. Transportation Congress, American Society of Civil Engineers; 1995. https://books.google.com/books?id=4yg3TOWVXRAC&pg=PA606&dq=B

ahia+HU,+Davies+R,+Martinez+V.+Recycling+of+Scrap+Tires+and+Plastic+Waste+in+Modification+of+Asphalt+Binders.&hl=fa&sa=X&ved=0ahUKEwi70YySupbfAhVEgM4BHcZlBMQQ6AEIJTAA#v=onepage&q=Bahia%20HU%2C%20Davies%20R%2C%20Martinez%20V.%20Recycling%20of%20Scrap%20Tires%20and%20Plastic%20Waste%20in%20Modification%20of%20Asphalt%20Binders.&f=false

[24] Madapati RR, Lee KW, Franco CA. Evaluation of Crumb Rubber in Asphalt. Transportation Congress, American Society of Civil Engineers; 1994. https://cedb.asce.org/CEDBsearch/record.jsp?dockey=0096981

[25] Kim S, Loh S, Zhai H, Bahia HU. Advanced characterization of crumb rubber modified asphalts using protocols developed for complex binders. In: Transportation Research Board 80th Annual Meeting; Washington D.C. Vol. 1767. 2001. pp. 15-24

[26] Gopal VT, Sebaaly PE, Epps J. Effect of crumb rubber particle size and content on the low temperature rheological properties of binders. In: Transportation Research Board 81st Annual Meeting; Washington D.C. 2002. pp. 13-17

[27] Edwards Y, Tasdemir Y, Isacsson U. Influence of commercial waxes and polyphosphoric acid on bitumen and asphalt concrete performance at low and medium temperatures. Materials and Structures. 2006;**39**(7):725-737

[28] Ho S, Zanzotto L, MacLeod D. Impact of different types of modification on low temperature tensile strength and critical of asphalt binders. In: Transportation Research Board 81st Annual Meeting; Washington D.C. Vol. 1810. 2002. pp. 1-8

[29] Jahromi SG, Khodaii A. Effects of nanoclay on rheological properties of bitumen binder. Construction and Building Materials. 2009;**23**:2894-2904

[30] Sim J, Park C, Moon DY. Characteristics of basalt fiber as a strengthening material for concrete structures. Composites Part B Engineering. 2005;**36**(6-7):504-512

[31] Ludovico MD, Prota A, Manfredi G. Structural upgrade using basalt fibers for concrete confinement. Journal of Composites for Construction. 2010;**14**(5):541-552

[32] Celauro C, Praticò FG. Asphalt mixtures modified with basalt fibres for surface courses. Construction and Building Materials. 2018;**170**:245-253

[33] Fiore V, Scalici T, Di Bella G, Valenza A. A review on basalt fibre and its composites. Composites. Part B, Engineering. 2015;**74**(Supplement C):74-94

[34] Morova N. Investigation of usability of basalt fibers in hot mix asphalt concrete. Construction and Building Materials. 2013;**47**(Supplement C):175-180

[35] Cai YC, Zheng YX. Experiment study of water stability of fiber-reinforced asphalt mixture. Advanced Materials Research. 2011:710-716. https://www.scientific.net/AMR.243-249.710

[36] Zheng Y, Cai Y, Zhang G, Fang H. Fatigue property of basalt fiber-modified asphalt mixture under complicated environment. Journal of Wuhan University of Technology-Materials Science Edition. 2014;**29**(5):996-1004

[37] Zheng YX, Cai YC, Zhang YM. Laboratory study of pavement performance of basalt fiber-modified asphalt mixture. Advanced Materials Research. 2011:175-179. https://link.springer.com/article/10.1007/s11595-014-1033-1

[38] Huang H, White TD. Dynamic properties of fiber-modified overlay mixture. Transportation Research Record. 2001;**1545**:98-104

[39] Zhao L, Chen J, Wang S. Using mineral fibers to improve asphalt and asphalt mixture behavior. In: Seventh International Conference on Traffic and Transportation Studies (ICTTS); Kunming, China. 2010. DOI: 10.1061/41123(383)129

[40] Wu S, Ye Q, Li N, Yue H. Effects of fibers on the dynamic properties of asphalt mixtures. Journal of Wuhan University of Technology-Materials Science Edition. 2007;**22**:733-736

[41] Qin X, Shen A, Guo Y, Li Z, Lv Z. Characterization of asphalt mastics reinforced with basalt fibers. Construction and Building Materials. 2018;**159**:508-516