

Review

A Comprehensive Literature Review on Polymer-Modified Asphalt Binder

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Abstract: Due to periodic variations in temperature and heavy traffic loading, hot-mix asphalt (HMA) pavements undergo considerable distress during their service life. The rheological properties of asphalt binder, when subjected to complex physical and chemical processes, make it stiff and sometimes brittle, which ultimately plays a huge part in pavement deterioration. This phenomenon is commonly known as asphalt aging. Incorporating polymer modifiers with virgin asphalt can work as an effective means to change the binder properties and alleviate the issues related to asphalt aging. Different types of polymers, including elastomers, plastomers, and reactive polymers, can be mixed in different combinations with the virgin asphalt to create polymer-modified binders (PMBs). In general, polymers are typically added to the virgin asphalt binder in PMB manufacturing at weight percentages ranging from 3% to 7%. Previous research suggests that many polymer-modified binders (PMBs) show great resiliency and perform extremely well during field and laboratory testing, although the complex nature of asphalt itself makes it significantly difficult to understand the relationship and compatibility of the asphalt–polymer system. This paper aims to develop a comprehensive literature review on the chemical aspects, microscopic structure, and compatibility of polymers with virgin asphalt. It was found that swelling, storage stability, blend morphology, and the polymer mixing technique play a great role in the compatibility of asphalt–polymer systems. Thermoplastic elastomers (e.g., styrene–butadiene–styrene) and plastomers (e.g., ethylene–vinyl acetate) are the most used polymer modifiers for asphalt binders. The compatibility of the polymer–asphalt system can be improved by sulfur vulcanization, antioxidants, hydrophobic clay minerals, functionalization, and reactive polymers, among other techniques.

Keywords: hot-mix asphalt; polymer-modified asphalt binder; asphalt–polymer system; compatibility; storage stability; blend morphology; thermoplastic elastomers; plastomers



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1. Introduction

Hot-mix asphalt (HMA) pavements are prone to three main types of distress (i.e., permanent deformation, fatigue cracking, and low-temperature cracking) during their service life, which are responsible for their poor performance. These types of distresses occur in flexible pavements because of traffic load and temperature differences that are associated with the rheological properties of asphalt. The alteration of the virgin asphalt binder's properties through the incorporation of polymer modifiers is an effective means to mitigate distress-related issues. The incorporated polymer should transfer its intended

properties to the polymer–asphalt system and alter the rheological and failure properties of the virgin asphalt, thereby mitigating the problems associated with rutting, fatigue, and thermal cracking. Rigidity, brittleness, elasticity, durability, resistance to accumulated damage, and storage stability are the fundamental properties of asphalt. The magnitude of these properties can be improved through the modification of asphalt binders [1,2].

Polymers are very large molecules with many atoms (copolymers) that include successive linking of one or more types of small molecules (monomers) into a chain or network structure (straight, linked, or crosslinked) [3]. The configuration and conformation of the monomers are responsible for the viscoelastic properties of the polymers. While the monomer configuration is changed when the chemical bonds are broken, the conformation is altered due to the rotation of molecules about the single bonds. The crosslinking phenomenon, which is the formation of weak chemical bonds between main chains through side chains, also affects the viscoelastic properties of the polymer [3]. A high degree of crosslinking induces “memory” within the polymer structure, which restricts the sliding of the main chains when elongated, which retain their initial shape after the stress is removed. Various polymer types can be added to virgin asphalt to modify its properties, including thermoplastic elastomers, plastomers, and reactive polymers, and polymer-modified binders (PMBs) are defined as mixtures of asphalt with one or more polymers. Polymers are usually added in percentages ranging from 3–7% by weight of the virgin asphalt during PMB production [4].

Researchers have made significant efforts to enhance the rheological and mechanical properties of asphalt binder through polymer modification. Numerous polymer-modified binders have been developed that provided promising performance both in the field and in the laboratory. However, the inherent complexity of asphalt makes it challenging for researchers to better understand the chemical structure and compatibility of polymer–asphalt systems. Therefore, an in-depth review of the existing literature was conducted in this study on the chemical aspects, microscopic structure, and compatibility of polymers with virgin binder. This in-depth literature review might benefit researchers and transportation agencies in better understanding the complex nature of PMBs, in addition to designing new PMBs that can better combat common distresses of asphalt pavements.

2. Objectives

The goal of this study was to provide an in-depth review of the existing literature on different aspects of asphalt binder modification through the incorporation of polymers. To achieve this goal, the objectives of this study included the following:

- Identifying the chemical composition and microstructure of virgin asphalt binder.
- Evaluating the factors that affect compatibility between virgin asphalt binder and polymer.
- Assessment of the common techniques for evaluating the compatibility of polymer–asphalt systems.
- Evaluating the current practice of enhancing compatibility.
- Identifying commonly used polymers for binder modification.

3. Overview of Asphalt

Asphalt is one of the oldest known engineering materials, and its first use as a gluing material dates back to 1800 BC [5]. For several decades, asphalt has been used as either a sealant or waterproofing agent in the roofing industry, or as a binding material for mineral aggregates in pavement construction [6]. The early users directly used naturally occurring asphalt that was found on the Earth’s surface, and the use of asphalt in pavements was rare [7]. In the USA, the extensive use of asphalt in the construction of flexible pavements began in the early 19th century due to the emergence of vacuum distillation technology, which allowed for the industrial production of artificial asphalt from crude petroleum [8]. At present, 85% of the almost 100 Mt of asphalt that is produced worldwide each year is applied in the paving industry. In pavement construction, asphalt works as a binding

material for aggregates to produce asphalt mixtures, also known as asphalt concrete or hot-mix asphalt (HMA). The performance of asphalt mixtures during the construction phase and the service life of the flexible pavements depend greatly on the small amount of asphalt (5% by the weight) used in HMAs. From a chemical perspective, asphalt derived from crude petroleum or found in natural asphalt is nearly solid at room temperature. However, it becomes soluble in toluene [5]. Asphalt is typically manufactured commercially in a refinery through the destructive distillation of crude petroleum oil [9]. In the first phase, the light components are separated by an atmospheric distillation, which is followed by the refinement of the residue under vacuum, pressure, and a temperature higher than the prior phase [10]. In addition to the typical distillation process, other less commercial methods of asphalt manufacturing include air-blowing [8,10], solvent deasphalting [11], and obtaining asphalt residue from a visbreaking unit [10].

4. Chemical Composition of Asphalt

The chemical structure of asphalt consists of hydrocarbons (i.e., aliphatic, aromatic, and naphthenic) and their byproducts [12]. The most dominant elements of asphalt are carbon (~90%) and hydrogen atoms (~10%) [13]. Heteroatoms (i.e., sulfur, oxygen, and nitrogen) and transition metal atoms (i.e., vanadium and nickel, and manganese) are also found in small quantities [5,6,10]. Sulfur (mostly polar) can be found in asphalt in the form of sulfides, thiols, and sulfoxides. Oxygen exists as ketones, phenols, and carboxylic acids, while nitrogen is found as pyrrolic, pyridinic, and amphoteric structures (i.e., 2-quinolones) [14,15]. Most metals exist in asphalt as metalloporphyrin complexes [15]. Asphalt is composed of 300–2000 chemical compounds with extremely variable molecular weight (ranging from 240–2400 g/mole) and polarity [12]. This extreme variability might be attributed to the origin and composition of crude oil. It is difficult to generalize the chemical composition of asphalt based on geographic location, as manufacturers often blend asphalts from various crude oil sources. The presence of various chemical compounds in asphalt at the microscopic level reveals a very complex picture; as a result, the entire chemical composition of asphalt has remained mostly unclear until today. The most popular method of studying asphalt composition was found to be the so-called “SARA method”. As per the “SARA method”, molecules in asphalt are divided into a limited number of fractions, including saturates (S), aromatics (A), resins (R), and asphaltenes (A), based on thin-layer chromatography with flame ionization detection (TLC-FID) [16]. In this method, asphalt components are grouped into two major fractions, namely, “solid” asphaltenes and “liquid” maltenes (see Figure 1). Maltenes are further subdivided into saturates, aromatics, and resins.

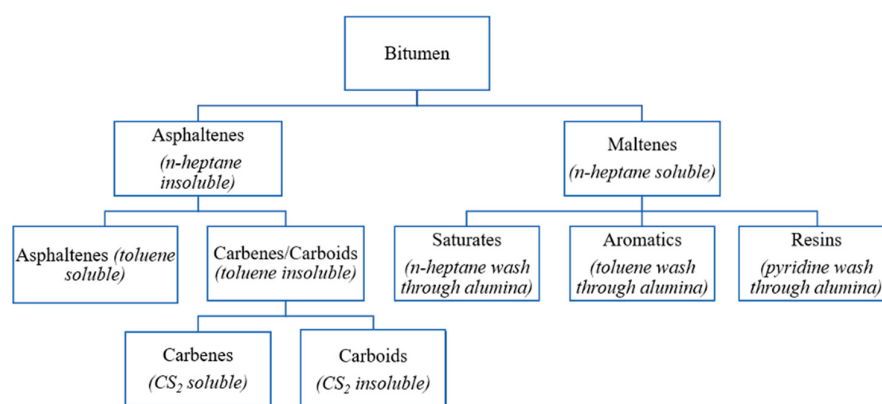


Figure 1. Grouping of asphalt molecules as per SARA method [17] (reprinted with permission from Ref. [17], open access).

The saturate (5–15 wt.% of paving asphalt) is a complex combination of polyalkyl compounds. The polyalkyl compounds are light-colored liquids at ambient temperature [18].

They include minor amounts of polar atoms or atomic rings, along with crystalline n-alkanes with various branching patterns and some lengthy aliphatic chains [5]. Although there is straight-run asphalt, saturate fractions from air-blown asphalt contain more long-chain paraffins than straight-run asphalt [19]. Since saturates are the lightest part of the maltenes, an increased saturate content causes a decrease in the complex shear modulus and an increase in the phase angle of asphalt [19]. Aromatics (30–45 wt.% of the paving asphalt) are light (yellow) to dark (red) liquids at ambient temperature and are the largest SARA fraction, functioning as a plasticizing agent for asphalt [19]. Resins (20 wt.% of the total asphalt) are dark brown solid components of asphalt that are soluble in n-heptane [20]. The chemical composition of resins resembles that of asphaltenes, but they have a lower molecular weight, higher polarity, and less condensed aromatic rings than asphaltenes [5]. Resins' chemical structure typically includes 2–4 fused aromatic rings that stabilize asphaltenes by working as a dispersing agent for the mutually immiscible asphaltenes and oils, along with improving the viscosity of the asphalt due to their high polarity [5,12]. Asphaltenes have fused aromatic rings and some pending aliphatic chains. These contribute to 5–25 wt.% of paving asphalt [21,22]. The existence of a fused aromatic structure is the unique property that distinguishes asphaltenes from other asphalt molecules. The presence of aromatic rings causes asphaltene molecules to become planar [1,23]. These planar molecules form covalent bonds (or π - π bonds) and produce graphite-like stacks [24,25]. When asphaltenes are put in a solvent, the aggregation of the asphaltene molecules occurs, and negatively charged “micelles” are formed [22]. These molecules increase the adhesiveness of the asphalt with the mineral aggregate. The surface activity of asphalt is also influenced by asphaltenes [22]. The molecular weight, aromaticity, polarity, and heteroatomic content increase in the order of saturates < aromatics < resins < asphaltenes [5]. SARA fractionalization has proven to be very useful, as asphalt researchers typically define the asphalt's chemistry by the relative amounts of these fractions. Various properties of SARA fractions, along with their elemental analysis, are summarized in Table 1.

Table 1. Properties and chemical compositions of SARA fractions (summarized from [5,11,22]).

Fractions	Saturates	Aromatics	Resins	Asphaltenes
wt.% of asphalt	5–20	40–65	± 20	5–25
Polarity	Non-polar	Non-polar	Highly polar	Highly polar
Color	-	Yellow to red	Dark brown	Black
Behavior	Viscous oil	Viscous liquid	Solid/semi-solid	Solid
Avg. MW (g/mole)	600	800	1100	800–3500
Solvent	<i>n</i> -Heptane	Toluene and toluene/methanol 50/50	Trichloroethylene	<i>n</i> -Heptane insoluble
Solubility parameter (MPa ^{0.5})	15–17	17–18.5	18.5–20	17.6–21.7
Density at 20 °C (g/cm ³)	0.9	1	1.07	1.15
Glass transition temperature (°C)	–70	–20	-	-
H/C	1.9	1.5	1.4	1.1
C (%)	78–84	80–86	67–88	78–88
H (%)	12–14	9–13	9–12	7–9
O (%)	<0.1	0.2	0.3–2	0.3–5
N (%)	<0.1	0.4	0.2–1	0.6–4
S (%)	<0.1	0–4	0.4–5	0.3–11

5. Internal Chemical Structure of Asphalt

Researchers have considered several methods to understand the internal chemical structure of asphalt throughout the past century. From a molecular point of view, the

colloidal model is the most frequently used to define the chemical composition of asphalt. This was first introduced at the beginning of the 20th century by Nellensteyn [26] and then further refined by Pfeiffer [27]. As per the colloidal model, asphalt is a colloid containing micelles and asphaltene particles. The internal structure and physical properties of asphalt are influenced by the asphaltene dispersed in the oily phase [28] (see Figure 2). A layer of hydrocarbon is centered around asphaltene. Through polar interactions, resins help the asphaltene to become stable. However, this only occurs in the oily phase [29]. In the maltene phase, asphaltenes work as a colloidal suspension [26]. The colloidal model resulted in the concepts of so-called “sol type” and “gel type” asphalts [27]. The “sol-type” of asphalt demonstrates high solvating ability, good portability of asphaltene micelles, high-temperature susceptibility, improved ductility, lower age-hardening potential, and low thixotropy [1]. The asphaltene content remains within 5–10% in this. As the asphaltene micelles are fully dispersed and remain non-interacting, their behavior resembles Newtonian behavior (Figure 3a) [27]. The “gel type” asphalts contain higher asphaltene contents (i.e., 20–35%) and exhibit a non-Newtonian behavior [1]. This non-Newtonian behavior could be caused by the gel structure. This is made of fully interconnecting asphaltene micelles (Figure 3b) [27]. “Gel type” asphalts have low-temperature sensitivity, low ductility, quick age-hardening, and significant thixotropy [1,5]. Even though an asphalt mix with “gel type” asphalt is better at avoiding rutting than one with “sol type” asphalt, it can be weaker and crack more easily [30–32].

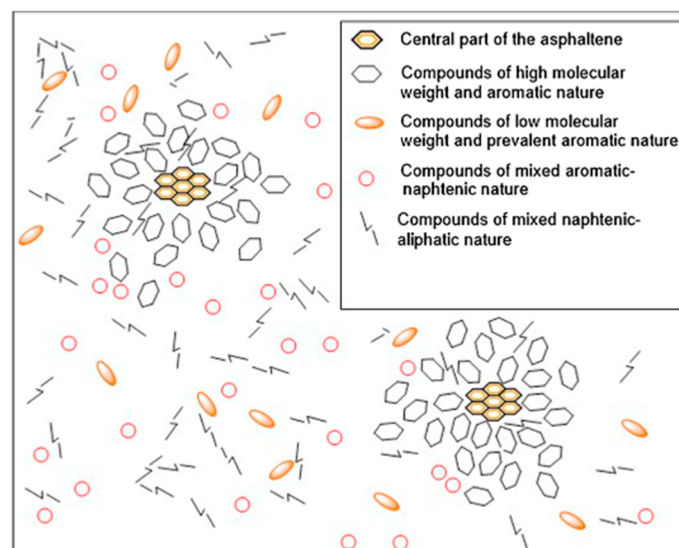


Figure 2. Visual representation of the colloidal structure of asphalt [33] (reprinted with permission from Ref. [33]).

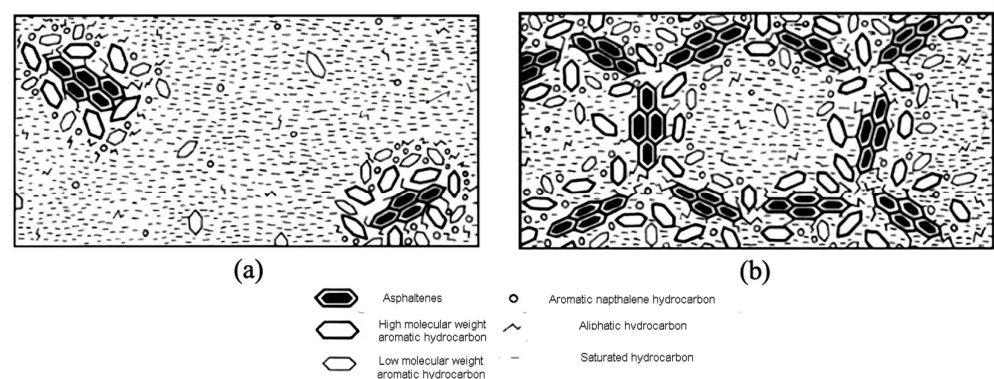


Figure 3. (a) “Sol-type” asphalt as per the colloidal model. (b) “Gel-type” asphalt as per the colloidal model [34] (reprinted with permission from Ref. [34], open access).

6. Compatibility of Polymer with Virgin Binder

The efficacy of binder modification is contingent upon bitumen and polymer “compatibility” [34]. When polymers are “incompatible” with the parent binder, the resulting heterogeneous mixture lacks cohesion and ductility and cannot contribute to the enhancement of the blend’s viscoelastic properties. All commercial PMBs are heterogeneous at the micron scale [35–38]). Some polymers are only partially compatible, necessitating the use of mechanical, thermal, and chemical processes to achieve a successful blend. In an ideal scenario, when a “compatible” polymer is added to bitumen, the resulting mixture should exhibit the intended properties of the polymer and not undergo phase separation during storage, transportation, and service. The morphology of the composite is another important consideration when discussing the “compatibility” of the polymer [4]. A stable and compatible asphalt–polymer system will exhibit a distinct overall arrangement of the composite components. Therefore, asphalt–polymer compatibility can be explained in terms of the degree of swelling and solubility of the incorporated polymer, along with the storage stability, composite morphology, and blending technique.

6.1. Degree of Swelling and Solubility

In an ideal polymer-modified binder, the polymer should retain its chemical architecture after combining with asphalt, whose molecules only determine the macroscopic network enlargement. The intended mechanical properties of the polymer can be effectively conveyed to the polymer-modified binder [5] if the expanded polymer network becomes continuous. Typically, the amount and size of asphaltenes, the amount and size of polymer molecules, and the aromaticity of the maltene phase influence the compatibility of an asphalt–polymer system [39,40]. Enhancing the binder properties is dependent on the interactions between the four SARA fractions and the polymer. Due to differences in density, polarity, and molecular weight, polymers and bitumen do not combine. Different SARA fractions interact variably with the polymer molecules, whose volume is increased by the aromatic components of maltenes [41]. This internal distillation process induces biphasic behavior in mixtures, and the resultant system morphology consists of a “polymer-rich phase” (PRP) and an “asphaltene-rich phase” (ARP) (see Figure 4). When the polymer is distended by a small number of asphalt molecules, the ARP becomes a continuous and dominant phase in which the PRP is dispersed, and the rheological properties of the resulting composite are virtually identical to those of the parent asphalt [5]. When the enlargement is sufficient, however, the so-called “phase inversion” occurs, where the PRP becomes continuous and the ARP is disseminated in the PRP [1]. In this instance, the internal structure of the polymer is preserved, and the likelihood of transferring the polymer’s intended properties to the composite increases. Nevertheless, phase inversion never guarantees compatibility, as any polymer incorporated in sufficient quantities has the potential to induce phase inversion [5]. Lastly, when complete swelling occurs, the ARP may cease to exist, which is permissible only if the polymer network remains intact during swelling. Complete solubility of the polymer in asphalt is undesirable, because asphalt consumes the polymer structure during dissolution, preventing the transfer of the macroscopic properties of the polymer to the mélange [1,13]. To preserve the original properties of a polymer that has been incorporated, a suitable degree of swelling and limited polymer solubility are essential.

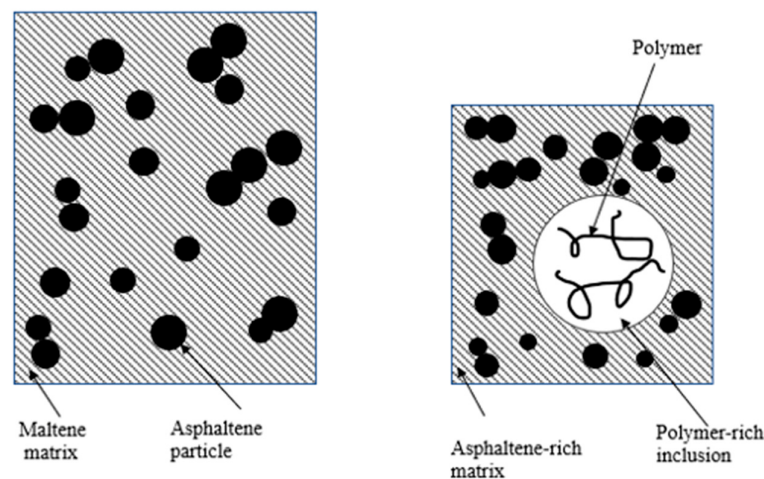


Figure 4. Effect of polymer modification on the colloidal structure of asphalt: original asphalt and the corresponding PMB with increased asphaltene content in the matrix [5] (reprinted with permission from Ref. [5]).

6.2. Storage Stability

The compatibility between the polymer and asphalt also depends on the storage stability of the polymer–asphalt system. To maintain the storage stability of polymer-modified binders, the polymers must be compatible with the asphalt binder. Incompatible mixtures can cause precipitation and phase separation, as the aggregates can alter the polymer’s uniform distribution throughout the binder matrix and, in turn, have an adverse impact on the PMB’s performance, e.g., the adhesiveness, elasticity, and crack resistance may degrade [1]. The swelling of polymers affects their storage stability. Due to the density difference between the phases, excessive swelling results in the formation of a thermodynamically unstable system in which the ARP and PRP tend to separate macroscopically. Even though, from a kinetic standpoint, a polymer–asphalt system is stable at low temperatures, the segregation of the ARP and PRP is more likely to occur when composites are stored for an extended period at high temperatures above the critical point without agitation [42]. Separation is brought about by coalescence and flocculation, resulting in the pure creaming of PRP [43]. Therefore, mechanical polymer dispersion is not always an efficient procedure for producing polymer-modified asphalt [44,45]. In addition, the combining time (or temperature) should be minimized to ensure economically efficient blending and to prevent the aging of the polymer and asphalt caused by a mixing process involving high temperatures and high shear. When the polymer particle size is small, Brownian motion of the polymer molecules prevents the gravitational separation of the polymer, resulting in a stable state of polymer within the bitumen matrix [42]. In contrast, polymer particles larger than 10 μm are effective at increasing asphalt binder viscosity [39]. While polymers with relatively high molecular weights have the potential to improve the properties of asphalt binders, they can substantially reduce the compatibility between the PRP and ARP, resulting in phase separation at high temperatures [41].

6.3. Blend Morphology

The morphology of the polymer–binder composite can also influence the compatibility. Due to the presence of aromatic compounds, asphalt viewed through a fluorescence microscope appears as a homogeneous material with a yellowish hue; the color gradation depends on the aromatic content [5]. In an asphalt–polymer system, the maltenes expand the polymer. This expansion causes the fluorescent molecules in the PRP to condense; therefore, the PRP in a biphasic system appears yellow [5]. The ARP appears yellow under a fluorescence microscope due to the migration of aromatic molecules to the polymer. Therefore, the overall morphology has a yellowish hue, with a distinct separation between

the brilliant yellow PRP and the darker ARP. The morphological properties are highly dependent on the sample temperature, chilling rate, and isothermal annealing durations [46]. Figure 5 depicts the typical morphology of asphalt–polymer mixtures obtained using a fluorescence microscope. All of the mixtures contained the same amount of polymer and were distinguished by their degree of enlargement. Figure 5a illustrates the worst-case scenario, in which the polymer is thoroughly dissolved in bitumen. Figure 5b depicts a desirable and structured “orange skin” morphology in which the PRP and ARP are indistinguishable. This form of morphology confirms the system’s high compatibility and corresponds to a positive effect of the polymer on the rheological properties of the composite, as well as its high-temperature storage stability. In Figure 5c, where phase inversion is evident and the ARP is dispersed in the PRP, a modest decrease in compatibility can be observed. This circumstance corresponds to the greater influence of the polymer on the composite’s properties, and the restricted ARP surface area has the potential to improve storage stability. Compatibility decreased further as the ARP’s dimensions increased (Figure 5d), resulting in a morphology in which the ARP and PRP were both continuous (Figure 5e). This co-continuous morphology corresponds to a separation that is inevitable during storage at high temperatures. A further decrease in interactions and enlargement results in a PRP-dispersed phase (Figure 5f), whose shape progressively changes to spherical, which corresponds to the minimum ARP–PRP interfacial area (Figure 5g). Blend morphology has the potential to be an acceptable method for visualizing and predicting asphalt–polymer system compatibility.

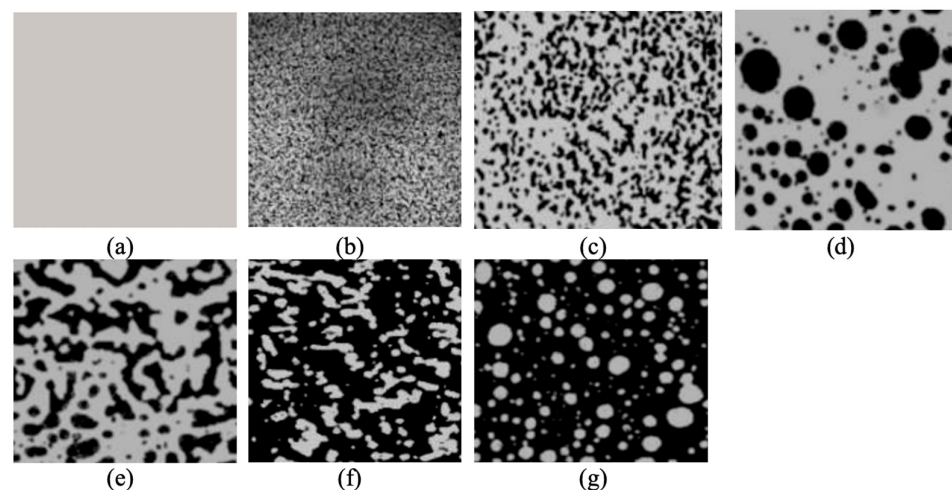


Figure 5. Typical blend morphologies obtained from fluorescence microscopy: (a) the limiting case and an undesirable situation where the polymer is completely dissolved in asphalt; (b) a desirable and structured “orange skin” morphology is observed where the PRP and ARP are indiscernible; (c) the presence of phase inversion is evident and the ARP is dispersed in the PRP; (d) compatibility further decreased with an increase in the ARP’s dimensions; (e) a morphology was obtained where the ARP and PRP were both continuous; (f) a further decline in the interactions and swelling leads to a PRP-dispersed phase, (g) the shape of which changes progressively to spherical, corresponding to the minimum ARP–PRP interfacial area [47] (reprinted with permission from Ref. [47]).

6.3.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a complex and mature electron microscopy technique used by scientists and engineers to investigate different materials’ surface microstructure and morphology at a higher magnification [48]. This technology is widely used for polymer-modified asphalt binders (PMBs) to examine their morphology and engineering properties [49]. The test can be conducted for PMBs using several steps: sample preparation, sample coating, placing in a vacuum chamber, electron beam scanning, and image formation. The sample should represent the principal materials and must be

clean. However, there is no foolproof method for preparing specimens; good practice calls for preserving them in places that are dry and clean, like sealed containers, vacuum packets, and desiccators [46]. After that, the sample is coated with a conductive material, for example, gold or carbon, to make a thin layer to prevent a charging effect and provide a conductive path for electrons [46]. The sample is placed in a vacuum chamber, and the SEM produces a beam of electrons that thoroughly scans the surface of the sample. As a result, the electrons interact with the sample and produce the emission of signals. The emitted signals are processed to make an image, which is analyzed to determine the morphology and microstructures of the PMBs [49–51]. SEM is an effective technology, and much research has been conducted to evaluate the morphology and microstructures of PMBs using SEM technology. For example, Muhammad Mubarak [52] (pp. 5–14) conducted SEM experiments to characterize and assess the structure of PMBs. Bhupendra Singh and Praveen Kumar [53] (pp. 633–641) used the test to simultaneously investigate the impact of polymer modification and aging on the asphalt binder. Manman Su et al. [54] (p. 103082) used the test to investigate the morphology of SBS-modified binders. Svetlana Shekhovtsova and Evgeniy Korolev [55] (p. 124591) used SEM to investigate the formation of a PMB structure when carbon nanoparticles were present. The surface properties and microstructure of PMBs can be learned through SEM [49]. This supports the creation and improvement of asphalt mixtures for various applications by assisting scientists and engineers in understanding the impact of polymers' addition on the performance and behavior of the binder.

6.3.2. Fluorescence Microscopy

Because the ARP and PRP have distinct UV-excitation responses [41], the blend morphology is typically derived from a fluorescence microscope (FM), which provides a direct measurement of the relative quantity and morphology of both the ARP and PRP. For the investigation of polymer-modified binders subjected to FM, the literature describes three distinct sample preparation techniques: the “drop”, “thin-film”, and “freeze-fracture” techniques. The “Drop” procedure is the simplest sample preparation technique [33]. In this method, a drop of a sample removed from a container is placed on a glass plate and allowed to cool to room temperature, and the morphology is analyzed via FM through either the bottom of the glass plate or a cover glass placed over the sample [33,41]. If the “drop method” is used to examine the effect of isothermal storage or cooling rate, it is referred to as the “thin-film” method, because a higher temperature is used in this method as compared to the “drop method”, where the sample is placed between two glass plates to form a very thin film (0.5 μm) [33]. According to the standard technique EN 13632 [51], also known as the “freeze-fracture” method, the mixture is heated and then stirred by hand to achieve uniformity [52]. The substance is then transferred to an aluminum receptacle encircled by a sand bath at the same temperature as that used during sample preparation. The sample is first chilled to the ambient temperature in the sand, and the thermal history of the material is determined, because this has a significant influence on the morphology of the composite [55,56]. Cooling is prolonged until the sample becomes brittle enough to be broken into fragments, and the resulting surface is examined using FM to determine the presence of continuity (or co-continuity) between the ARP and PRP. To date, FM is the most valuable technique for understanding the surface morphology of polymer-modified binders; it provides a rapid, efficient, and cost-effective picture of the composite [47,57–70].

6.3.3. Atomic Force Microscopy

Atomic force microscopy (AFM) is another popular technique to study asphalt morphology. AFM is a very-high-resolution type of scanning probe microscopy that can measure the morphology, phase, friction, and mechanical properties of asphalt [68]. In the case of morphology and phase, asphalt-polymer blends are evaluated in the tapping mode of operation using rectangular silicon cantilevers [70,71]. For most AFM measurements, samples of very small quantities are heated and placed on the center of a glass slide. The

sample on the coverslip is again heated up to 150 °C in 2 min so that it covers the entire glass surface in the form of a film. It is then cooled to room temperature in a closed chamber for 24 h, and images are taken with the microscope [72]. The advantage of the AFM technique is that it allows for the visualization of the precise details of the asphalt's morphology using simple techniques of sample preparation that conserve the original colloidal structure and morphology of the asphalt [73]. Moreover, the AFM technique does not rely on optical transparency as it does for optical microscopy, and the resolution is not limited by the wavelength of light [40].

6.3.4. Polarized Optical Microscopy

Polarized optical microscopy (POM) is an additional technique for visualizing the morphology of a polymer-modified binder using a micrograph image derived via visible light and the unique photon properties [72]. The asphalt binder in POM is heated at a rate of 10 °C/min to 160 °C, maintained at 160 °C for 10 min, and then chilled to room temperature. The POM images were acquired 24 h after sample preparation [73]. The use of confocal laser scanning microscopy (CLSM) [71] is an additional method for analyzing the morphology of mixtures. By compressing the polymer–asphalt mixture between two glass plates, samples of each type of polymer-modified asphalt were created [74], and images were captured for morphological analysis using a laser microscope in transmission mode and a helium–neon or –argon laser [75].

6.4. Mixing Technique

The method of combining polymers and bitumen also affects their compatibility. The combining technique affects the rheological properties of the blend, and optimizing the mixture temperature/time and agitation level is essential for obtaining a blend with the desired properties [44,46]. In the literature used by the researchers to produce the blend, the “wet method” and the “dry method” were identified as the two predominant blending techniques [47,48]. The “wet method” entails combining a latex polymer with asphalt at high temperatures and then mixing the resulting mixture with aggregates during the production of HMA [1]. This method is straightforward and facilitates a significant expansion of polymers by bitumen molecules. However, mixing using the “wet method” may entail vigorous mixing at high temperatures, which may oxidize the bitumen components and alter the rheological properties of the mixture. In contrast, polymer granules or fragments are combined with aggregates prior to the addition of virgin asphalt in the “dry method” of preparing HMA [1]. However, in this study, mixing techniques using the “dry method” are not discussed, as it does not involve producing a PMB; rather, it is often used to obtain modified asphalt mixtures.

It is challenging to combine polymers and asphalt during the manufacture of polymer-modified binders, because their viscosities differ significantly at high temperatures. Shearing breaks polymer particles into smaller particles during blending. High shear and low shear have been defined in the literature as the two primary shearing procedures [50]. As shown in Figure 6, the high-shear mixing technique reduces the size of polymer particles through mechanical and hydrodynamic shearing. During combining, the temperature is increased so that the polymer can be dissolved in the asphalt and a homogeneous polymer–asphalt system can be created. Low shear is preferable for blending powdered and liquid modifiers in a straightforward mixing vessel with a paddle stirrer. In this method, mingling is restricted to the expansion and dissolution of bitumen with the polymer at a constant temperature. The optimal conditions for blending the polymer and enhancing its compatibility with bitumen are the lowest mixing temperature and the shortest mixing time [5].

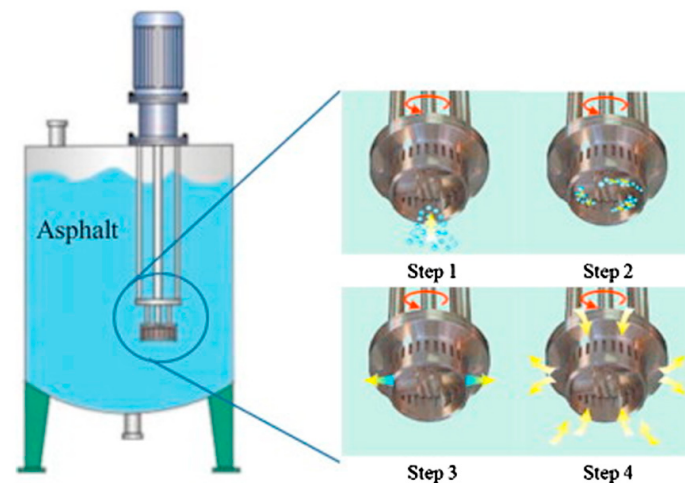


Figure 6. Schematic illustration of a high-shear mixer [76] (reprinted with permission from Ref. [76]).

7. Evaluation of the Storage Stability

7.1. Tube Test

The “tube test” that simulates the storage of binders at high temperatures according to ASTM D7173–11 [77] is the most common storage-stability testing procedure. In this process, the polymer-modified binder is dispensed to a height of 110 mm in a vertical aluminum “toothpaste tube” measuring 160 mm in height and 33 mm in diameter on average. The binder is retained in the tube for three days at 180.5 °C without stirring. During this storage time, the PRP migrates to the top of the tube, while the ARP settles to the bottom. The tube is removed from the oven after three days, chilled vertically to room temperature, and then cut horizontally into three equal segments. While the middle portion is discarded, the top and bottom softening points are determined using the ring-and-ball method, and their difference (S) is calculated. A mixture is considered stable if S is below 3 °C. It is important to note that the tube test does not accurately represent the actual storage conditions, as manufacturers store polymer-modified asphalt in a storage vessel with continuous stirring before blending with aggregates [78]. Another disadvantage of the tube test is that it was designed specifically for polymer-modified binders and may not be applicable to other types of modified binders [40]. When a minor amount of polymer is introduced to a binder, S can remain below the limiting value while still exhibiting considerable phase separation [40]. Moreover, S values marginally below the permissible limit have the potential to modify other mechanical and rheological properties of the modified binder [74]. Consequently, if the tube test is utilized, it should be accompanied by morphological evaluation and the determination of the viscoelastic properties of the top and bottom sections of the polymer–asphalt combination.

Utilizing the separation index (I_s) or “percentage of separation” based on the rheological properties of the top and bottom sections is an alternative method for determining the softening point. The I_s and “percentage of separation” are determined according to Equations (1) and (2), respectively:

$$I_s = \log \left(\frac{G_b^*}{G_t^*} \right) \quad (1)$$

where:

I_s = separation index [40];

G_b^* = complex modulus of the bottom section measured at 25 °C and a frequency of 10 rad/s;

G_t^* = complex modulus of the top section measured at 25 °C and a frequency of 10 rad/s.

$$\% \text{ separation} = \frac{\left(\frac{G^*}{\sin \delta}\right)_{\max} - \left(\frac{G^*}{\sin \delta}\right)_{\text{avg}}}{\left(\frac{G^*}{\sin \delta}\right)_{\text{avg}}} \quad (2)$$

$$\left(\frac{G^*}{\sin \delta}\right)_{\max} = \text{higher value of } (G^*/\sin \delta) \text{ between the top and bottom sections;}$$

$$\left(\frac{G^*}{\sin \delta}\right)_{\text{avg}} = \text{average } (G^*/\sin \delta) \text{ of the top and bottom sections.}$$

7.2. Segregation and Ease of Remixing Test

The “segregation test” and the “tube test” are conceptually comparable. In this procedure, samples are stored for 48 h at 180 °C in 375 mL metal cans before being chilled to room temperature [79]. After the cans have cooled, the degree of separation is determined by measuring the softening points of the top and bottom halves and calculating the *S* value. The “ease of remixing test” is used to determine whether a phase-separated asphalt–polymer system can regain its initial homogeneous state following a remix [80,81]. Polymer-modified binders are permitted to fail the segregation test if they pass the Australian specification’s test for convenience of combining. Similar to the segregation test, the samples are stored for 48 h at 180 °C in 375 mL metal cans. Then, the metal can is transferred to a heated plate, and the binder is manually agitated at a rate of 100 movements per minute for 10 min using a flat-bladed spatula, simulating field-standard mixing protocols. Equation (3) calculates the segregation (*S*) and ease of remixing (*E*) from the softening points of the top and bottom halves of the metal cans:

$$S \text{ or } E = \frac{200(S_t - S_b)}{(S_t + S_b)} \quad (3)$$

7.3. Laboratory Asphalt Stability Test (LAST)

The laboratory asphalt stability test (LAST) is a viable alternative to the so-called tube test because it provides a more realistic storage environment observed in the field [40]. The LAST apparatus was created by scaling down a vertical storage tank with a 20,000-gallon capacity that was manufactured by a well-known asphalt-related equipment manufacturer (see Figure 7). The LAST test facilitates the optimization of the temperature, agitation level/speed, and storage period incorporated during the determination of the polymer-modified binder’s storage stability [76,82–85]. The testing protocol is capable of handling 400–450 mL samples in which binders are subjected to static storage and then to high mechanical agitation, under external heat, simulating the extreme conditioning steps [78]. Then, over the course of 48 h, samples are collected from various locations, and the separation ratios (R_s) or degradation ratios (R_d) between the top and bottom are calculated using Equations (4)–(7).

$$R_{sHT} = \frac{\left(\frac{G^*}{\sin \delta}\right)_t}{\left(\frac{G^*}{\sin \delta}\right)_b} \quad (4)$$

$$R_{sIT} = \frac{(G^* \sin \delta)_t}{(G^* \sin \delta)_b} \quad (5)$$

$$R_{dIT} = 0.5 \frac{\left(\frac{G^*}{\sin \delta}\right)_t + \left(\frac{G^*}{\sin \delta}\right)_b}{\left(\frac{G^*}{\sin \delta}\right)_{in}} \quad (6)$$

$$R_{dHT} = 0.5 \frac{(G^* \sin \delta)_t + (G^* \sin \delta)_b}{(G^* \sin \delta)_{in}} \quad (7)$$

where:

HT = high-grade temperatures;
 IT = intermediate-grade temperatures;
 in = subscript that represents the initial state at time = 0.

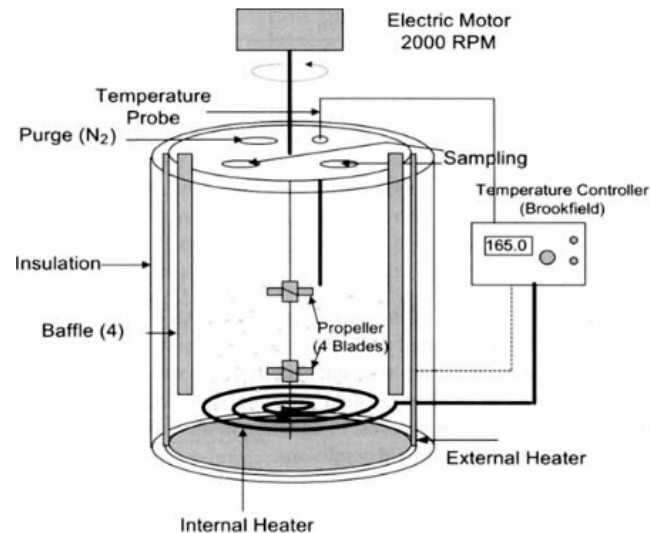


Figure 7. LAST test apparatus [86] (reprinted with permission from Ref. [86]).

7.4. Dynamic Shear Rheometer (DSR) Test

The dynamic shear rheometer (DSR) test is a widely used method for evaluating the rheological properties of polymer-modified asphalt binders and the compatibility between asphalt and polymers [87]. In other words, a dynamic shear rheometer (DSR) is used to measure viscosities at medium-to-high temperatures [88]. A sample is selected as a representative of the polymer-modified asphalt binder, and the sample is heated, typically at 135 degrees Celsius, to ensure that the sample is in a liquid state while testing [89]. The core apparatus of the DSR is a cylindrical mold equipped with parallel plates. The gap in the plates is determined based on test requirements. The liquid sample is poured into the mold [89]. The DSR instrument is also equipped with an apparatus to create different temperature and loading conditions that simulate modified asphalt conditions. However, the DSR can perform a temperature sweep test that reveals the rheological properties of the modified asphalt binder for a range of temperatures. The DSR can also perform a frequency sweep test to determine the binder's complex share modulus, representing the PMB's viscous and elastic behavior [90,91]. The DSR test generates stress and strain measurements. The results of the DSR test can be used to estimate rheological properties, compatibility, stiffness, and resistance to deformation. The rheology results of the DSR test can be used to prepare a Cole–Cole diagram and master curve [92]. The Cole–Cole diagram enables researchers to evaluate the rheological properties of PMBs, such as recoverability, deformation resistance, etc. [93,94]. The master curve can be used to predict the performance of PMBs, characterize the material, control the quality, and so on [38,40]. Tao Wang et al. [95] (p. 408) investigated the feasibility of evaluating the low-temperature characteristics of styrene–butadiene–styrene (SBS)-modified asphalt employing the dynamic shear rheometer (DSR) technique. Zhuang Zhang et al. [30] determined the rheological properties of polymer-modified aged samples using the DSR test. Di wang et al. [96] performed a DSR test for a wide range of temperatures and frequencies to assess the rheological qualities of PMBs. The benefit of this approach is the ability to quickly assess the low-temperature performance of asphalt using the DSR test, which can minimize testing resources and testing time [29]. The DSR test provides comprehensive rheological properties; it can be conducted for a wide range of temperatures, is a non-destructive method, and can predict performance. To increase the dimensions of the complex shear modulus, the DSR has to be

combined with the BBR [97]. In addition, the sample preparation and standardization are challenging in this test. The DSR test provides a reliable and effective way to assess the rheological characteristics of polymer-modified asphalt binders.

7.5. Multiple Stress Creep Recovery (MSCR) Tests

Multiple stress creep recovery (MSCR) is commonly used for evaluating the rheological properties of polymer-modified asphalt binders, providing valuable information on the viscous and elastic characteristics of the binder for various temperature and loading conditions. Over the past 10 years, the MSCR test has grown in popularity, particularly for polymer-modified binders. It offers significant benefits for identifying high-quality binders like polymer-modified bitumen [86,98–100]. At first, the sample is prepared by blending the base asphalt with the polymer modifier, where the bonding may involve mixing and heating to achieve homogeneity [101]. To ensure that the sample reaches thermal equilibrium, the sample is conditioned at a specific temperature, typically 10 to 60 degrees Celsius. A constant axial loading is applied to the binder by a rheometer [91]. Due to the application of loading ranging from a few seconds to a few minutes, the sample PMB deforms, which is called creep testing [92,93]. Afterward, the stress is released, and the rate and extent of recovery to the original dimensions are measured, which is called recovery testing. The creep and recovery tests are repeated for low-to-high stress levels. The output data are analyzed to determine the elastic and viscous behavior of the PMB [101–104]. Laurent Porot et al. [89] (pp. 1–14) conducted an MSRP test on different PMBs at high temperatures, where he found that compared to standard criteria, MSCR performed better at differentiating between complex binders. Binshuo Bao et al. [105] (p. 304) conducted an MSCR test to investigate the nonlinear and linear viscoelasticity of SBS-modified asphalt binder and its mastic. Danial Nasr et al. [106] (p. 127069) conducted an MSCR test to investigate the rheological characteristics of PE-modified asphalt binder, where the authors found improvements in the modified asphalt. The MSCR test has the significant advantage of removing the need for tests like elastic recovery, toughness, force ductility, and perseverance, and the procedure is specifically prepared to characterize PMABs. Information on the asphalt binder's performance and formulation can be obtained from a single MSCR test [107]. There are some limitations of the test, such as it being time-consuming, as well as limitations in temperature and stress level. However, MSCR is an outstanding technique for studying the viscoelastic behavior of polymer-modified asphalt binders.

7.6. Linear Amplitude Sweep (LAS) Test

The linear amplitude sweep (LAS) test is a widely used rheological test to investigate the linear viscoelastic characteristics of polymer-modified asphalt binders (PMBs) with varying strains of cyclic loading conditions [108]. In other words, the linear amplitude sweep (LAS) test is an advanced method to examine the fatigue performance of asphalt binders [109]. The base asphalt and polymer modifier are blended using suitable proportions to achieve a homogeneous mixture of samples. The sample is conditioned at a particular temperature to achieve thermal equilibrium. After that, the sample is loaded in a rheometer equipped with a coaxial cylinder and a parallel plate system. The test starts by applying a minor strain to a more significant strain amplitude, and the response is recorded. The stress and strain data are recorded and analyzed for important information about linear viscoelastic behavior [110–112]. Much research has been conducted to characterize polymer-modified asphalt binders using the LAS test. Bhupendra Singh and Praveen Kumar [97] (pp. 3691–3705) applied the LAS test on a PMB to investigate the quality of the binder. Mingjing Yue et al. [100] (p. 123054) conducted the LAS test to assess the durability and recovery capabilities of SBS-modified asphalt binder. Huan-Yun Zhou et al. [91] (p. 3986) conducted the LAS test to evaluate the rheological properties of PE-modified asphalt binder. The LAS test offers many advantages when conducted on PMBs, such as providing the linear viscoelastic range, quick execution of the test, and providing comprehensive rheological characteristics. Conversely, the test has some drawbacks, such as

limited strain amplitude range, loading conditions, and limited temperature; additionally, standardization is challenging, and the prediction range is limited [101,102]. However, the LAS test effectively investigates the linear viscoelastic behavior of polymer-modified asphalt binders [112–117].

8. Current Practice of Enhancing Compatibility

8.1. Sulfur Vulcanization

Sulfur vulcanization is a chemical process that creates a stable polymer network in asphalt by crosslinking polymer molecules and also couples polymer to asphalt by forming sulfide or polysulfide bonds. These bonds are so strong that they typically do not dissolve at high temperatures, enhancing the blend's storage stability. Sulfur vulcanization is limited within asphalt binders modified by unsaturated polymers, i.e., SBS copolymer, due to the chemical reactions between sulfur and unsaturated bonds in the polymer, which are the basis for sulfur's linkage with polymer modifiers. The use of sulfur improves the elasticity, resistance to rutting, and rheological properties of polymer-modified binders. However, sulfur vulcanization has some drawbacks, such as an increased susceptibility to oxidative aging, the production of a hazardous gas (hydrogen sulfide) during vulcanization, and the poor recyclability of modified binders.

8.2. Antioxidants

Frequently, polymer-modified binders are susceptible to oxidation, and the use of antioxidants can be advantageous. Binder modification typically employs various types of antioxidants, such as hindered phenols, phosphites, and organic zinc compounds, which retard oxidation by scavenging free radicals or breaking the hydroperoxides formed during oxidation [87,88]. These intermediates are extremely reactive and significantly contribute to oxidation. However, the high cost and limited flux of antioxidants in bitumen limit the use of antioxidants in binder modification.

8.3. Hydrophobic Clay Minerals

Hydrophobic clay minerals contain clay platelets that can prevent the modified binders from aging by resisting the entry of oxygen. By diminishing the difference in density between polymer modifiers and asphalt, these particles also enhance the blend's storage stability. Montmorillonite and kaolinite are the most frequently used clay minerals in polymer modification.

8.4. Functionalization

To improve the storage stability, aging resistance, adhesion to aggregates, stiffness at high temperatures, and cracking resistance at low temperatures of the polymer/asphalt system, functionalization is the chemical addition of specific functional groups to the polymer. By forming hydrogen bonds or chemical bonds with asphalt's components, for example, the additional functional groups may improve compatibility. Functionalization is feasible via anastomosis. Maleic anhydride (MAH), methacrylic acid (MA), and glycidyl methacrylate (GMA) are frequently used to graft polymer modifiers.

8.5. Reactive Polymers

Polymer modifiers, including reactive ethylene polymers and isocyanate-based polymers, are employed in asphalt modification, and they are thought to chemically react (rather than physically merge or interact) with asphalt components. Ethylene-glycidyl acrylate (EGA) copolymers and random terpolymers of ethylene, GMA, and an ester group (usually methyl, ethyl, or butyl acrylate) are the most frequently reported reactive ethylene polymers. Polymers' compatibility with asphalt is thought to be enhanced by the presence of acrylate groups, which are thought to increase the polarity of the polymer, and epoxy rings, which are thought to react with specific functional groups (such as carboxylic acid groups) in asphalt. The low-temperature characteristics, however, are not enhanced. Gela-

tion risks in modified asphalt may also be caused by interactions between isocyanate-based polymers.

9. Chemical Analysis of Polymer-Modified Asphalt Binders

Chemical analysis of polymer modified asphalt binders (PMBs) determines their chemical composition, properties, and structure. Though there are several methods available for the chemical analysis of PMBs, the most commonly used methods are Fourier-transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC).

9.1. Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) is a recognized approach to assess the chemical-related phenomena that arise during the manufacture of the binder, as well as the molecular structure of the materials and their consequences on the functionality of the modified bitumen [118–121]. An FTIR spectrometer simultaneously obtains a broad variety of high-resolution spectrum data. The test can be conducted in six steps: sample preparation, instrumentation, data acquisition, spectrum interpretation, analysis, and quantification. The desired PMB is dissolved in an appropriate solvent to produce a thin film or solution, because a typical FTIR test includes a technique called diffuse reflectance inspection (DRIFTS), which requires a powdered sample, and the roughing angle inspection specification (RARS) method demands a specimen with a thin film layer [122]. The test is performed using an FTIR spectrometer. The sample is placed in the sample holder of the spectrometer. The goal of FTIR is to obtain information about the amount of infrared light absorbed by the sample under examination at a specific wavelength range [15,110]. Depending on the surroundings, mid-infrared light ($400\text{--}4000\text{ cm}^{-1}$) causes molecules to vibrate. Every molecule, regardless of whether linear or not, possesses $3N-5$ or $3N-6$ normal vibrations, depending on the number of atoms in the molecule, which are prone to infrared absorption. In this instance, a photon's energy is in resonance with the energy disparity between the vibrational ground state and the first stimulated vibrational state. The primary vibration is excited as the photon is canceled. The transmission absorption spectra are recorded in this way [110,112,113]. Further analysis of the detected spectrum enables the production of the FTIR results. Many researchers have conducted FTIR tests on polymer-modified asphalt binders. Muhammad Mubarak [50] (pp. 5–14) conducted FTIR tests to characterize and examine the components of a polymer-modified asphalt binder. Peng Lin [114] (p. e02211) conducted the test to understand how fibers affect the performance and aging susceptibility of higher-volume polymer-modified asphalt mixers. Dongmei Zhang et al. [123] (p. 126522) conducted the test for the analysis of the chemical properties of aged composite nanomaterials in SBS-modified bitumen. Chi-Su Lim et al. [111] (p. 5743) conducted the test to compare the characteristics of asphalt binders used with the wax-based warm-mix additives ethylene–vinyl acetate (EVA) and styrene–butadiene–styrene (SBS). FTIR spectroscopy is the most effective way to monitor differences in the chemical structure of an old asphalt binder and measure the effects of oxidation [124,125]. This method is very useful for identifying and quantifying polymers, the interaction between polymer and asphalt, chemical changes during aging, and quality control. The test has some limitations, e.g., the test sampling chamber is small, which may cause some restrictions, the mounted objects might block the IR beam, and it is unlikely to obtain precise results because many materials totally absorb infrared light [126].

9.2. Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) involves separating dissolved molecules according to their size with the help of their elution from a column packed with a porous gel, aiming to estimate the molecular weight distributions and averages [127,128]. It can be defined as a form of molecular sieving chromatography, in which materials are broken down into their component parts by passing through a porous column's packaging after being dissolved in a solvent. The sample separates because its components travel through the

stationary phase at different rates depending on their ability to penetrate different pores—a procedure known as differential partitioning [117,118]. PMBs are employed in a variety of implementations, including coatings and asphalt. They are composed of a base binder—for example, polymer or resin—that is combined with a polymer additive to improve its qualities. The GPC technique can be implemented to examine the polymer, including its weight distribution, in the binder. For PMBs, the test can be conducted in several steps: prepare the polymer-modified asphalt solution, separate the injected asphalt solution, select the packing materials and arrange the columns, select the detector, and run the GPC test. The asphalt solution is made by dissolving the asphalt sample in a solvent [129]. Tetrahydrofuran (THF) is the solvent most commonly utilized for asphalt binders, due to its superior repeatability when compared to other solvents, like toluene [130]. After the sample has completely dissolved in the solvent, suspended particles and unresolved components are removed by filtering the dissolved asphalt solution [131]. Polytetrafluoroethylene (PTFE) syringe filters with varied sieve sizes are the most widely used filters [132]. The main instrument of the GPC test is the column, which is filled with packing materials of different pore sizes. The compatibility between the packing materials and the mobile phase is considered when selecting the packing material [118]. After that, the detector is selected to detect the molecules separated from the samples [133]. Light scattering (LS), differential refractive index (DRI), viscometry, and ultraviolet (UV) are the most used detectors, of which the DRI is the most frequently used [118]. Finally, the prepared sample is injected through the GPC instrument to pass into the columns, where they are detected by detectors aiming to examine the concentration of the polymer and information about molecular weight. The data are further analyzed to obtain a chromatogram, which is used to estimate the molecular weight [134]. Much research has been conducted to examine the properties of PMBs. Giacomo Cuciniello [135] (pp. 372–396) conducted GPC tests to determine the rheological and microstructural properties of SBS-modified asphalt binders. Lu Zhou et al. [123] (p. 04021158) applied the GPC test to investigate the mechanism and quantification of SBS-modified asphalt binder. Yuetan Ma et al. [136] (p. 161089) investigated the weather-aging effect of PE-modified asphalt binder using the GPC test. The advantages of the test are that it provides molecular weight distribution, the separation efficiency is high, and it can provide polymer concentration information. The test may not directly provide the information about the interaction between the polymer and asphalt, the solvent and detector selection is sensitive, and it needs specialized equipment [137].

10. Commonly Used Polymers in Binder Modification

Numerous efforts have been made by researchers to study the effects of polymer modification on the mechanical and rheological properties of the modified binders. The polymers that have been used in modifying asphalt binders can be broadly categorized into two groups, i.e., thermoplastic elastomers and plastomers. Thermoplastic elastomers' structure is generally linear and is characterized by weak inter-chain linkages [12]. They become rubbery under heat, become glassy after cooling, can resist permanent deformation over stretching, and elastically recover once the load is removed [41,138–141]. This important property of thermoplastic elastomers has resulted in the higher success of binder modification than with plastomers [1]. On the other hand, plastomers, having limited reversible elasticity, are more rigid as compared with thermoplastic elastomers and exhibit brittle failure. Figure 8 represents a classification of the polymers that are used in binder modification.

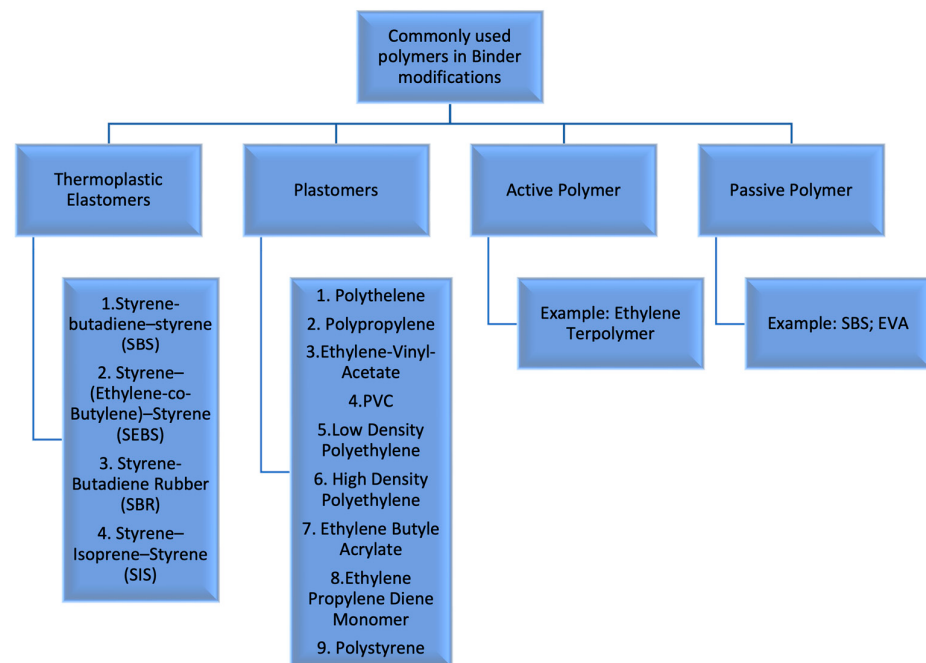


Figure 8. Classification of polymers used in binder modification [1,12] (reprinted with permission from Refs. [1,12]).

10.1. Thermoplastic Elastomers

The most popular thermoplastic elastomers that have been extensively used to modify asphalt binder properties are styrene–butadiene–styrene (SBS) copolymers, because of their exceptional glass transition temperature (T_g) and their effects on the rheological properties of the modified binder at high temperatures [142]. As shown in Figure 9a, the chemical structure of SBS copolymers, whether linear or radial, is biphasic, where glassy polystyrene (PS) ($C_6H_5CH=CH_2$) domains are attached by rubbery polybutadiene (PB) segments ($CH_2=CH-CH=CH_2$) [143,144]. This system is stable at temperatures between the glass transition temperatures of the PB ($\sim -95^\circ C$) and PS ($\sim 100^\circ C$). The rheological behavior of the SBS copolymer–asphalt blend depends on various factors, i.e., the nature and glass transition of the oil, the molecular structure of the SBS, and the polymer/oil ratio [145]. The interaction of PB occurs through its π -electrons with positively charged groups in asphalt, while the interaction of PS occurs through its aromatic protons with electron-rich groups in asphalt [146]. These interactions result in a three-dimensional (3D) network (see Figure 9b) in which PS domains act as physical crosslinks and increase the strength of the system [47]. The hard PS end blocks are responsible for the high tensile strength and resistance of SBS at high temperatures, whereas the rubbery PB mid blocks are responsible for its elasticity, fatigue resistance, and flexibility at low temperatures [37].

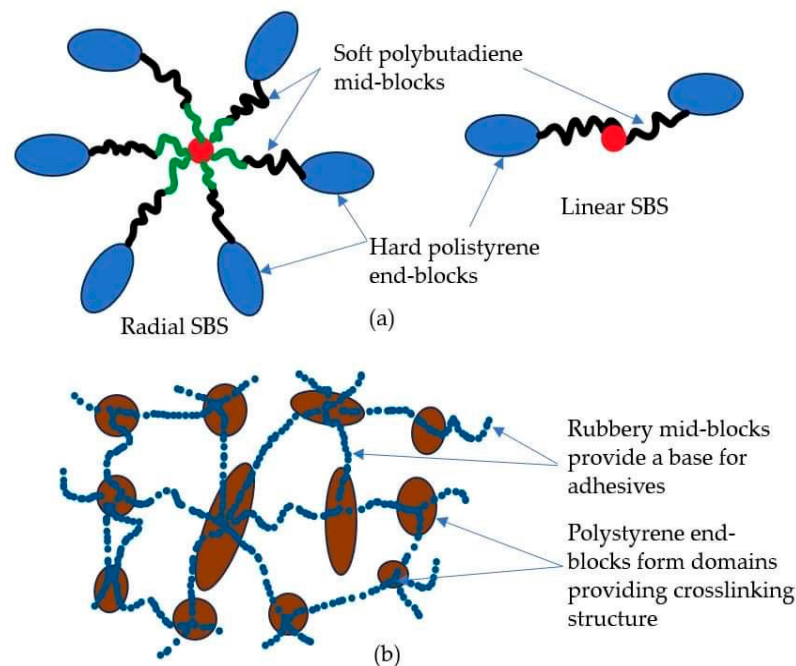


Figure 9. Styrene–butadiene–styrene (SBS) copolymer: (a) Chemical structure and (b) 3D network [12,147,148] (reprinted with permission from Refs. [12,147,148], open access).

The morphology of SBS-modified asphalt binders can demonstrate a continuous ARP with a dispersed PRP, co-continuous phases, or a continuous PRP with dispersed ARP globules, depending on the concentration of the incorporated polymer [149,150]. At high SBS copolymer concentrations, SBS becomes the dominant phase, and the rheological and engineering properties of the blend are changed. It was found from the previous studies that when 5–6% SBS is incorporated in asphalt, the so-called “phase inversion” takes place [151,152]. Care should be taken while choosing the optimal SBS copolymer content in asphalt, as lower polymer concentrations may lead to a lack of the required engineering properties, while higher concentrations may lead to phase separation during the storage period [1].

Using SBS copolymers in binder modification has various tangible benefits. SBS-modified asphalt binders have exhibited satisfactory performance against permanent deformation at high temperatures [141,153–157], fatigue cracking [158–160], and thermal cracking at low temperatures [160–163]. Additionally, HMAs produced with SBS copolymer demonstrated better resistance to moisture damage [164,165]. However, this thermoplastic elastomer has some drawbacks too. SBS copolymer was found to be highly vulnerable to heat, oxygen, and ultraviolet (UV) light [166]. To overcome this problem, antioxidants (zinc dialkyl dithiophosphate (ZDDP), zinc dibutyl dithiocarbamate (ZDBC), and naphthenoid oil) are used to impede the oxidation of the blends by breaking hydroperoxides and scavenging radicals [167]. Another limitation of the SBS-polymer-modified asphalt is the phase separation tendency during high-temperature storage [168,169]. Various additives have been used to improve the storage stability of SBS polymer–asphalt blends, including phosphorus-based compounds [169], montmorillonite composites [69,170], sulfur-based additives [171], polystyrene [172], kaolinite clay [172], tall oil pitch (TOP) [173], GMA [174], and ground tire rubber (GTR) [175].

SBS copolymer is highly susceptible to degradation by heat, oxygen, and ultraviolet (UV) light. Styrene–ethylene/butylene–styrene (SEBS) triblock copolymers were introduced to overcome the problems associated with SBS copolymer. SEBS triblock copolymer is synthesized by simple hydrogenation of the middle block of the styrene–butadiene–styrene (SBS) structure [6]. For SEBS-modified asphalt concrete, a concentration of 3–4% was observed to have the optimized rheological and engineering properties [1]. The mor-

phology seen in the SEBS-modified asphalt is similar to the morphology of SBS-modified asphalt [176]. SEBS-modified asphalt exhibits similar improvements in rheological properties to SBS-copolymer modified asphalt binder. SEBS is more effective than SBS in enhancing the rutting resistance of asphalt binder but less effective in improving the fatigue properties [177]. SEBS also has some limitations, such as compatibility problems [7]. For example, the ethylene/butylene blocks in SEBS have a tendency to crystallize, which further limits its compatibility with asphalt [125]. SEBS-modified asphalt binder can either show improved [178] or reduced compatibility and storage stability compared to SBS-modified asphalt binder [179].

10.2. Plastomers

The use of polyethylene is very common in binder modification due to the economy and its potential to improve the properties of asphalt binders [40]. Ethylene–vinyl acetate (EVA) is a copolymer in the form of random-chain hydrocarbon molecules, as shown Table 2. EVA is produced by the copolymerization of ethylene with vinyl acetate (VA). EVA copolymer is a thermoplastic material that resembles elastomers in softness and flexibility. Compared with polyethylene, the presence of polar acetate groups as short branches in EVA disrupts the closely packed crystalline microstructure of the ethylene-rich segments, reduces the degree of crystallization, and increases the polarity of the polymer, which are all believed to be beneficial to improving the storage stability of modified asphalt by some researchers [6]. The properties of EVA copolymers are dependent on VA content. When the VA content is low, the degree of crystallization is high, and the properties of EVA are quite similar to those of LDPE. As the vinyl acetate content increases, EVA tends to present a biphasic microstructure with a stiff polyethylene-like crystalline phase and a rubbery VA-rich amorphous phase [180]. The higher the VA content, the higher the proportion of the amorphous phase. As the VA content increases, the crystallinity decreases, and the polarity of the EVA and its compatibility with asphalt are enhanced [6]. When polyolefin/polyethylene materials are incorporated in asphalt binder, they are swelled by the light components of asphalt, and a biphasic structure is created where polyolefin is dispersed in the continuous ARP [181]. Two interlocked co-continuous phases are desirable here, with the potential to enhance the rheological and mechanical properties of the blend. Although phase inversion occurs at high polymer concentrations (5–15%), the concentration should be approximately 5% by the weight of the asphalt for paving applications [182].

The use of polyethylene-based polymers (e.g., EVA) in asphalt binder is beneficial in such terms as high-temperature properties, low-temperature cracking resistance, flexural stiffness, fatigue life, and water resistance [183–192]. These can also be considered to be effective modifiers to improve thermomechanical resistance, elasticity, and adhesion properties [140]. However, due to its non-polar and aliphatic nature, this polymer type is almost completely immiscible with asphalt, which is polar and aromatic [1]. Various techniques are used to enhance the miscibility/compatibility of the blend, including the use of chemical grafting and chlorination [193,194]. However, polyolefin materials do not enhance the elasticity of asphalt, because of their plastomeric nature [88]. The most common polymer modifiers used for paving applications, along with their advantages and limitations, are summarized in Table 2.

Table 2. Commonly used polymer modifiers, along with their advantages and limitations.

Categories	Examples	Advantages	Limitations
Thermoplastic elastomer	Styrene–butadiene–styrene (SBS)	Improved rutting resistance Lower fatigue cracking Lower low-temperature cracking Lower susceptibility to moisture damage Better dispersibility in asphalt Reduces the stiffness of the blend due to oxidation Maintains the mechanical properties for a long time Enhances short-term and long-term aging resistance	High cost Low tolerance to heat, oxygen, and ultraviolet (UV) light Storage instability at high temperatures
	Styrene–(Ethylene-co-Butylene)–Styrene (SEBS)	Improved rutting as compared with SBS Higher tolerance to heat, oxygen, and ultraviolet (UV) light than SBS	Increased cost of hydration Poor fatigue performance Compatibility and storage stability are not entirely known
	Styrene–Butadiene Rubber (SBR)	Enhanced ductility at low temperatures Increased viscosity High elastic recovery Good adhesive and cohesive properties	Less effective in improving the high- and low-temperature properties of asphalt as compared with SBS copolymer Poor compatibility and phase separation High aging susceptibility
	Styrene–Isoprene–Styrene (SIS)	Better aging resistance Good asphalt–aggregate adhesion Improved storage stability Better performance compared to SBS binder in terms of viscosity, rutting, and cracking resistance	Need an asphalts with high aromatic and low asphaltene contents
Plastomers	Polyethylene (PE)	Environmental and economic benefits Improved rutting performance Better low-temperature cracking resistance, High flexural stiffness Improved fatigue life Good water resistance Aging-resistant	Hard to disperse in asphalt Phase separation No elastic recovery
	Ethylene–Vinyl Acetate (EVA)	Easily dispersed in asphalt Good compatibility Excellent water resistance ability Better storage stability with a lower VA content and higher melt index (MI)	Less temperature-susceptible than LDPE-modified asphalt. At sufficiently high modifier content (~9%), EVA-modified asphalt shows less temperature susceptibility than SBS-modified asphalt Poorer elastic recovery than SBS copolymer

11. Sustainable Approaches to Binder Modification

11.1. Incorporation of Waste Polymers in Binder Modification

In just 10 years, the consumption of polymer products has increased by 60%, from 230 million tons in 2009 to 368 million tons in 2019. This propensity results in a substantial waste stream that must be properly managed to safeguard the environment in order to encourage a circular economy, which would reduce production costs [129,136,195]. The incorporation of waste polymers with virgin asphalt may improve environmental sustainability by minimizing the amount of plastic and rubber waste, energy use, and the extraction of virgin asphalt, which is generated from crude oil. Almost all waste

plastics (such as polyethylene tetrathalate (PET), polystyrene (PS), polypropylene (PE), etc.) can be processed using the wet technique for binder modification; however, polyvinyl chloride (PVC) cannot be mixed with virgin asphalt, due to the risk of deleterious chloride emissions [196].

In a study by Pradhan et al. [197], waste polystyrene (PS) was utilized to modify the asphalt binder. The longevity of the asphalt could potentially be increased by adding PS to the asphalt binder, but there were issues with the paving process, and particularly with miscibility and phase separation. Researchers investigated these issues by modifying the virgin binder by including both waste polystyrene and trans-polyoctenamer (TOR) polymer. Sulfur was also utilized as a crosslinking agent throughout this modification process. Waste polystyrene (PS) and trans-polyoctenamer (TOR) were combined with the virgin binder at a mass ratio of 2:1, creating a modified binder known as polyoctenamer-modified polystyrene binder (PS-1). Then, the authors utilized 0.1%, 0.5%, and 1% sulfur as the crosslinking agent to produce four different bitumen-modified mixture samples. According to the outcomes of the penetration and softening point tests, the addition of additives led to a slight increase in the virgin binder's stiffness. The addition of sulfur substantially enhanced the modified binders' elastic recovery and storage stability capabilities, allowing for the efficient anchoring of polymeric additives inside the asphalt matrix. As shown by the lower Jnr values and better average% recovery in the MSCR tests, the additives also showed enhanced high- and moderate-temperature characteristics. In the BBR tests, the modified binders showed less stiffness and higher m-values than the virgin binders. The best additive content for the crosslinking agent was 0.1% in PS-2, which outperformed the other evaluated binders in terms of rheological performance [196].

A very recent study conducted by Vargas et al. [198] aimed to develop a suitable asphalt additive by pyrolyzing plastic wastes such as HDPE and PP. It was discovered that only HDPE formed a wax that had a negligible effect on the bitumen's flashpoint when PP and HDPE polymers were pyrolyzed. Then, both virgin asphalt and pyrolyzing plastic-waste-modified bitumen with 5% polypropylene were used to assess the wax formulation. According to the softening point and consistency measurements, the inclusion of wax enhanced the bitumen's tolerance to higher temperatures. Furthermore, even though the wax made the bitumen more rigid, its impact was not as great as the polymer's. As a result, the wax-modified binder outperformed the polymer-modified binder in terms of fatigue life and resistance to breaking at low temperatures. When the wax concentration reached 7%, segregation in the PMB decreased by 17% and did not negatively affect the segregation in the virgin bitumen. Additionally, it was discovered that the pyrolytic wax made from HDPE reduced the bitumen's viscosity, requiring less energy to compact and mix the asphalt mixes. These results led to the conclusion that 7% is the ideal wax content for virgin bitumen and PMB. Segregation and increased viscosity were two major issues with the use of plastic waste as a bitumen component that were addressed using pyrolytic wax. Additionally, it was shown that pyrolysis pretreatment, as opposed to dry mixing, could permit better plastic utilization. Utilizing the pyrolyzing wax to reduce the temperature for mixing and compaction is a novel finding that has not been observed before. This technique has the potential to reduce the environmental effect of producing asphalt by reducing plastic waste and energy [198]. Another study conducted by Hu et al. [199] investigated the feasibility of using polyethylene waste material tape as a bitumen mixture modifier. Researchers found that increasing the waste tape content in the bitumen mixture led to improved performance against rutting. Although the fatigue performance of the additive showed a positive trend at lower strain levels, increasing the waste tape content by 6% weight showed a downward trend in the fatigue performance. Hu et al. also found that waste-tape-modified bitumen showed poor performance against low-temperature cracking, and this modification can only be applicable where the temperature in general does not go below 32 degrees Fahrenheit [198].

Rahman et al. [200] conducted a review of the use of recycling waste in asphalt concrete and bitumen mixtures. In this review, the authors summarized how recent research has

effectively incorporated plastics into binders, improving their rutting and fatigue performance. For example, using tire rubber powder can effectively improve the high-temperature performance of the asphalt binder, whereas the combination of waste cooking oil with palm oil fuel has the potential to replace the traditional bitumen binder by 5% [200,201].

The use of polymer-modified binders (PMBs) is limited to the surface layer of high-volume roads due to their higher market cost [200]. Reclaimed polymers can therefore be an alternative to reduce the production cost of polymer-modified asphalt binders. Brasileiro et al. conducted a review study to compile the latest enhancements of producing “Reclaimed-Polymer modified binder (RPMB)”. The authors of the paper summarized how the most researched reclaimed polymers that are being used are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), ethyl vinyl acetate (EVA), and ground tire rubber (GTR). It was found that polyethylene (PE) and ground tire rubber (GTR) are the most frequently used in producing RPMBs, as they are more available, stable, and have lower melting points than the mixing temperature [202].

11.2. Incorporation of Biopolymers in Binder Modifications

Due to their potential to improve the functionality and sustainability of asphalt pavements, the use of biopolymers in asphalt binder modification is essential. Biopolymers, which are made from renewable resources, are essential for creating environmentally acceptable and highly effective asphalt mixtures for creating sustainable road infrastructure. The two categories of biodegradable polymers are separated based on the method of degradation, i.e., synthetic and natural biopolymers [203].

Synthetic polymers are generally obtained from petroleum resources. Often these are referred to as biodegradable polymers. Synthetic polymers can be separated into oil- and bio-based polymers and are not very widely used in asphalt binder modification [203–205]. On the other hand, natural biopolymers, often referred to as “Bioplastics”, can be mixed with the virgin asphalt and reduce the % of bitumen in the mixture [206]. The biodegradability of natural biopolymers varies depending on the source, i.e., plants/animals/microorganisms or commercially synthesized biological materials [203]. As the scope of this review is to discuss different polymers that are being used in asphalt binder modification, this section only discusses the “Biopolymers” that are currently being used in the asphalt industry. The most abundantly used biopolymers are called polysaccharides. Polysaccharides are formed by the linking of multiple monosaccharide molecules through glycosidic connections. Using polysaccharides to modify the virgin binder’s properties in warm-mix asphalt (WMA) have already shown great promise by enhancing the mixture’s durability and resistance to temperature; also, algae-derived polysaccharides (alginates) have shown the ability to rejuvenate aged asphalt in reclaimed pavement (RAP) [207–209]. Table 3 presents some recent knowledge about the incorporation of biopolymers in bitumen modification.

Table 3. Recent literature about the incorporation of biopolymers in bitumen modification.

Major Class	Biopolymers	Recent Literature Mentioning the Use of Biopolymers
Polysaccharides	Chitosan Derived from chitin, which is found in different insects and shells [209,210]. Chitosan is an FDA-approved biopolymer used as a food additive [210].	Mallawarachchi et al. used chitosan to partially replace the emulsifier by 10%–20% by weight. The chitosan–emulsifier mixture was then used to create an asphalt emulsion, and the results showed that the positively charged chitosan–amines and negatively charged asphaltenes interacted and increased the viscosity and stability of the mixture [208].
	Natural Fibers Generally derived from animals or plant bodies. Previous research shows that fibers reinforce the composite materials by incorporating their fibrous features in the structure of the composite materials [210,211].	Kundal et al. added 0.4% sisal fiber with 5% bitumen content to asphalt mixtures. They found that the stability of the mixture increased until 0.4% but started to decrease after that [212]. Oyedepo et al. conducted similar research in 2021 and found that the stability of the mixture was highest when 0.2% sisal fiber was used [213]. Bonica et al. concluded that fiber derived from different sources of cellulose increased the rutting resistance in the asphalt mixture [214].
	Starch One of the most commonly used biopolymers from the polysaccharide group. Two types of glucose, namely, amylose and amylopectin, make up this biopolymer, and the flexibility and strength of materials made from starch increase with the amount of amylose present [215,216].	Research conducted by Porto et al. showed that starch, when mixed with bitumen at 4.8% by weight, enhanced the mixtures rigidity and increased the resistance to high temperatures [206]. A recent study by Komba et al. verified the previous research and concluded that bitumen treated with 5%, 10%, and 16% starch improved the elasticity and rheological properties of the mixture [217]. Both studies concluded that starch-modified mixtures can be produced at lower temperatures and in less time [202,206,216].
Natural rubber (NR)	Most of the natural rubber used in bitumen modification is derived from a very specific tree called <i>Hevea brasiliensis</i>. NR is an elastomer that resembles milky, runny latex from tree sap [218].	In a research study conducted by Krishnapriya et al., the authors used 2% natural rubber by weight in bitumen modification, where the results showed improved resistance to rutting and the fatigue performance of the modified bitumen enhanced significantly [219]. Shaffie et al. conducted similar research, and the researchers found that incorporating 8% natural rubber in the bitumen modification reduced the stripping phenomena [20]. In general, utilizing natural rubber in bitumen modification has been proven to be economical and environmentally friendly [51,220–222].

12. Summary and Conclusions

This study presents a comprehensive assessment of the literature encompassing various aspects of polymer-modified binders (PMBs). Achieving compatibility between the virgin binder and the polymer is essential for the successful modification of asphalt binders. The swelling, storage stability, blend morphology, and polymer mixing method are some of the elements that have an impact on the compatibility of the polymer–asphalt system. Careful consideration of these factors is imperative during the PMB production. Scanning electron microscopy (SEM), atomic force microscopy (AFM), fluorescent microscopy, and polarized optical microscopy were found to be effective techniques for evaluating the morphology of polymer–asphalt blends. The laboratory asphalt stability (LAST), dynamic shear rheometer (DSR), and multiple stress creep recovery (MSCR) tests were identified as some suitable methods for assessing the storage stability of PMBs.

Thermoplastic elastomers such as styrene–butadiene–styrene (SBS) and plastomers like ethylene–vinyl acetate (EVA) are some of the most widely used polymers in virgin asphalt modification. Numerous techniques, including sulfur vulcanization, antioxidants,

hydrophobic clay minerals, functionalization, and reactive polymers, can be used to increase the compatibility of the polymer–asphalt system.

This study also reviewed some recent literature about the use of recycled and waste polymers in binder modification. This was found to be a practical way to reduce the buildup of plastic and rubber waste, minimize energy use, and lessen dependency on virgin asphalt made from crude oil. Asphalt pavements can be made more useful and sustainable by using biopolymers made from renewable resources, including chitosan, natural fibers, starch, and natural rubber (NR). These sustainable practices of binder modification not only benefit the environment but also have the potential to improve the performance, affordability, and sustainability of asphalt pavement. The practicality of employing various waste/recycled and bio-based materials and their effects on the rheological and physical properties of asphalt binders and mixtures should therefore be the focus of future research.

This in-depth literature review may benefit researchers and transportation agencies in better understanding the complex nature of PMBs, in addition to designing new PMBs that can better combat common distresses of asphalt pavements.

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