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Review

Bitumen and Bitumen Modification: A Review on Latest Advances

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Abstract: This synthesis explores the state-of-the-knowledge and state-of-the-practice regarding the latest updates on polymer-modified bitumens (PmBs). The information in this study was gathered from a thorough review of the latest papers in the literatures related to modified bituminous materials, technologies, and advances. For this purpose, the paper is presented in two principle sections. In the first part, the bitumen itself is investigated in terms of chemical structure and microstructural systems. In the second part, the paper focuses on bitumen modification from different aspects for assessing the effectiveness of the introduced additives and polymers for enhancing the engineering properties of bitumen in both paving and industrial applications. In conclusion, the knowledge obtained in this study has revealed the importance of the chemical composition of base bitumen for its modification. It can be declared that while some polymers/additives can improve one or some aspects of neat bitumen properties, they can lead to compatibility problems in storage and production. In this respect, several studies showed the effectiveness of waxes for improving the compatibility of polymers with bitumen in addition to some benefits regarding warm mix asphalt (WMA) production.

Keywords: polymer-modified bitumens (PmBs); chemical structure; microstructural systems; spectroscopy; compatibility

1. Introduction

1.1. Bitumen Functionality

According to the European specification (EN 12597), bitumen is defined as a virtually involatile, adhesive, and waterproofing material derived from crude oil, or present in natural asphalt, which is completely or nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperatures [1]. It is well-accepted that the original characteristics of bitumen are highly dependent on its production and processing procedure, as well as bitumen crude oil characteristics [2]. Good crude oils and proper distillation processes can enhance bitumen properties. Generally, heavier crude oil gives higher bitumen yields [3]. Therefore, having a complete knowledge on the bitumen characteristics from different aspects is of paramount importance. This knowledge proves to be more important when, for some bitumen applications, some difficulties such as discontinuity in phase, mal-dispersion, and instability with polymers/additives make it challenging in the production and application of bituminous materials.

From a commercial point of view bitumen is a low-cost thermoplastic material that has been widely used in roofing and pavement application, paving mixtures, and industrial products for a long time. In both paving and industrial applications, the bitumen should be resistant to climate and more demanding traffic loads, for which reason rheological properties play a key role in different aspects [4–6]. From a functional point of view, the bitumen has to be fluid enough at high temperature (≈160 °C) to be pumpable and workable to allow for a homogeneous coating of aggregate upon mixing. Moreover, it has to be stiff enough at high temperatures to resist rutting (according to the local temperatures, ≈60 °C). Finally, it must remain soft and elastic enough at low temperatures to resist thermal cracking [4]. All the mentioned requirements are almost opposite, and most of the available neat bitumens would not provide all the needed characteristics together. Moreover, in some applications, the performance of conventional neat bitumens may not be satisfactory considering the required engineering properties because it is brittle in a cold environment and softens readily in a warm environment. This limited performance temperature range is the main drawback to neat bitumen, limiting its use for both roofing and road paving applications. In addition, as the traffic speed and load has dramatically increased, unplanned overloading has notably shortened the life of asphalt pavements, increasing its costs of maintenance and risks to users. Hence in order to enhance the performance properties of neat bitumen, to date, a variety of additives have been introduced and some have been used successfully for many applications. Modifiers and additives have been used to boost bitumen performance include: polymers, chemical modifiers, extenders, oxidants and antioxidants, hydrocarbons, and anti-stripping additives. The following sections are dedicated to the discussion about bitumen chemistry composition in order to describe the main features and mainly to describe the additives used over the last few decades of research, providing a comprehensive and in-depth coverage of the science and technology of bitumen modifiers.

1.2. Bitumen Chemistry

From a chemical point of view, bitumen is defined as a viscous viscoelastic liquid (at room temperature) consisting essentially of hydrocarbons and their derivatives, which is totally soluble in toluene, substantially non-volatile, and softens gradually when heated [7]. It comprises a very great number of molecular species that vary widely in polarity and molecular weight [8,9]. Elemental analysis show that bitumen composition is primarily determined by its crude oil source and it is difficult to give a specific geographical generalization [10,11] (many suppliers also mix bitumen from different sources as well). This has been shown in a wide research by SHRP (Strategic Highway Research: Special Report) [12]. Based on this report, the main constituents of bitumen are carbon, which varies from 80 to 88 wt% and hydrogen ranging from 8 to 11 wt%. In addition, Heteroatoms and transition metal atoms (principally vanadium and nickel) are generally presents: sulfur (0 to 9 wt%), nitrogen (0 to 2 wt%), oxygen (0 to 2%), vanadium up to 2000 ppm, and nickel up to 200 ppm [10,13,14].

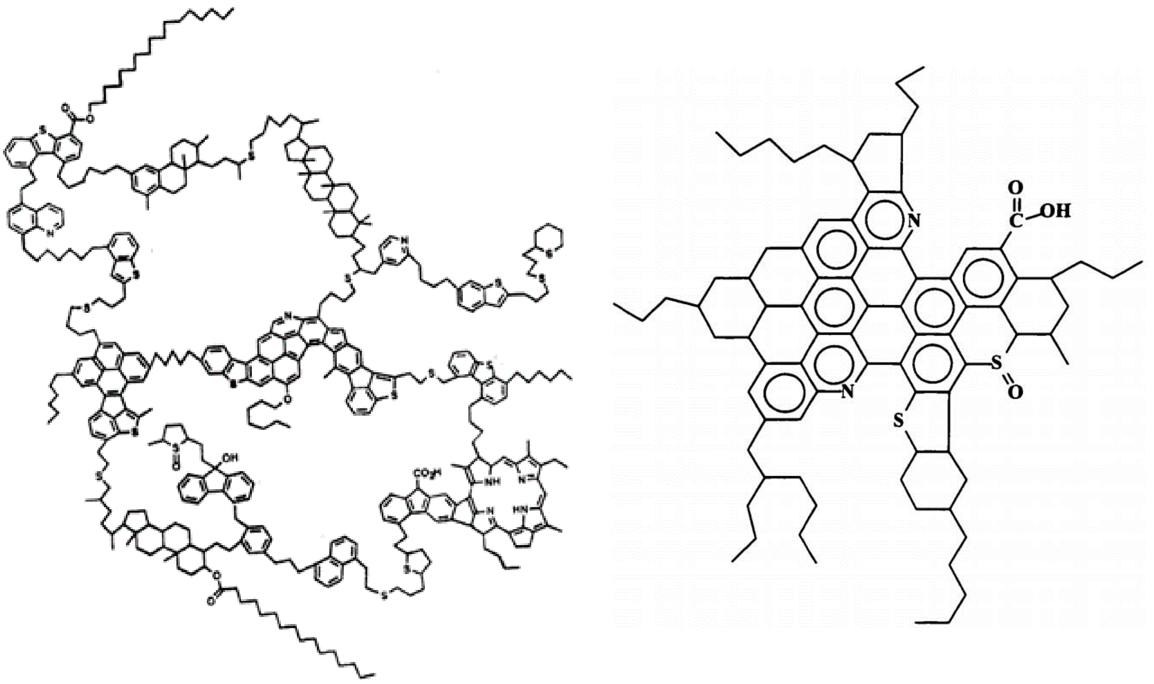
From a molecular point of view, the main compounds of the polar heteroatoms above are: sulphides, thiols and sulfoxides, ketones, phenols and carboxylic acids, pyrrolic and pyridinic compounds, and most metals form complexes such as metalloporphyrins [14]. Molecular weight distribution analysis shows that bitumen is a complex mixture of about 300 to 2000 chemical compounds (medium value 500–700) making a complete chemical characterization very difficult. For this reason, bitumen is generally fractionated by simpler methodologies, which allow two principal constituents to be identified:

I Asphaltenes
II Malthenes (also called petrolenes)

Maltenes are then classified into saturate, aromatic, and resin, which together with asphaltene are known as the bitumen SARA (Saturate, Aromatic, Resin, Asphaltene) fraction. The relative abundance of the SARA fractions allows the bitumen chemical composition to be related with its internal structure and some of its macroscopic properties [15]. However, it should be noted that changes in experimental conditions (especially eluent nature) significantly affect the proportion of every bitumen fraction [10,16]. It is, therefore, important to specify the experimental setup condition for comparing the various chemical compositions of bitumen, even though they show some common features and overall properties that remain substantially unchanged.

1.2.1. Asphaltenes

Asphaltenes, whose percentage in bitumen varies from 5 to 25% are amorphous brown/black solids at room temperature with particle dimensions between 5–30 μm, insoluble in n-heptane, but soluble in toluene [17,18]. Asphaltene contains oxygen, nitrogen, sulfur, and heavy metals (V, Ni, etc.) in the form of complexes such as metallo-porphyrins with long aliphatic chains (up to 30 carbon atoms), and pyrrolic and pyridinic rings. As demonstrated by UV-fluorescence spectroscopy [19,20], Fourier transform infrared spectroscopy (FTIR) [20,21], X-ray raman spectroscopy [22], and NMR spectroscopy [20,23,24], asphaltene molecules consists of fused aromatic rings, most probably between 4 to 10 units, together with some aliphatic chains as ring substituents, as shown in Figure 1.



(**a**) (**b**)

Figure 1. Asphaltene hypothetical structure: (**a**) Archipelago structure, and (**b**) continent structure (reprinted from [25,26] with the permission of the American Chemical Society and OnePetro).

Owing to the presence of many condensed aromatic rings, asphaltenes form an almost planar structure that can associate by π–π bonding interaction to form graphite like structures (see Figure 2) [21,27].

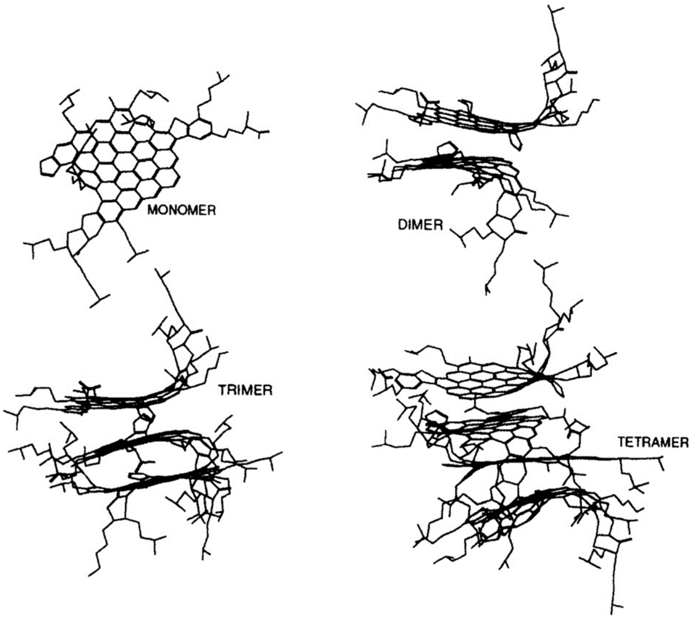
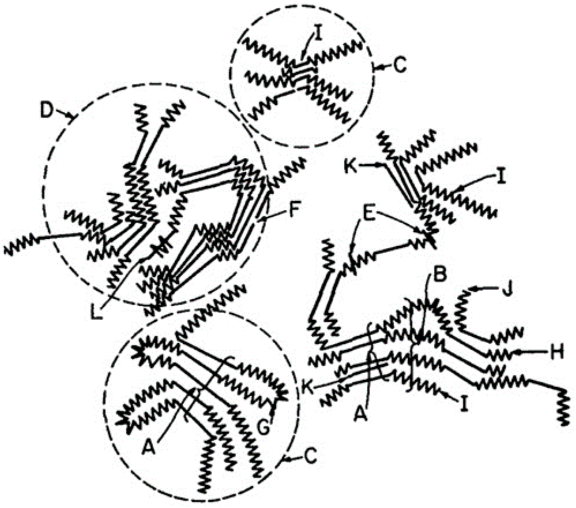


Figure 2. Monomeric, dimeric, trimeric, and tetrameric structure of a Venezuelian asphaltene molecule (reprinted from [28] with permission of the American Chemical Society).

X-ray diffraction spectra of solid asphaltenes [29–31] have shown two main peaks: one amorphous at a $2\theta = 19°$, mainly due to the aliphatic structures of the molecules, and a very wide diffraction peak at $2\theta = 26°$, corresponding to the Bragg angle scattering of the (0,0,2) planes of graphite, meaning that the graphite-like crystals of asphaltene aggregates are very small [4]. As reported by Yen et al. [30] based on the half-width of the diffraction peak, they estimate the graphite-like structure size in the order of 2–5 nm with an average of five-unit sheets (see Figure 3).



A: Crystallite, B: Chain bundle, C: Particle, D: Micelle, E: Weak link, F: Gap and hole, G: Intracluster, H: Intercluster, I: Resin, J: Single layer, K: Petroporphyrin, L. Metal

Figure 3. Yen model of solid asphaltenes (reprinted from [28], with permission of the American Chemical Society).

Asphaltene aggregation is still maintained in solvent, where they associate to form the so-called “micelles” [14,32–35] whose size is principally determined by the solvent nature, asphaltene content, and temperature [28,29,35]. Asphaltene graphite-like stacking of the molecules has as consequences a high degree of electron delocalization, giving an overall negative charge [27,36] a permanent electrical charge [37], and a dielectric constant between 5 and 7 [38–40]. Finally, asphaltene association also has particular effects on the rheological behavior of bitumen [41–43]. A more detailed study on the asphaltene nature can be found in [44].

1.2.2. Saturates

The saturated components in bitumen typically are within 0–15 wt% of the overall fraction. From a chemical point of view, saturates are complex mixtures of polyalkyl structures in which straight chain paraffins prevail as shown by FTIR measures [21]. Saturated fractions from blown bitumen are richer in long-chain paraffins than those from straight-run bitumen [45]. The saturate fraction is a mixture of pure aliphatics (linear and cyclic) [4]. As the content of saturates increases a decrease in the complex shear modulus and an increase in the phase angle of bitumen is expected because the saturate fraction is the lightest part of the maltenes, whereas the latter are a liquid part of bitumen which is complemented with solid asphaltenes [45,46].

1.2.3. Resins

Resins are dark brown solid (or semi-solid) compounds characterized by particle sizes of 1–5 nm, soluble in n-heptane, and structurally and compositionally similar to asphaltenes, except for a lower molar mass [47]. Resins are present in an amount ranging from 30 to 45 wt% and sometimes can be more polar than asphaltenes, but with less condensed aromatic rings [17]. Their polar nature enhances the adhesive properties of bitumen, but their principal role is as dispersing agents for the asphaltene macromolecular structures and oils, which are mutually insoluble. When bitumen is oxidized, resins gain oxygen molecules and the similarity of their structure to asphaltenes is enhanced. The bitumen characteristics are determined largely by the resins' asphaltene ratios [48].

1.2.4. Aromatics

Aromatic oils are dark brown viscous liquids containing low molecular weight aromatic compounds. They have a slightly aliphatic carbon skeleton with lightly condensed aromatic rings and a molar mass ranging between 300 and 2000 g/mol. Aromatic oils make the highest fraction (40–65%) of bitumen. They have a high solvent power relative to high molecular weight hydrocarbons. Together with saturated oils they are considered as the plasticizing agents of bitumen [17].

2. Bitumen Polymers

Polymers are macromolecules synthesized through chemical reaction between smaller molecules (monomers) to form long chains. The physical properties of the resulting polymer are determined by the chemical structure of the monomers and by their sequence inside the polymer. A combination of two different monomers that can be in a random or block arrangement gives a so-called copolymer. Polymers include a broad range of modifiers with elastomers and plastomers being the most commonly-used types. Polymer-modified bitumens (PmBs) are produced by the mechanical mixing or chemical reactions of a bitumen and one or more polymer in a percentage usually ranging from 3% to 10%, relatively to the weight of bitumen. In the first case, the mixtures are said to be simple, because no chemical reactions occur between the two partners in the system. In this case, the polymer is considered as a filler which gives specific properties to the mixture. In the second case, the mixtures are said to be complex, because chemical reactions or some other interaction occurs between the two partners in the system [49].

Modified bitumens are characterized as a two-phase system: bituminous, prevalently as asphaltenic matrix, and polymeric matrix, which has been investigated from two different points of view.: (1) the complex interaction mechanism between bitumen and additive and (2) the influence of different type of bitumen modifiers aiming to study the rheological performance characteristics, temperature sensitivity, morphology, thermal behavior storage stability, and aging of the resulting PmBs.

From a bitumen/polymer interaction mechanism point of view, according to Polacco et al. [50], polymer modification results in a thermodynamically unstable but kinetically stable system in which the polymer is partially swollen by the light bitumen components (maltenes) and can swell up to nine times its initial volume [51]. Competing for bitumen's light fractions, polymers tend to induce the micelles aggregation of the asphaltenes or to increase their degree of association, according to the nature of the original bitumen. At high temperatures, a relatively low viscosity of the melted micro-heterogeneous polymer-modified bitumen allows the substances with similar structure and polarity to form their domains: the swollen polymers and the asphaltenes. However, the thermodynamic instability of this system induces a phase separation (or sedimentation) under the influence of the gravitational field. Therefore, associated asphaltene micelles can settle to the bottom of the blend during static hot storage. According to this mechanism, the degree of phase separation of polymer modified binders can be influenced by storage conditions such as temperature and time. As shown by Lu et al., the phase separation will mainly be governed by the nature of the base bitumen and the characteristics and content of the polymer [8]. To date, different types of additives and polymers have been used for bitumen modification [52]. Table 1 summarizes the most common types of additives used as bitumen modifiers.

Table 1. Examples of additives used to modify bitumen (reconstructed from [52] with the permission of Thomas Telford).

Type of Modifier	Examples	Abbreviation
thermoplastic elastomers	Styrene–butadiene elastomer	SBE
	Styrene–butadiene–styrene elastomer (linear or radial)	SBS
	Styrene–ISOPRENE–STYRENE elastomer	SIS
	Styrene–ethylene–butadiene–Styrene elastomer	SEBS
	Ethylene-propylene-diene terpolymer	
	Isobutene–isoprene random copolymer	IIR
	Polyisobutene	PIB
	Polybutadiene	PBD
	Polyisoprene	PI
latex	Natural rubber	NR
thermoplastic polymers	Ethylene–vinyl acetate	EVA
	Ethylene–methyl acrylate	EMA
	Ethylene–butyl acrylate	EBA
	Atactic polypropylene	APP
	Polyethylene	PE
	Polypropylene	PP
	Polyvinyl chloride	PVC
	Polystyrene	PS
thermosetting polymers	Epoxy resin	
	Polyurethane resin	PU
	Acrylic resin	
	Phenolic resin	
chemical modifiers	Organometallic compounds	
	Sulfur	S
	Phosphoric acid, polyphosphoric acid	PA, PPA
	Sulfonic acid, sulfuric acid	
	Carboxylic anhydrides or acid esters	
	Dibenzoyl peroxide	
	Silanes	
	Organic or inorganic sulfides	
	Urea	
recycled materials	Crumb rubber, plastics	
fibers	Lignin	
	Cellulose	
	Alumino-magnesium silicate	
	Glass fibers	
	Asbestos	
	Polyester	
	Polypropylene	PP
adhesion improvers	Organic amines	
	Amides	
anti-oxidants	Phenols	
	Organo-zinc or organo-lead compounds	
natural asphalts	Trinidad Lake Asphalt	LA
	Gilsonite	
	Rock asphalt	

In Table 2 are summarized the most common used modifiers found in the literature, which are discussed in this paper.

Table 2. Different categories of polymers mainly used in bitumen modification.

Thermoplastics Polymers (see Section 2.1)	Polyethylene (PE) Polypropylene (PP) Ethylene-Vinyl-Acetate (EVA) PVC EBA
Thermoplastic Elastomers (see Section 2.2)	Styrene-Butadiene-Styrenhe-Block copolymers (SBS) Styrene-Isoprene-Styrene-Block copolymers (SIS)
Thermosets (see Section 2.3)	Epoxy resin Polyurethane resin Acrylic resin Phenolic resin
Natural and Synthetic Rubbers (see Section 2.4)	Styrene-Butadiene rubber (SBR) Natural rubber Polydiolefins Reclaimed Tire rubber
Bitumen Chemical Modifier (see Section 3)	Sulphur (S) Polyphosphoric acid (PPA) Reactive Polymers Maleic Anhydride (MAH) Nanocomposite Modifiers
Warm Mix Asphalt methodology (see Section 4)	

Each of these groups associate with different pros and cons as a bitumen additive. In addition to the large group of polymers, other bitumen modifiers, such as polyphosphoric acid (PPA), sulfur, maleic anhydride, and different kinds of clays, have been introduced and experienced, in this respect, some success.

2.1. Thermoplastics Polymers

Polyolefinic plastomers, also known as thermoplastics, whose category includes: Polyethylene (PE), polypropylene (PP), ethylene vinyl acetate (EVA), ethylene butyl acrylate (EBA), and polyvinyl chloride (PVC). Polyethylene which can be found in in three forms; low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE) are the most common plastomers. The use of plastomers as polymers to obtain PmBs arose as a consequence of the high costs of the styrenic polymers and the degradation phenomena due to their unsaturations. On the contrary, polyolefinic plastomers have a low cost and high availability presenting also higher stability than styrenic ones. Polyolefin polymers addition generally increases the bitumen stiffness and a good rutting resistance [53,54]. For these reasons plastomers play a leading role in PmBs in which they represent about 15% of the reference market. Reclaimed polyethylene is recovered from low-density domestic waste PE carry bags. Punith and Veeraragavan investigated an 80/100 paving-grade bitumen with different PE ratios [55]. The blends were tested using Hamburg wheel track tests, resilient modulus tests, an indirect tensile test, and an unconfined dynamic creep test. The results analysis showed that the PE-modified asphalt mixtures exhibited better performance characteristics than conventional mixtures. Even though polyethylene and polypropylene are the most common plastomers used, their non-polar nature results in compatibility problems with bitumen also sharpened by their tendency to crystallize which deeply restricts the interaction with bitumen [4,56]. In addition to compatibility problems of thermoplastics, these kinds of polymers also failed to increase the bitumen elasticity [53]. In an attempt to avoid the problems of compatibility and crystallization, other kinds of thermoplastics have been introduced. Principally, these modified polymers are obtained by inserting acetate groups, producing ethylene vinyl acetate (EVA) with vinyl acetate group content higher than 14%, ethylene methyl acrylate (EMA), and ethylene butyl acrylate (EBA). Esters groups of these polymers have the double advantage of increasing the polarity and reducing their crystallization tendency, disrupting the closely packed crystalline microstructure [50]. Both factors increase the bitumen compatibility and storage stability of the blend. In general, relative to the compatibility of plastomers with the bituminous matrix, it is believed that the higher the ester fraction is, a lower crystallinity is achieved. However, the crystallinity degree must be carefully balanced. If the crystallinity degree is to low, the lattice formed tends to be disrupted early after the crystals are interlocked with the bituminous fraction. In the EVA case, the optimal crystallinity degree is obtained using vinyl-acetate percentage ranging from 14% to 28%. However, despite the enhanced properties obtained by using EVA and other similar polymers, like compatibility, the problem of elastic recovery of polymer-added bitumen still remains [50,53,57]. Furthermore, the glass transition temperature of EVA which is dependent on the acetate content is not low enough to improve significantly the low-temperature properties of bitumen [58]. In this respect, Ameri et al. demonstrated that bitumen resistance to low-temperatures cracking can be increased by an amount of added EVA ranging between 2% to 4%, whereas it is decreased adding about 6% of EVA [59].

2.2. Thermoplastic Elastomers Modified Bitumen

Thermoplastic elastomers can resist permanent deformation over stretching, and elastically recovers once the load is removed [53,60]. Generally, thermoplastic elastomers used as modifiers are block copolymers of mono- or di-olefins. As mono-olefin unit the styrene molecule is used as mesomer, whereas as diolefin the butadiene or isoprene unit are normally used. The corresponding elastomers are called styrene butadiene styrene (SBS), styrene isoprene styrene (SIS), styrene-ethylene/butylene-styrene (SEBS).

Thermoplastic elastomer structure is generally linear and is characterized by weak inter-chain linkage. However, radial SBS copolymer are widely used as a bitumen modifier. Figure 4 represents the linear and radial SBS structures.

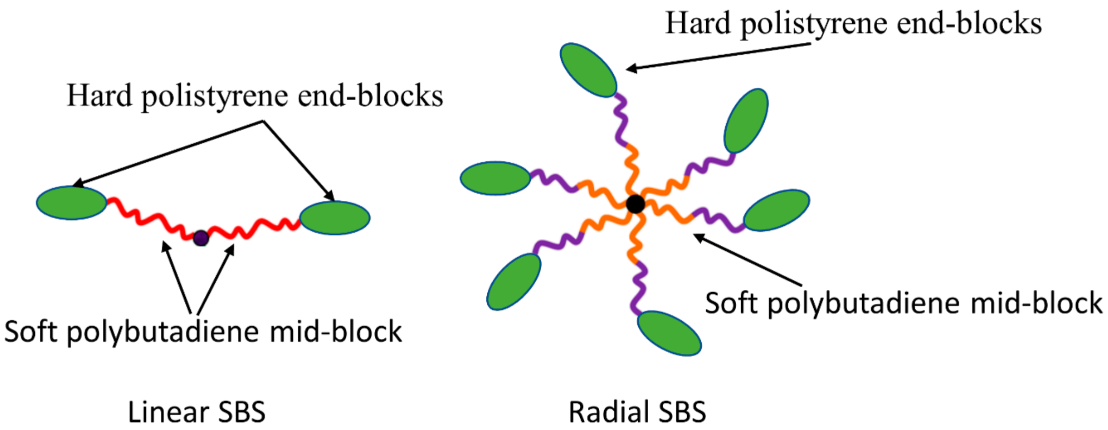


Figure 4. Representation of linear and radial SBS (reconstructed from [61] open access).

As can be seen in Figure 4 the linear polymer is characterized by two polystyrenic blocks linked to a two-polybutadiene block, while in the radial structure polystyrene blocks make a radial configuration around the polybutadiene block. This structure distinction is decisive because it characterizes the final performances of the blend. It has been noted that radial structure offers a higher system stability and a better redistribution of the elastic and viscous components of bitumen. The elastic and sturdiness feature of styrenic elastomers are due to a three-dimensional lattice formed by the physical interlocking of the molecules. The three-dimensional vertexes of the lattice are formed by polystyrenic blocks, which form separated domains in a rubber matrix formed by polybutadiene units. A schematic representation is shown in Figure 5.

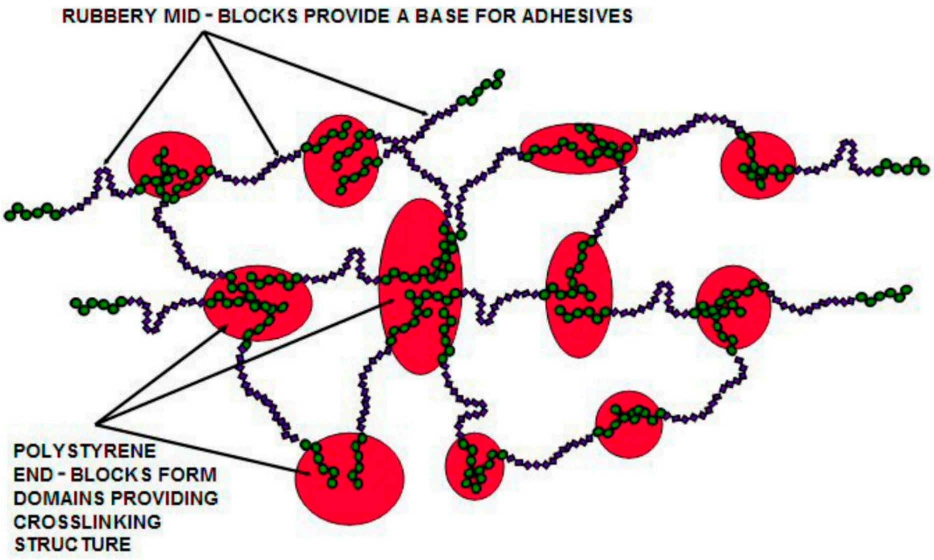


Figure 5. Schematic representation of styrene-butadiene block copolymer morphology (reprinted from [62]).

Polystyrenic blocks are responsible for the sturdiness of the polymers while polybutadiene blocks give elasticity. At temperatures above the glass transition of polystyrene (Tg = 100 °C) the latter softens with a consequent weakness of the PS domains. This allows an easier bitumen treatment. Upon cooling to room temperature, styrenic blocks reaggregate to re-form rigid domains restoring sturdiness and elasticity. Once SBS polymer is added, some interactions happen between the bitumen and SBS. Polystyrene blocks swell by absorbing light components of bitumen, which causes the hardening of the bitumen [63,64].

The repeatedly reported excellent properties, relatively good dispersibility in bitumen (dependent on the base bitumen composition), and acceptable cost have made SBS popular as a bitumen modifier. Many studies showed that the addition of SBS to the bitumen increases the softening point, decreases the penetration slightly, lessens the thermal susceptibility, increases the viscosity and decreases the Frass breaking point. It has also been observed that SBS moderates the increasing of stiffness due to the oxidation process simulated by short and long-term aging maintaining almost unaltered virgin bitumen properties also following RTFOT (Running Thin Film Oven Test) treatments.

The SBS concentration plays a fundamental role in polymer-added bitumen properties. Bitumen modification can be done by adding up to 7% of elastomers and, in some cases, different polymers can be used contemporarily. For soft and medium modifications polymer quantities are less than 4.5% (about 3% for soft modification and 4.2% for medium modification). For hard modifications added quantities are higher than 5%, while at low concentrations, SBS is dispersed as a discrete phase in bitumen, increasing the SBS concentration results in a phase inversion and two interlocked continuous phases are obtained: the bitumen rich phase and SBS rich phase typically shown in Figure 6. The latter is characterized by two sub-phases: one formed by a swollen polybutadiene matrix and polystyrene domains [63].

In spite of many proven benefits regarding the use of SBS copolymers for bitumen modification, they are still far from perfect. For example, the compatibility between bitumen and SBS is not always that good and storage instability of SBS modified bitumen was reported even for bitumens containing a low quantity of polymer [66–68]. In other words, the same level of compatibility may not be obtained with different base bitumen as in the example shown in Figure 7. In this respect, Airey has observed a competition between thermoplastic elastomers and asphaltenes to absorb the light components of bitumen in SBS/bitumen blends [64]. An insufficient amount of light components induces phase separation in modified bitumen. It was also noted that to produce a compatible and stable SBS modified bitumen a high aromatic content in the latter could be helpful [69]. In this respect, it has been observed that an improvement in compatibility between SBS and some bitumens with low aromatic content could be achieved by the addition of aromatic oils [65]. However, too high an aromatic content (70–80%) in modified bitumen can lead to swelling and anti-plasticization (i.e., an increase in its glass transition temperature) of some polystyrene blocks [70], which is not good for the resulting properties of the modified bitumen. Lu et al. concluded that for the bitumens containing 50–60% of aromatic components, blends with linear SBS provide greater stability than those with radial SBS copolymer [71].

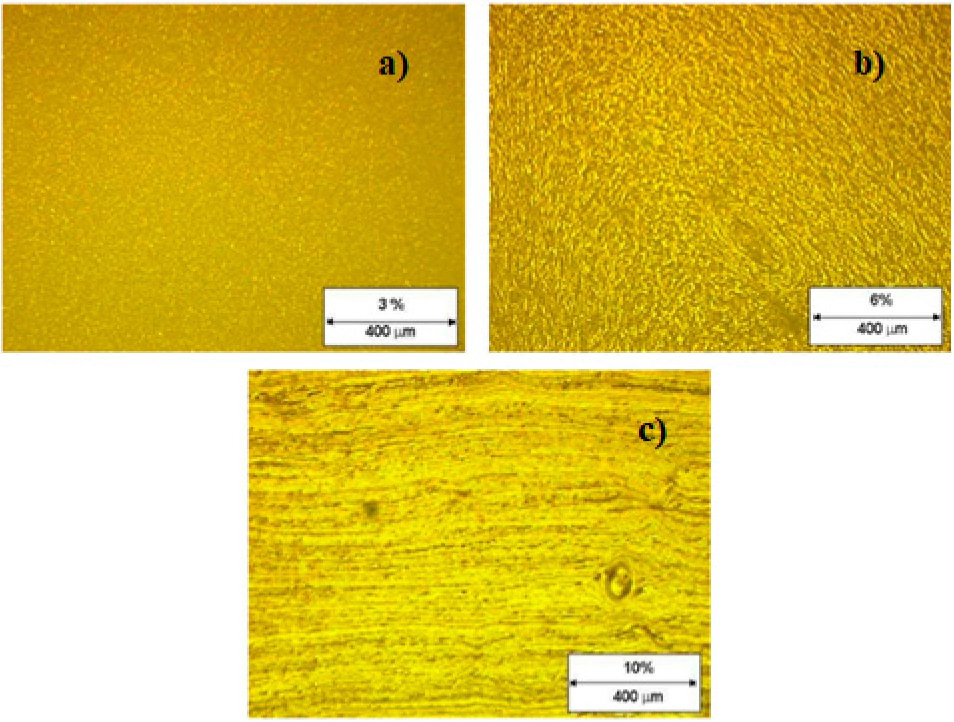
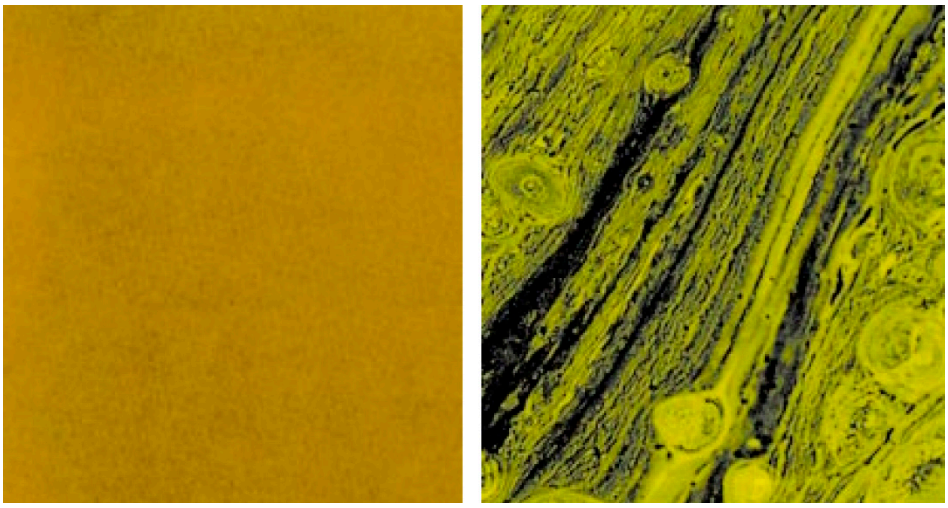


Figure 6. Dispersion of: (**a**) 3%, (**b**) 6%, and (**c**) 10% (*w*/*w*) of linear SBS obtained by fluorescence microscopy (reprinted from [65] with the permission of the American Chemical Society).



(**a**) (**b**)

Figure 7. (**a**) A compatible system with 4% SBS and (**b**) an incompatible system with 4% of SBS content (reprinted from the Shell Bitumen Industrial Handbook with permission of SHELL Publisher).

In addition to polymer chemical structure and concentration, it has been shown that the molecular weight of the polymer is also of paramount importance to bitumen/polymer compatibility. It has been shown that, an increase in molecular weight decreases entropy and blend stability. In this respect, linear and radial SBSs with similar S/B ratios were used by Lu et al. to study their respective blend stability. It has been observed that the use of the linear SBS produces a higher-stability blend than the radial one. This was ascribed to the lower molecular weight of the linear SBS used than the branched one. However, as Polacco et al. declares it is doubtful that a significant difference would have been observed if the linear and branched copolymers had similar molecular weights due to differences in molecular structure [46].

2.3. Thermosets

Thermosetting plastics (TP)—two liquid compounds (resin and hardener) — are first blended together and then with the bitumen a few seconds before application as surface coating/surface dressing (main use) or before mixing with aggregates for the production of hot asphalts (occasional use) [72]. Thermosetting plastics are polymers that turn into a solid state while heated or impose hardness. Before hardening, TP molecules have a linear structure, the same as thermoplastics molecules, but the size of their molecules is significantly smaller. TP molecules are chemically active. They contain either double (unsaturated) bonds or other chemically active groups. Therefore, under certain conditions (at heating, irradiation, or adding hardeners) thermosetting molecules react with each other and form a continuous network. Epoxy, phenol-formaldehyde, carbamide, polyester, silicone, and other resins belong to TP [73]. It has been shown that when epoxy thermosets polymers are blended with bitumen the modified bitumen displays the properties of the epoxy rather than those of the bitumen [74]. Since the epoxy bitumen presents the properties of the thermosetting polymer, the available time to use the modified bitumen is limited and is determined to a great extent by the mixing temperature. The higher the temperature, the shorter is the time of use. After producing, the thermosetting bitumen begins to 'cure' and increase its strength (hardens) once it is applied. The curing time is according to ambient temperatures. The higher the ambient temperature, the longer is the curing time. Once curing is completed, future temperature increase, which would soften the conventional bitumen, does not affect the hardness of the thermosetting bitumen at all. The completely cured bitumen is designated as an elastic material having no viscous behavior. Even though the PmBs with thermosetting plastics have relatively high adhesion to the mineral particles and great strength they are not common for paving applications. This is because firstly, when entering these polymers, owing to the imposed hardening, the technological properties of PmB are almost immediately deteriorated; secondly, the rigidity of the PmB is increased at low temperatures, which results in increased thermal sensitivity; thirdly, the use of TP complicates the system and raises its price; and finally, the effectiveness of thermosetting plastics appears usually at their large quantities in bitumen (more than 10 wt%). Asphalt mixtures produced with thermosetting polymer-modified bitumen have excellent adhesive ability, excellent resistance to deformation, excellent fatigue performance, and high stiffness modulus.

2.4. Natural and Synthetic Rubber

2.4.1. Natural Rubber

Natural rubber polymer could be easily synthesized through the chemical reaction of isoprene molecules. The resulting compound, the cis-1,4-polyisoprene with a chemical formula of $(C_5H_8)_n$ with high molecular weight is analogous to natural rubber [75,76]. In each repeated unit of polyisoprene, the double bond presence makes the polymer easily undergo a vulcanization process. This consists in the addition of sulfur to change the properties of natural rubber into a thermoset [77]. From a physical point of view, the presence of complex molecular chains of polyisoprene gives natural rubber a large elasticity and resilience characteristics [78]. For practical application of natural rubber, vulcanization is needed. However, in this process rubber creates disulfide bonds between chains, limiting its degree of freedom and the chains speedily tighten. Thus, the rubber is harder and less extensible because of an increasing in elastic force [79].

Natural rubber latex has been applied in the bitumen industry for over 30 years and is perceived to have potential for improving bitumen binder performance by improving thermal sensitivity, flexibility, stability, and stripping. In terms of thermal sensitivity, while at low temperatures it helps to dissipate the developed stress, preventing asphalt concrete cracking, at high temperatures it acts as a membrane, controls the asphalt flow, enhancing shear resistance [80]. In addition, its inherent elastomer properties proved that natural rubber latex has great potential for improving the long-term pavement performance of asphalt concrete [81].

It has been found that rubberizing asphalt concrete not only increases the rut resistance, but also enhances fatigue life with the increase in resilient modulus [82,83]. In addition to improving the mechanical and performance properties of asphalt concrete, in a study using both the Marshall method and a gyratory compacter it has been shown that natural rubber decreases the optimum binder content in asphalt concretes, increasing its density and stability [84]. From another point of view, liquid natural rubber (LNR) was found to be more efficient than latex for the aim of modifying bitumen binders. This is mainly because LNR blends easier with a binder, which results in a homogeneous binder [85]. In this form, natural rubber has more benefits compared to its conventional form, and the properties of the blend are comparable to those produced with synthetic rubbers.

Despite the benefits regarding the use of natural rubber in bitumen binder modification, there are some drawbacks that limit its use on a large industrial scale. Natural rubber is a highly valuable biomaterial compared to other biopolymers, hence natural rubber has been commercialized into synthetic rubber. This is mainly because of the huge difference between the available produced amount and the demand. From another point of view, even if several studies showed some benefits about the bitumen binders modified with natural rubbers for paving applications, there are still some doubts regarding to asphalt concrete performance and mechanical properties throughout the performance temperature range [86,87].

2.4.2. Synthetic Rubber

Synthetic rubber is a man-made rubber which is produced in manufacturing plants by synthesizing it from petroleum and other minerals. Synthetic rubber is basically a polymer or an artificial polymer. It has the property of undergoing elastic stretch ability or deformation under stress, but can also return to its previous size without permanent deformation. Styrene butadiene rubber (SBR), polyisoprene, and polybutadiene, polychloroprene, and tire rubber are some of the synthetic rubbers commonly used today. From the mentioned categories, synthetic rubber obtained from end-of-life tires (ELTs) are common for producing rubberized bitumen binders for both paving and industrial application. To date many studies have investigated synthetic rubbers from different points of view. From these studies, it can be concluded that many factors can influence the performance and mechanical properties of rubberized binders including: the size and content of rubber [88–90], the chemical structure [91,92], particles surface properties (ambient granulating or cryogenically crushed tire rubber) [93], blend production method and temperature [94,95].

Among the aforementioned factors, probably the most important one is the optimum percentage of rubber in the binder. Many research works have been conducted comparing the performance and mechanical properties of mixtures containing different amounts of rubber. However, it greatly depends on the application method (dry or wet), when it is used in asphalt mixtures and the characteristics of the base binder. Regarding rubberized bitumen, ASTM D6114 defines asphalt rubber (rubberized bitumen) as material consisting of the virgin binder and a minimum of 15% crumb rubber (by the weight of total blend) [96]. In addition, many studies concluded that while a low rubber content, around 4% (to the weight of bitumen), has almost no effect, or at least no significant effects on the performance and mechanical properties of the binder, more than 20% was found to be unsuitable.

3. Bitumen Chemical Modifiers

Systematic investigation of mechanical, rheological, and aging properties, temperature sensitivity, morphology, and thermal behavior of different PmBs has shown some advantages and drawbacks [6,97–111]. First of all, it has been shown that polymer modification improves some of the properties of bitumen, such as better elastic recovery, higher cracking resistance at low temperatures, and higher rutting resistance at high temperatures [96,97,102]. Secondly, some drawbacks have been observed, such as thermal instability and PmB's phase separation problems [68,79]. The first attempts to overcome the PmB's drawbacks were started in the early 1990s, when Giavarini et al. claimed that PmBs could be stabilized by adding polyphosphoric acid (PPA) [112]. They also believe that PPA could help to improve storage stability of polypropylene-modified bitumens by changing the bitumen structure from sol to gel. From then, various attempts have been made to remove the drawbacks of the PmBs. In addition to physical blends of bitumens and polymers, another way to improve the binder properties is through chemical modification, which uses the chemical agent as an additive to modify the characteristics of pure bitumen.

To date many chemical agents have been introduced for the target of bitumen modification, such as: organo-metallic compounds [113,114], sulfur (S) [66,115–121], polyphosphoric acid (PPA) [122–124], sulfonic acid [125], carboxylic anhydrides [126–128], silanes [129,130], thiourea dioxide [131], nanocomposite-modified bitumen [132–140], and reactive polymers [141–155]. However, from the above-mentioned chemical compounds only a few of them have been used practically. Sulfur (S), polyphosphoric acid (PPA), reactive polymers, maleic anhydride (MAH), and polymer/clay or polymer/layered silicate (PLS) nanocomposites are the most common chemical agents.

3.1. Sulfur Modifier

The early applications of sulfur as a modifier involve its use in large quantities without other materials, such as polymers [115,116]. Some commercial products, named as "sulfur extended bitumen" (e.g., Shell Thiopave®, Shell Brands International AG, Baar, Switzerland [52]) are obtained using this methodology, in which many parameters should be considered. Among the factors that control the reaction between sulfur and bitumen, the mixing temperature plays a determinant role. Below 140 °C sulfur can be incorporated into the bitumen molecules or can form hydrogen sulfide via dehydrogenation reaction. Higher temperatures allow C–S bond formation promoting a dynamic vulcanization of bitumen. It induces bridge formation within aromatic and naphthenic components modifying the chemical composition and colloidal structure of bitumen. Some authors also suggested that sulfur could self-polymerize when added to the binder [156]. However, nowadays, sulfur is added in very small quantities to bitumen where the polymers are the main modifiers. Some studies [120,121] have also shown that sulfur vulcanization made the PmBs more susceptible to oxidative aging and concluded that it is not a good idea to use sulfur as a sole additional modifier.

The first studies that used a small quantity of sulfur to increase the polymer/bitumen interaction date from the early 1970s when Petrossi proposed a method for preparing a rubber-modified bitumen. He blends bitumen with rubber (natural or synthetic) at 145 to 185 °C and after slightly reducing the temperature (125 to 160 °C) added 0.3 to 0.9% (by the weight of rubber) of sulfur. A free-radical vulcanization accelerator is also added to aid vulcanization [157]. Later on, Maldonado [158] proposed a different procedure starting with the preparation of a homogeneous PmB by stirring bitumen and SBS for 2 h at 130 to 230 °C and then adding 0.1 to 3 w/w% of sulfur and stirring for another 20–60 min. However, the exact reaction of sulfur-polymer-bitumen system is not completely clear. It was supposed that sulfur crosslinks the polymer molecules and links polymer and bitumen through sulfide and/or polysulfide chemical bonds. This assumption comes from the well-known process of vulcanization of unsaturated rubbers.

Further investigation on this topic was carried out by Wen et al. [117,118]. They prepared a low-viscosity homogeneous bitumen/SBS/sulfur blend by heating it to a temperature of 120 °C. This limits the occurrence of reactions between bitumen and sulfur or the vulcanization of SBS. Finally, an increase in the temperature in the range of 150 to 180 °C allow these reactions to start. Possible evidence of this fact is that, unlike the two binary systems, an increase of the torque to maintain a constant rpm for the ternary bitumen/SBS/sulfur blend was necessary. The authors also hypothesized a vulcanization of both the unsaturated rubber and the functionalized bitumen components by the aid of sulfur, which creates interconnections between the polymer and bitumen. It has been claimed that these connections increase blend storage-stability by linking the polymer with the bitumen components through covalent chemical bonds. Later, Martınez-Estrada et al. [159] reported more indirect evidence for vulcanization. In this study a detailed rheological characterization of bitumen/SBS/sulfur and bitumen/SB/sulfur blends was performed. The importance of the homogeneity of the blend before sulfur addition has been also highlighted. In this respect a fast vulcanization, and consequently a useless material, could be observed if a too early sulfur addition is carried out. An appropriate sulfur bridge distribution is also important for a good chemical compatibility. To avoid freezing the blend's morphology at an earlier stage, good polymer dispersion and swelling must be achieved before network formation. Finally, the risk of gelation must be avoided. An "anti-gelling" adjuvant with the formula R-X, where R is a $C_{2–50}$ monovalent organic radical and X is an acidic function (carboxylic, sulfonic, phosphoric) has been used. Other solutions were proposed by Chevillard et al. and Ho et al. [160,161].

Many studies have shown that the use of sulfur as modifier improves the properties of some PmBs. In this respect it has been shown that sulfur enhances the storage stability, the elasticity, the deformation resistance, and some rheological properties of the PmBs [66,119,162]. From the rheological point of view, PmBs added with sulfur show a "more elastic" behavior compared to the ones without sulfur [66,118,163]. However, the use of sulfur as a chemical modifier has shown some drawbacks. First of all, the reaction of sulfur with polymer modifiers is based on the chemical reactions between sulfur and the double bonds of the polymer, so the use of sulfur is limited to PmBs modified by unsaturated polymers. The risk of obtaining nonhomogeneous PmBs during the polymer and sulfur addition into bitumen, is due to the difficulty of distributing the sulfur throughout the mixture. Moreover, local over-vulcanization of the polymer was detected. Replacing elemental sulfur with a more bitumen soluble polysulfide like di-hydrocarbyl polysulfide, represents a possible solution to this problem [164]. However, the emission of the hazardous health gas hydrogen sulfide during preparation of the bitumen/polymer mixes is the main drawback to the use of elemental sulfur. Hydrogen sulfide could be generated during sulfur vulcanization through the abstraction of hydrogen atoms in both bitumen and polymer modifiers, especially at high temperatures [165–167]. Some researchers argued that the gaseous emission is relatively small and most manufacturers know how to deal with the associated risks and dangers. The use of other sulfur-based agents as alternatives to elemental sulfur was introduced to eliminate, or at least reduce, such emissions. Compounds like benzothiazole sulfonamides, di-thiocarbamates, thiuram sulfates, morpholine sulfates, and caprolactam sulfates. Zinc mercaptobenzothiazole, zinc oxide, and dithiodimorpholine, as well as compositions without elemental sulfur, such as mercaptobenzothiazole, zinc oxide, mixed polythiomorpholine zinc 2-mercaptobenzothiazole, and dithiodimorpholine, were reported [168–170]. Nevertheless, the undesired formation of hazardous hydrogen sulfide has been observed also using this sulfur source. Shell Oil Company [171] used a disulfide that does not release sulfur at high temperature mixing. It has been claimed that the disulfide, instead of a conventional source of free sulfur, enhances compatibility between the polymer and bitumen. Diaryl disulfides were firstly proposed. However, all these additives are so expensive that they have not, in general, been used commercially. Finally, the poor recyclability of sulfur PmBs is another problem with sulfur vulcanization. All these drawbacks limit the application of sulfur vulcanization in PmB.

3.2. PPA-Based Techniques

Among the different acids that can be used to improve bitumen properties through chemical modification, polyphosphoric acid (PPA) has been studied in numerous papers and patent publications [172–185]. From a chemical point of view PPA is an oligomer of phosphoric acid (H_3PO_4), with no free water, which may have more than 10 repeating units [122].

The bitumen modification of PPA appears to be a complex physico chemical process, and the resulting properties may be strongly dependent on the bitumen nature. The difficult investigation of the reactions between the bitumen molecules and PPA is due to the large number of molecules with different chemical structures and their possible interactions. In this respect, an NMR investigation has shown that PPA tends to revert to orthophosphoric acid after mixing with bitumen [123]. Orange et al. claim that PPA neutralizes polar interactions between the asphaltene molecules, by protonation of basic sites or through esterification [186]. Co-polymerization, alkyl aromatization of saturates, and so on are other classes of reactions that have been proposed. A more detailed description can be found in [4,122,186]. From a thermal and rheological point of view bitumen/PPA blends [185–188] have shown an increased high-temperature performance with no significant changes in the low-temperature ones. It has been also found that PPA can improve the storage stability of PmBs. Giavarini et al. [112] used three ethylene–propylene copolymers of different molecular weights (MWs) and crystallinity to modify four different bitumens. In all cases, at a minimum amount of 3 %wt. of PPA added polymer segregation showed a remarkable reduction.

However, it should be noted that this improvement could be dependent on many factors, like polymer type and the quantity of PPA, as shown recently by Zhang and Hu [189].

3.3. Reactive Polymer Modifiers

Reactive polymers, also known as reactive ethylene terpolymers (RET) because of their ethylene-based structure, are polymer-based compounds grafted with reactive groups derived from, glycidyl methacrylate (GMA), acrylic acid, etc. The use of these types of polymer has been introduced to increase the compatibility between polyolefin (e.g., PE, PP, etc.) and bitumen by creating covalent linkages. Polymer grafting is a good solution and often simple to realize because it involves a single-step melt process. However, a possible drawback is the uncontrolled and undesired crosslinking of unsaturated polymers because of the radical mechanism of the grafting. Therefore, saturated polymers, such as styrene-ethylene-butylene-styrene (SEBS), PE, PP, etc., are more suitable for this process.

Owing to acrylic functionalization, the use of reactive polymers showed some advantages, like increased polarity and reactivity. However, higher costs compared to the other types of polymers and gelation problems due to the rather high number of reactive groups on a single macromolecule are the mainly-reported disadvantages that have been observed. To overcame these drawbacks, the amount of RET that could be used is around 2 to 2.5% and, in many cases, is even lower than 1% by weight [143]. Owing to these problems RETs are not ideal as bitumen modifiers, because the overall effect on the performances can be quite poor [143,190,191]. Therefore, their use could be mainly for increasing the compatibility between bitumen and other polyolefins, as shown by Yeh et al [144]. In this respect, using differential scanning calorimetry (DSC), they demonstrated an improvement in the bitumen/polymer interactions relative to unfunctionalized PP. Recently, two poly(ethylenebutylacrylate-glycidylmethacrylate), known as Elvaloy®AM and Elvaloy®4170 (produced by DuPont, Wilmington, DE, USA), were blended with neat bitumen in order to study the blend storage stability [192]. After high-temperature storage a complete homogeneity of all the samples was observed. This indicates the use of RET basically guarantees the storage stability, although under severe conditions of temperature and storage time another study has shown the instability of the blend [193]. Low-density polyethylene (LDPE) was used to compare the storage stability properties of blends prepared by using LDPE before and after grafting with GMA [148]. As can be observed from Figure 8 the use of GMA-grafted LDPE shows a higher stabilizing effect than LDPE.

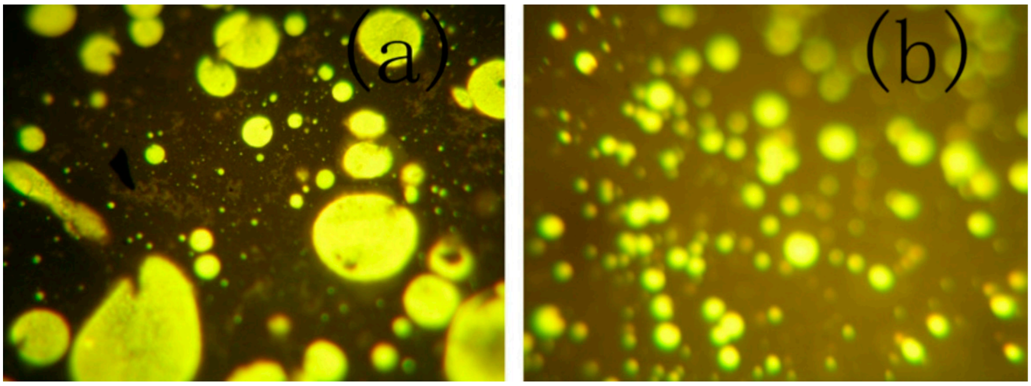


Figure 8. Fluorescence microscopy images showing the morphology of: (**a**) the LDPE and (**b**) GMA-g-LDPE blends (reprinted from [148] with permission of Elsevier).

Finally, a particular mention goes to silicon-based polymers like polyoxyalkylene with reactive silicon groups which form siloxane bonds by the silanol condensation reaction [194].

3.4. Maleic Anhydride

Maleic anhydride (MAH) is an unsaturated cyclic (five atom ring) compound with molecular formula $C_4H_2O_3$. It has been widely used as a bitumen modifier and bitumen-polymer compatibilizer. MAH-bitumen interaction is characterized by complex mechanisms (copolymerization with bitumen molecules [126] or Diels-Alder reactions [195,196]). Nevertheless, it has been shown that meaningful physical properties change of bitumen are induced by MAH. In this respect Nadkarni et al. [197] studied a bitumen containing different amounts of MAH in terms of dynamic mechanical analysis (DMA), melt viscosity, and softening point. The results have shown that the chemical modification of bitumen with MAH improves the cracking resistance at low temperature and cohesive strength at high temperature.

Chemical reactions between MAH and bitumens were also investigated by comparing the effects of MAH and the related di-acids and anhydrides such as succinic anhydrides (SAH). The results of FTIR and gas chromatography-mass spectroscopy analysis showed the presence of two acid groups (-COOH) for both MAH and SAH. This leads to the conclusion that the two anhydrides undergo ring opening to give the corresponding di-acid. Moreover, in the case of MAH, the disappearance of the double IR bond signal was noticed. This fact could be explained by its reaction (or coordination) with bitumen molecules [126].

From another point of view, several studies have shown that the rheological properties of the blends obtained by adding to a bitumen MAH, SAH and different di-acids follow the order: MAH > SAH ~ dicarboxylic acids > monocarboxylic acid.

These results suggest the hypotheses that the two carboxylic acid groups are able to link two bitumen molecules. The better result obtained by adding MAH to the bitumen was hypothesized to be due to the double bond of MAH that interacts by coordination or other bonding mechanism to the bitumen molecules creating an additional linking. However, a recent study has shown controversial results about the MAH-bitumen reaction. In this respect, new FTIR analysis has shown that the IR band due to the MAH ring was retained during the MAH-bitumen reaction [127]. This observation, leads to the hypotheses that both Diels–Alder and π–π charge-transfer mechanism are involved instead of a ring opening process. The π–π charge-transfer process was possible because of the polynuclear aromatic nature of asphaltenes which act as donors in the charge-transfer processes. However, although the high reactivity of MAH could be used to improve the bitumen properties by promoting its interactions with polymers, this high reactivity raises drawbacks related to its handling and storage. A solution to these problems is achieved by synthesizing a polymer–MAH in advance and then modifying the bitumen with this modified polymer, namely creating a reactive polymer (see Section 3.3). However, a further purification step is needed to eliminate unreacted MAH monomers, increasing the costs.

Recently Becker et al. [198], compared storage stability of PmBs prepared using SBS, SEBS, and two commercial SEBS-grafted MAH with different MAH content. SEBS-grafted MAH showed the best storage stability, although it did not improve significantly the rheological behavior of the binder.

3.5. Nanocomposite Modifiers

Polymer/layered silicate nanocomposite (PLS) (aka polymer/clay nanocomposites) has been, and are still, widely used in polymer science research. Layered silicate can improve the polymer properties, such as mechanical properties, heat resistance, decreasing gas permeability and flammability, and increasing biodegradability [199–201]. The most commonly used silicates for preparation of PLS nanocomposites are hectorite ($M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$) and montmorillonite (MMT; $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$) that belong to the same general family of phyllosilicates. As shown in Figure 9 they have a crystal structure made up of layers composed of two tetrahedrally-coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate.

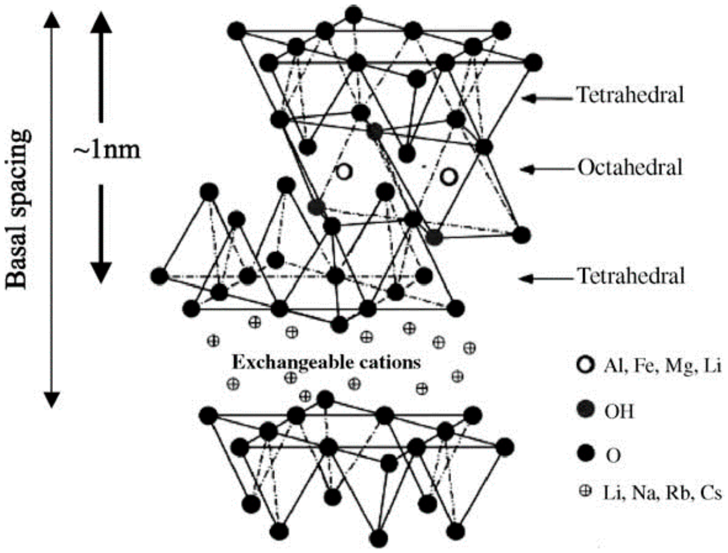


Figure 9. Structure of a 2:1 phyllosilicate (reprinted from [199] with the permission of Elsevier).

Due to the hydrophilic nature of layered silicates, it is very difficult to disperse them into polymer matrix and in most cases separation into two discrete phases takes place. The most common way to overcome this problem is to replace the interlayer cations (Na^+, K^+, etc.) with cationic surfactants, such as alkyl ammonium or phosphonium, preferably with long alkyl chains. The surfactants have a double role: (1) reducing the surface energy of the inorganic host and (2) improving the wetting characteristics of the polymer matrix. Additionally, their functional groups can react with the polymer matrix, and in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix [202,203]. Increasing interactions between the polymer and the layered silicate in PLS nanocomposites led to the dispersion at the nanometer level of organic and inorganic phases. As a result, nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally-filled polymers.

Furthermore, depending on the strength of interfacial interactions between the polymer matrix and layered silicate, three different types of PLS nanocomposites are thermodynamically achievable (see Figure 10):

I Intercalated nanocomposites: these are obtained by the insertion of few molecular layers of polymer into the layered silicate structure. From the crystallographic point of view this insertion occurs in a regular way.

II Flocculated nanocomposites: conceptually, this is the same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge–edge interaction of the silicate layers.

III Exfoliated nanocomposites: in these compounds the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on clay loading.

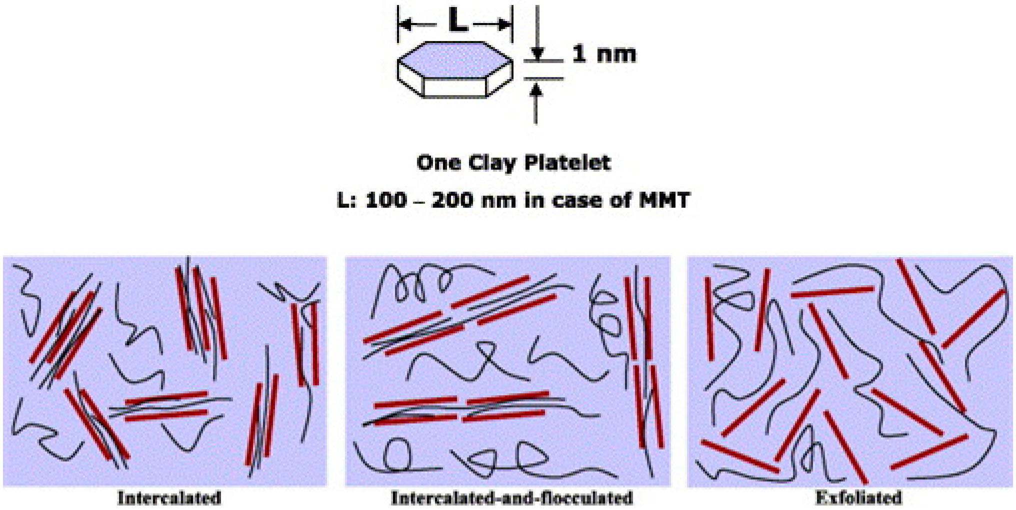


Figure 10. Illustration of three different types of polymer/layered silicate nanocomposites (reprinted from [199] with the permission of Elsevier).

The preparative methods of PLS can be divided into three main groups according to the starting materials and processing techniques. 1) From solution: the layered silicate is first swollen in a solvent of the polymer, such as water, chloroform, or toluene. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in PLS nanocomposite. 2) In situ polymerization: the layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step. 3) Melt intercalation method: this involves an annealing process, statically or under shear, of a mixture of the polymer and an organically-modified layer silicate (OMLS) above the softening point of the polymer. This method has great advantages over the other two. First, it is environmentally benign due to the absence of organic solvents. Second, it is compatible with current industrial process. The melt intercalation method allows the use of polymers which were previously not suitable for in situ polymerization or solution intercalation.

In several studies, clays were used as compatibilizer agents in polymer blends. In this respect, clay localizes at the interfacial bitumen-polymer region reducing the interfacial tension. As a consequence, the “minor phase-dispersed” particles lose the typical rounded shape they possess in the pure polymer blends, and a finer dispersion is obtained [204–213]. Based on this fact, the studies have been focused mainly on their effects on the compatibility between bitumen and polymers. As the results have shown a considerable increase in the bitumen/polymer compatibility, it has been suggested that using ternary bitumen/polymer/clay (BPC) systems, the PmB’s performances may be improved. In particular it has been claimed that the use of PLS in PmBs has mainly two effects: (1) improving the aging resistance of PmB with barrier properties of the dispersed clay platelets and (2) enhancing the storage stability of PmB by decreasing the density difference between polymer modifiers and bitumen [68].

The Bitumen–Polymer–Clay Ternary System

Among the three preparatory methods of PLS described above, melt intercalation is the one that can be easily applied to bitumen modification due to its compatibility with current industrial processes and with all types of thermoplastic polymers. Bitumen, polymer, and clay can be mixed in a single step known as physical mix (PM) (see Figure 11). Otherwise, two consecutive steps could be employed: (1) nano-composite preparation and (2) addition to a bitumen. Globally, the process is known as master batch (MB). The use of one (PM) or the other (MB) method is very important and can give different results.

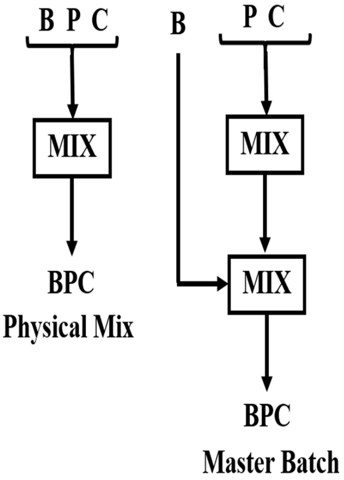


Figure 11. Schematic representation of the two mixing processes: physical mix and master batch (reprinted from [46] with the permission of Elsevier).

These two methods were applied and studied in different research works, in which different polymers and clays were reported for the production of bitumen/polymer/composites (BPC). SBS and kaolinite [132], SBS and organobentonite [214], poly(styrene-b-ethylene-b-butene-b-styrene) (SEBS) and kaolinite [133], and LDPE or EPDM and silica [134] were the primary compounds which have been studied. In all the previously reported cases, different ratios of polymer-clay nanocomposites were firstly prepared and successively added to bitumen. Storage stability, blend morphology, and mechanical and rheological properties of the BPCs were characterized. Tube tests to evaluate the storage stability of the blend were made. In all cases, storage stability was observed. To justify these results, it has been hypothesized that clays tend to reduce the density gap between the polymer rich phase (PRP) and bitumen asphaltene rich phase (ARP) by locating themselves preferentially in the PRP phase. However, this was not directly supported by experimental evidence.

In this respect, the recorded values of softening points are certainly consistent with this interpretation being considered as evidence. Ouyang et al. [133] lists the softening points of the top and bottom sections of the tube test for the bitumen/SEBS/kaolinite mixes (see Table 3).

As can be seen from Table 3, for a given SEBS content, the ΔS parameter whose magnitude is indicative of the blend stability (higher magnitude equals lower stability), decreases as clay content increases. Moreover, for the sample of 4% SEBS this difference become negative indicating that the Polymer Rich Phase (PRP) migrates toward the bottom of the tube. At high clay contents, negative values for the ΔS were obtained. This could be explained by considering that the polymeric rich phases become heavier than the asphaltenic rich phase (ARP). A balance of PRP and ARP densities obtained at well-defined clay amounts, inducing a storage stability. An LDPE-modified bitumen also has shown a similar effect [134]. However, storage stability is not simply due to a decrease in density difference between the PRP and ARP phases. Several studies have shown that compatibility between bitumen and polymer also plays a fundamental role [215]. Therefore, the improved storage stability can be ascribed mainly to two factors: decrease in density difference between the PRP and ARP phases and, to a greater extent, to a real bitumen/polymer compatibilizing effect. Furthermore, the preparation procedure also plays an important role. As can be seen from Table 3, the only mix found unstable during the high-temperature storage was prepared using the PM method. This, in accordance with the idea that the clay resides preferentially in the PRP leads to a conclusion that only with a pre-formed nanocomposite storage stabilization could it be achieved.

Table 3. SEBS/KC-modified bitumen storage stabilities at high-temperature (from Table 4 of [133] with the permission of Elsevier).

Formulation		**S (°C)**		
SEBS %(w/w)	SEBS/KC (w/w)	Top (S_t)	Bottom (S_b)	ΔS
3	100/0	53.0	50.0	3.0
3	100/50	52.5	52.8	−0.3
4	100/0	57.0	53.8	3.2
4	100/10	56.5	50.8	5.7
4	100/30	55.0	52.0	3.0
4	100/50	55.5	55.8	−0.3
4	100/50 [a]	59.0	52.0	7.0
4	100/70	52	52.5	−0.5
5	100/0	70.5	58.0	12.5
5	100/50	57.0	58.0	−1.0
6	100/0	85.0	67.5	17.5
6	100/50	59	60.5	−0.5

[a] Mix prepared using PM. $\Delta S = S_t - S_b$.

This point was confirmed by other researchers who studied different systems, such as a styrene-butadiene rubber (SBR) with a palygorskite- and organo-modified palygorskite clays [216]. This paper studied the storage stability of the blends and the importance of the preparation procedure. Polacco et al. [136] investigated the internal structure and nanocomposite nature of the blends. In this research a neat bitumen (NB) and SBS were modified with OMMT (Cloisite 20A, referred to simply as 20A) through melt mixing, obtaining two blends of bitumen/clay and polymer/clay: (1) SBS/20A, (2) NB/20A. Ternary blends were then prepared using both PM and MB methods: (3) NB/SBS/20A PM, and (4) NB/SBS/20A MB. Figure 12 reports the X-ray diffractometry (XRD) characterization, which was performed on virgin materials (bitumen, polymer, and clay) and blends. A comparison between the binary blend NB/20A and the 20A alone shows that the clay's interlayer spacing almost doubled. This was attributed to bitumen intercalation. A partial exfoliation of the stacks can also be seen. Moreover, storage tests showed the absence of phase separation, confirming a high degree of interaction between NB and 20A.

As shown by the XRD pattern, intercalated nanocomposites were also obtained in the SBS/20A binary blends. The interlayer spacing was found to be independent of the clay quantity, but it was lower than that of NB/20A blends. This suggests that the clay had higher compatibility with the bitumen compared to the polymer. Regarding ternary blends, XRD patterns show that both mixing processes (PM, MB) give intercalation with interlayer spacing equal to that obtained by mixing bitumen and clay without the polymer. This may indicate that the degree of intercalation is substantially determined by the bitumen molecules and is independent of the mixing sequence. This could be explained by considering that the polymer chains are present in a very small amount compared to the bitumen molecules and they interact with a limited amount of clay stacks. Therefore, polymer chains, even if already intercalated between some of the clay platelets, are not expected to inhibit the interactions between clay and the small and abundant bitumen molecules. On the contrary, the ability of the polymer molecules to intercalate the clay stacks is strongly influenced by the mixing sequence. Finally, once the clay-polymer interactions are established, bitumen molecules are not necessarily expected to substitute the polymer chains in clay interlayers. For these reasons the similarity in the XRD spectra does not necessarily mean a similarity in the internal structure of PM and MB mixes.

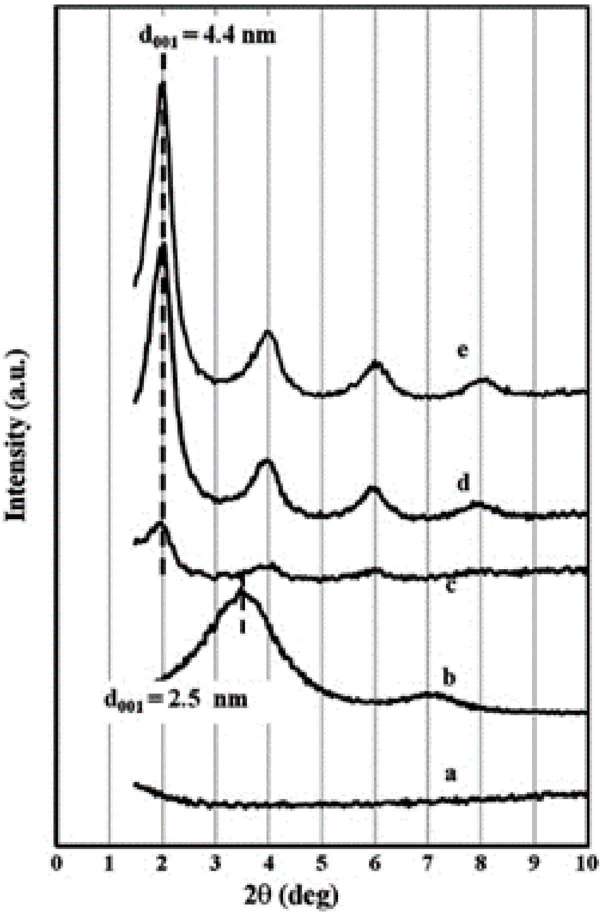


Figure 12. XRD pattern of neat bitumen, Closite 20A, SBS/20A, B/20A, B/SBS/20A (PM) and B/SBS/20A (MB) (reprinted from [136] with the permission of Elsevier).

From a morphological point of view, Figure 13 shows three different systems: (a) the binary NB/SBS blend, (b) NB/SBS/clay PM blend, and (c) NB/SBS/clay MB blend. As can be seen NB/SBS blend is characterized by a biphasic morphology, which results in high-temperature storage instability. The NB/SBS/clay PM blend still shows a biphasic pattern, but the smaller microdomains indicate an improved compatibility and stability of the system. A further improvement of the morphology is observed for the NB/SBS/clay MB blend, which has the canonical aspect of a perfectly compatible PmB pattern. In addition, Figure 13a,b show the important role of clay, which favors the contact between the polymer chains and those bitumen molecules that would otherwise be confined in the ARP. Clays acts as the substrate where polymer and asphaltene molecules come into contact, reducing the differences in composition between the PRP and ARP phases.

Later, Sureshkumar et al. [217,218] prepared different PmBs using EVA as a polymer and studied the effect of two different organoclays: 20A and another OMMT known as Dellite 43B (namely referred to as 43B). Figure 14 shows the fluorescence microscopy images of the blends studied.

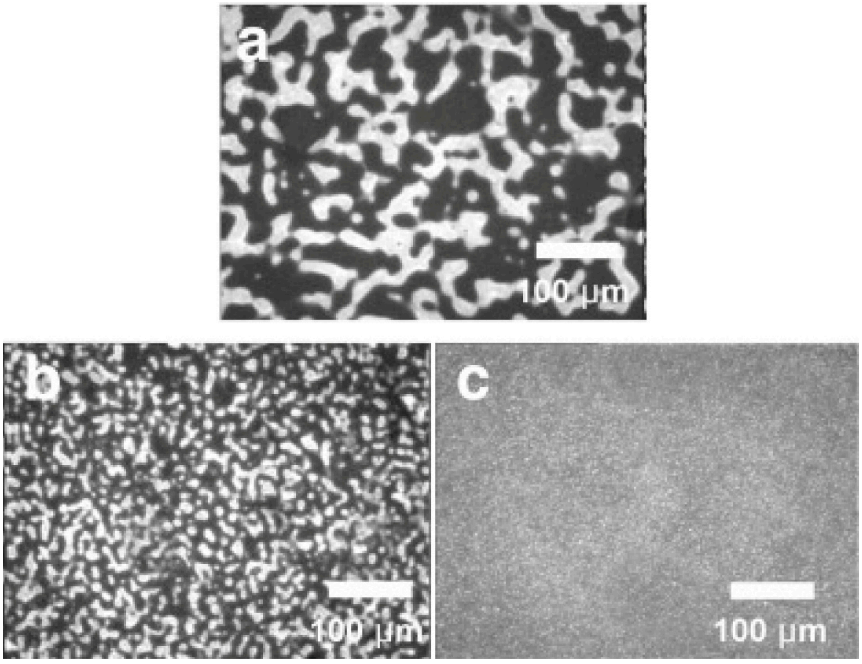


Figure 13. Fluorescence Images of (**a**) BA/SBS, (**b**) BA/SBS/20A PM, and (**c**) BA/SBS/20A MB (reprinted from [46] reprinted with the permission of Elsevier).

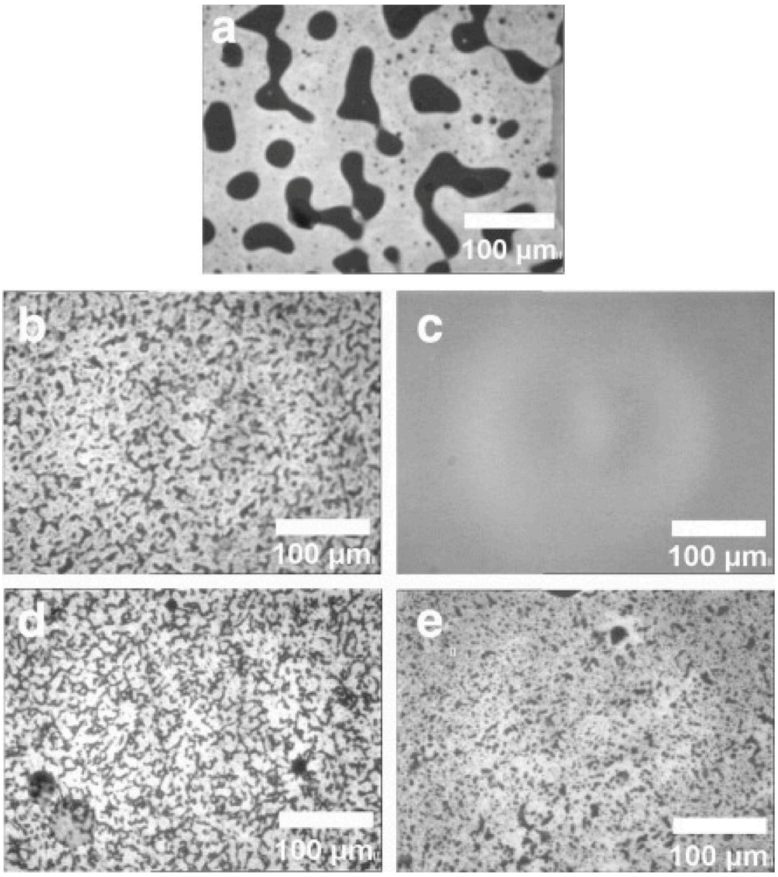


Figure 14. Fluorescence images of (**a**) BA/EVA, (**b**) BA/EVA/20A PM, (**c**) BA/EVA/20A MB, (**d**) BA/EVA/43B (PM), and (**e**) BA/EVA/43B (MB) (reprinted from Figure 1 of [217] with the permission of Elsevier).

The pictures show results similar to those described for SBS. However, clay 43B has a compatibilizing effect less pronounced than 20A. The differences observed among the blends prepared using PM or MB are reflected in the macroscopic behavior. Rheological tests have shown an improvement in thermo-mechanical properties of the ternary blend prepared using MB. Therefore, the MB procedure is preferable to the PM since it guarantees better homogeneity, stability, and mixture performance. However, the PM has the advantage of being simpler from a practical point of view because it involves a single step using classic paving equipment.

4. PmBs in Warm Mix Asphalt (WMA) Technology

A new kind of polymer-modified bitumen technology has been introduced in recent years. It combines the classic ones (PmB) with the warm mix asphalt technique (WMA). One of the methodologies employed to shift from hot mix asphalts to warm ones is based on the use of waxes. This is due to the fact that above their melting temperature, they act as plasticizers, while at low temperatures they crystallize and act as fillers [4,219,220]. While the PmB is well consolidated the WMA is relatively new, but rapidly growing, due to its economic and environmental advantages. Compared with classic hot mix asphalts (HMA), warm mix ones, in general, are characterized by lower fuel consumption and costs, lower production of greenhouse gases, fumes, and odors, which improve the environmental impact and working conditions, extension of haul distances, and good workability during laying and compaction [219]. Although naturally present as constitutive components of all crude oil products [221,222] and studied in the technical literature, where bitumen wax content [223–225], crystallization properties [226], chemical structure [227,228], and influences on bitumen and bitumen mixture properties [220,223,229–234] were analyzed, waxes affect the binder performances. For example, wax melting can soften bitumen at high service temperature, reducing rutting resistance of the pavement, while at low temperatures wax crystallization can increase stiffness and sensitivity to fatigue and thermal cracking [219,223,234]. Nowadays there is an increase development about warm polymer modified bitumen which can maintain the advantages of both technologies (WMA and PMB) although this is not an easy task because waxes used as warm modifiers reduce the high temperature viscosity while increasing the low temperature stiffness and polymers do basically the contrary [219]; simply adding the two modifiers does not guarantee the enhancement of bitumen properties like those obtained by adding single ones. For example, a ternary mixture bitumen/polymer/wax has significantly different properties (like viscoelasticity) from those predictable by superposing the effect of wax and polymer only and the final warm effect and performances of the binder will be determined by the interactions between the three components. Scientific studies on this ternary mixture are still limited. Edwards et al. [235] for example, studied the addition of paraffinic waxes to a polymer-modified mastic bitumen, showing that a 4% wax addition improves workability of the mastic bitumen without affecting its performances. Kim et al. [236,237] studied the artificial long- and short-term aging of a PmB mixed with wax additives. Other studies analyzed the properties and pavement performance, compacting temperatures, long-term performance [238], fatigue characteristics [4], thermo-mechanical properties [239], and viscosity and rheological properties [240]. Rossi et al. [219] conducted a preliminary investigation by mixing bitumen, SBS, and three typologies of wax chosen among the three categories: paraffinic (obtained by Fischer-Tropsch process), partially oxidized and maleic anhydride functionalized. By morphological and calorimetric analyses and solubility tests they were able to characterize blend behavior related to wax type. In particular, they found that paraffinic waxes preferentially reside in the polymer-rich phase and slightly enhance the bitumen polymer compatibility. Partial oxidation tends to aggregate with the asphaltene rich phase reducing compatibility with the polymer, while functionalized wax, although not clear where they are located, has a considerable compatibilizing effect strongly altering the colloidal equilibrium of the bitumen polymer blend.

5. Concluding Remarks

This paper summarizes the findings obtained from an extensive literature review focused on the basic aspects related to different types of bitumens, processing technologies and polymers, chemical and nanocomposite-modified bitumen characterizations' pros and cons, as well as identifying corresponding areas of study for future perspectives. The comprehensive review implies that the relative abundance of the bitumen SARA fractions results in significant differences in bitumen chemical composition and further mechanical properties. It is evident that different types of processing of crude oil result in bitumens with different chemical compositions. This also has a great influence on the compatibility with any polymer through polymer modification.

The author believes that the widespread use of the PmB technologies within the road pavement industry is advisable considering the genuine shortcomings of neat bitumens and the heavy-duty pavements of current transportation networks.

The review conducted on the different kinds of PmBs can be concluded as the follows:

- While plastomer-modified bitumens are suitable for improving the permanent deformation resistance of the bituminous compounds and asphalt concrete mixtures over high stresses, the absence of elasticity at low temperature limited the application of these bitumins.
- The field recorded data, as well as experimental works, showed that plastomer-modified bitumens, such as polyethylene and polypropylene, are the most common plastomers resulting in compatibility problems. This is due to their non-polar chemical nature.
- Despite the thermal and aging stability of plastomer-modified bitumens due to the absence of double bonds, the main problem resides in the stability of the blend (polymer + bitumen) during storage and difficulties to disperse them homogenously in the bitumen matrix.
- Thermoplastic elastomer copolymers, owing to their elastic component, are usually more effective than plastomers for bitumen modification in pavement applications. The modification ranges from low-modified containing 3% polymer to a high level with polymer content of 7%.
- Bitumen modification via styrene butadiene styrene (SBS) as the most commonly used elastomer has numerous benefits, including the improved thermal susceptibility, increased softening point, and slight decrease of penetration value at 25 °C. In addition, it has been observed that SBS can moderate the increase of stiffness due to oxidation processes.
- Bitumens modified with thermosetting polymers show a high elasticity and no viscous behavior. Asphalt mixtures produced with thermosetting polymer-modified bitumen have excellent adhesive ability, excellent resistance to deformation, excellent fatigue performance, and high stiffness modulus. Even though the PmBs with thermosetting plastics have relatively high adhesion to the mineral particles and high strength they are not common for paving applications. This is because the technological properties of PmB are almost immediately deteriorated by these polymers due to their hardening properties; secondly, the rigidity of the PmB is increased at low temperatures, which results in increased thermal sensitivity; thirdly, the use of TP complicates the system and raises its price; and, finally, the effectiveness of thermosetting plastics usually appears due to their large quantities in bitumen (more than 10 wt%)
- Natural rubber latex has potential for improving bitumen binder performance by enhancing the thermal sensitivity, flexibility, stability, and stripping. In addition, its inherent elastomeric properties proved its high potential in improving long-term pavement performance of asphalt concrete by increasing rutting resistance, fatigue life, etc. Natural rubber also decreases the optimum binder content in asphalt concretes, increasing its density and stability. However, natural rubber is a highly valuable biomaterial compared to other biopolymers, hence natural rubber has been commercialized into synthetic rubber. This is mainly because of the very large difference between the available produced amount and the demand. Still, there are some doubts regarding asphalt concrete performance and mechanical properties throughout the performance temperature range

- The synthetic rubber/bitumen system was investigated from a different point of view. It can be concluded that many factors can influence the performance and mechanical properties of rubberized binders including: the size and content of rubber, the chemical structure, particles surface properties (ambient granulating or cryogenically crushed tire rubber), blend production method, and temperature. A low content of rubber, around 4% (to the weight of bitumen) has almost no effect, or at least no significant effects, on the performance and mechanical properties of the binder, while more than 20% was found to be unsuitable.
- In spite of the proven advantages regarding the use of polymers in bitumen modification systems, several research works showed the difficulties regarding the incompatibility with the bitumen. Phase separation could occur in such modified bitumen.
- Several research works showed that the stability of the PmBs is highly dependent on the asphaltene and aromatic content of base bitumen: the less asphaltene, the more stable the modified compound that can be expected. However, polymer chemical structure and reactivity are also of paramount importance in bitumen/polymer system compatibility.
- Various solutions to remove drawbacks to currently used polymer modifiers, among which the use of chemical modifiers received great attention, have been employed in the last few decades. These solutions overcome some disadvantages of PmBs, but most cause some new problems. Thus, more research needs to be carried out in the future to solve these problems and find new ways to modify bitumen effectively and cheaply.
- Finally, few research works showed the effectiveness of waxes in improving some of the characteristics of base bitumens and modified bitumens. In addition, the presence of a determined amount of wax could improve the polymer compatibility.

Considering the variety of the conclusions, especially regarding the bitumen chemical characteristics and related engineering properties, further studies are required to be able to fully integrate the aspects related to bitumen functionality and obtain conclusions concerning many challenges on this topic.

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References

1. *European Committee for Standardization EN 12597: Bitumen and Bituminous Binders-Terminology*; European Committee for Standardization: Brussels, Belgium, 2000.
2. Paliukait, M.; Vaitkusa, A.; Zofkab, A. Evaluation of bitumen fractional composition depending on the crude oil type and production technology. In Proceedings of the 9th International Conference "Environmental Engineering" Selected Papers, Vilnius, Lithuania, 22–23 May 2014.
3. Read, J.; Witheoak, D. *The Shell Bitumen Handbook*, 5th ed.; Thomas Telford Publishing: London, UK, 2003.
4. Lesueur, D. The Colloidal Structure of Bitumen: Consequences on the Rheology and on the Mechanisms of Bitumen Modification. *Adv. Colloid Interface Sci.* **2009**, *145*, 42–82. [CrossRef] [PubMed]
5. Olli-Ville, L. Low-Temperature Rheology of Bitumen and Its Relationships with Chemical and Thermal Properties. Ph.D. Thesis, School of Engineering, Aalto University, Espoo, Finland, 2015.
6. D'Melo, D.; Taylor, R. Constitution and Structure of Bitumens. In *The Shell Bitumen Handbook*, 6th ed.; Hunter, R.N., Self, A., Read, J., Eds.; ICE Publishing: London, UK, 2015; ISBN 978-0727758378.
7. McNally, T. Introduction to polymer modified bitumen (PmB). In *Polymer Modified Bitumen Properties and Characterisation*, 1st ed.; McNally, T., Ed.; Woodhead Publishing: Sawston, UK, 2011.
8. Lu, X.; Isacsson, U.; Ekblad, J. Phase Separation of SBS Polymer Modified Bitumens. *J. Mater. Civ. Eng.* **1999**, *11*, 51–57. [CrossRef]

9. Petersen, J.C. Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art. *Transp. Res. Rec.* **1984**, *999*, 13–30.
10. Branthaver, J.F.; Petersen, J.C.; Robertson, R.E.; Duvall, J.J.; Kim, S.S.; Harnsberger, P.M.; Mill, T.; Ensley, E.K.; Barbour, F.A.; Schabron, J.F. *Binder Characterization and Evaluation-vol 2 Chemistry*; SHRP Report A-368; National Research Council: Washington, DC, USA, 1994.
11. Mortazavi, M.; Moulthrop, J.S. *SHRP Materials Reference Library*; SHRP report A-646; National Research Council: Washington, DC, USA, 1993.
12. *Strategic Highway Research: Special Report 260. Committee for Study for a Future Strategic Highway Research Program, Strategic Highway Research*; Transportation Research Board Special Report 260; National Research Council: Washington, DC, USA, 2001.
13. Jiménez-Mateos, J.M.; Quintero, L.C.; Rial, C. Characterization of petroleum bitumens and their fractions by thermogravimetric analysis and differential scanning calorimetry. *Fuel* **1996**, *75*, 1691–1700. [CrossRef]
14. Speight, J.C. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, NY, USA, 1999.
15. Ashoori, S.; Sharifi, M.; Masoumi, M.; Salehi, M.M. The Relationship between SARA Fractions and Crude Oil Stability. *Egypt. J. Pet.* **2017**, *26*, 209–213. [CrossRef]
16. Rostler, F.S. *Fractional Composition: Analytical and Functional Significance*; Hoiberg, A.J., Robert, E., Eds.; Krieger Publishing Company, Huntington: New York, NY, USA, 1979; Volume 2, pp. 151–222.
17. Corbett, L.W. Composition of asphalt based on generic fractionation, using solvent deasphaltening, elution-adsorption chromatography and densimetric characterization. *Anal. Chem.* **1969**, *41*, 576–579. [CrossRef]
18. Speight, J.C. Petroleum asphaltenes. Part 1. Asphaltenes, resins and the structure of petroleum. *Oil Gas Sci. Technol.* **2004**, *59*, 467–477. [CrossRef]
19. Mullins, O. Optical Interrogation of Aromatic Moieties in Crude Oils and Asphaltenes. In *Structures and Dynamics of Asphaltenes*; Mullins, O., Sheu, E.Y., Eds.; Plenum Press: New York, NY, USA, 1998; pp. 21–77. ISBN 978-1-4899-1615-0.
20. Piéri, N. Etude du Vieillissement Simulé et In-Situ des Bitumens Routiers Par IRTF et Fluorescence UV en Excitation-Emission Synchrones. Ph.D. Thesis, Aix-Marseille University, St-Joseph, France, 1995.
21. Scotti, R.; Montanari, L. Molecular structure and intermolecular interaction of asphaltenes by FT-IR, NMR, EPR. In *Structures and Dynamics of Asphaltenes*; Mullins, O., Sheu, E.Y., Eds.; Plenum Press: New York, NY, USA, 1998; pp. 79–113. ISBN 978-1-4899-1615-0.
22. Bergmann, U.; Mullins, O.C.; Cramer, S.P. X-Ray Raman spectroscopy of carbon in asphaltene: Light element characterization with bulk sensitivity. *Anal. Chem.* **2000**, *72*, 2609–2612. [CrossRef]
23. Michon, L.; Didier, M.; Jean-Pascal, P.; Bernard, H. Estimation of average structural parameters of bitumens by ^{13}C Nuclear Magnetic Resonance spectroscopy. *Fuel* **1997**, *76*, 9–15. [CrossRef]
24. Sheremata, J.M.; Gray, M.R.; Dettman, H.D.; McCaffrey, W.C. Quantitative molecular representation and sequential optimization of Athabasca asphaltenes. *Energy Fuels* **2004**, *18*, 1377–1384. [CrossRef]
25. Murgich, J.; Abanero, J.; Strausz, O. Molecular Recognition in Aggregates Formed by Asphaltene and Resin Molecules from the Athabasca Oil Sand. *Energy Fuels* **1999**, *13*, 278–286. [CrossRef]
26. Mullins, O. Review of the Molecular Structure and Aggregation of Asphaltenes and Petroleomics. *Spe J.* **2008**, *13*, 48–57. [CrossRef]
27. Becker, J.R. *Crude Oil Waxes, Emulsiones and Asphaltenes*; PennWell: Tulsa, OK, USA, 1997.
28. Dickie, J.P.; Yen, T.F. Macrostructures of the Asphaltic Fractions by Variuos Instrumental Methods. *Anal. Chem.* **1967**, *5213*, 1963–1968.
29. Speight, J.C. Molecular Models for Petroleum Asphaltenes and Implication for Asphalt Science and Technology. In Proceedings of the International Symposium on the Chemistry of Bitumens, Rome, Italy, 5–8 June 1991; pp. 154–207.
30. Yen, T.F.; Erdman, J.G.; Pollack, S.S. Investigation of the Structure of Petroleum Asphaltenes by X-Ray Diffraction. *Anal. Chem.* **1961**, *33*, 1587–1594. [CrossRef]
31. Sadeghi, M.A.; Chilingarian, G.V.; Yen, T.F. X-Ray Diffraction of Asphaltenes. *Energy Sources* **1986**, *8*, 99–123. [CrossRef]
32. Sheu, E.Y.; De Tar, M.M.; Storm, D.A. Surface activity and dynamics of asphaltenes. In *Asphaltene Particles in Fossil Fuel Exploration, Recovery, Refilling and Production*; Sharma, M.K., Yen, T.F., Eds.; Plenum Press: New York, NY, USA, 1994; pp. 115–121.

33. Roux, J.N.; Broseta, D.; Demésans, B. Study of asphaltene aggregation: Concentration and solvent quality effects. *Langmuir* **2001**, *17*, 5085–5092. [CrossRef]
34. Pryanto, S.; Mansoori, G.A.; Suwono, A. Measurement of property relationships of nano-structure micelles and coacervates of asphaltene in a pure solvent. *Chem. Eng. Sci.* **2001**, *56*, 6933–6939. [CrossRef]
35. Mullins, O. *Structures and Dynamics of Asphaltenes*; Mullins, O., Sheu, E.Y., Eds.; Plenum Press: New York, NY, USA, 1998; ISBN 978-1-4899-1615-0.
36. Fotland, P.; Anfindsen, H. Conductivity of asphaltenes. In *Structures and Dynamics of Asphaltenes*; Mullins, O., Sheu, E.Y., Eds.; Plenum Press: New York, NY, USA, 1998; pp. 247–266.
37. Taylor, S.E. The electrodeposition of asphaltenes and implication for asphaltene structure and stability in crude and residual oils. *Fuels* **1998**, *77*, 821–828. [CrossRef]
38. Swanson, J.M. A contribution to the physical chemistry of the asphalts. *J. Phys. Chem.* **1942**, *46*, 141–150. [CrossRef]
39. Marruska, S.; Rao, B.M.L. The role of polar species in the aggregation of asphaltenes. *Fuel Sci. Technol. Int.* **1987**, *5*, 119–168. [CrossRef]
40. Fotland, P.; Anfidsen, H.; Fadnes, F.H. Detection of asphaltene precipitation and amounts precipitated by measurement of electrical conductivity. *Fluid Phase Equilib.* **1993**, *82*, 157–164. [CrossRef]
41. Mozaffari, S.; Tchoukov, P.; Atias, J.; Czarnecki, J.; Nazemifard, N. Effect of Asphaltene Aggregation on Rheological Properties of Diluted Athabasca Bitumen. *Energy Fuels* **2015**, *29*, 5595–5599. [CrossRef]
42. Mozaffari, S.; Tchoukov, P.; Mozaffari, A.; Atias, J.; Czarnecki, J.; Nazemifarda, N. Capillary driven flow in nanochannels—Application to heavy oil rheology studies. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *513*, 178–187. [CrossRef]
43. Fang, L.; Shaghayegh, D.; Nelya, A.; Charles, M.; Sanjoy, B.; Pauchard, V. Mixture Effect on the Dilatation Rheology of Asphaltenes-Laden Interfaces. *Langmuir* **2017**, *33*, 1927–1942.
44. Duran, J.A.; Casas, Y.; Xiang, L.; Zhang, L.; Zeng, H.; Yarranton, H.W. Nature of Asphaltene Aggregates. *Energy Fuels* **2018**, *1*. [CrossRef]
45. Gawel, I.; Czechowski, F. Study of saturated components in asphalt. *Pet. Sci. Technol.* **1997**, *15*, 729–742. [CrossRef]
46. Polacco, G.; Filippi, S.; Merusi, F.; Stastna, G. A review of the fundamentals of polymer-modified asphalts: Asphalt/polymer interactions and principles of compatibility. *Adv. Colloid Interface Sci.* **2015**, *224*, 72–112. [CrossRef] [PubMed]
47. Koots, J.A.; Speight, J.G. Relation of petroleum resins to asphaltenes. *Fuel* **1975**, *54*, 179–184. [CrossRef]
48. Yarranton, H.W.; Fox, W.A.; Svrcek, W.Y. Effect of Resins on Asphaltene Self-Association and Solubility. *Can. J. Chem. Eng.* **2007**, *85*, 635–642. [CrossRef]
49. Boutevin, B.; Pietrasanta, Y.; Robin, J.J. Bitumen-Polymer Blends for Coatings Applied to Roads and Public Constructions. *Prog. Org. Coat.* **1989**, *17*, 221–249. [CrossRef]
50. Polacco, G.; Stastna, J.; Biondi, D.; Zanzotto, L. Relation Between Polymer Architecture and Nonlinear Viscoelastic Behaviour of Modified Asphalts. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 230–245. [CrossRef]
51. Walkering, C.P.; Vonk, W.C.; Whiteoak, C.D. Improved Asphalt Properties Using SBS modified Bitumens. *Shell Bitum. Rev.* **1992**, *66*, 9–11.
52. Rodrigues, C.; Hanumanthgari, R. Polymer modified bitumens and other modified binders. In *The Shell Bitumen Handbook*, 6th ed.; Hunter, R.N., Self, A., Read, J., Eds.; ICE Publishing: London, UK, 2015; ISBN 978-0727758378.
53. Becker, Y.; Méndez, M.P.; Rodríguez, Y. Polymer Modified Asphalt. *Vis. Tecnol.* **2001**, *9*, 39–50.
54. Polacco, G.; Berlincioni, S.; Biondi, D.; Stastna, J.; Zanzotto, L. Asphalt Modification with Different Polyethylene-Based Polymers. *Eur. Polym. J.* **2005**, *41*, 2831–2844. [CrossRef]
55. Punith, V.S.; Veeraragavan, A. Behaviour of asphalt concrete mixtures with reclaimed poly ethylene as additive. *J. Mater. Civ. Eng.* **2007**, *19*, 500–507. [CrossRef]
56. Lesueur, D.; Gérard, J.-F. Polymer modified Asphalts as Viscoelastic Emulsions. *J. Rheol.* **1998**, *42*, 1059–1074. [CrossRef]
57. Isacsson, U.; Lu, X. Testing and Appraisal of Polymer Modified Road Bitumens-State of the Art. *Mater. Struct.* **1995**, *28*, 139–159. [CrossRef]
58. Stastna, J.; Zanzotto, L.; Vacin, O.J. Viscosity Function in Polymer-modified Asphalts. *J. Colloid Interface Sci.* **2003**, *259*, 200–207. [CrossRef]

59. Ameri, M.; Mansourian, A.; Sheikhmotevali, A.H. Investigating Effects of Ethylene Vinyl Acetate and Gilsonite Modifiers Upon Performance of Base Bitumen Using Superpave Tests Methodology. *Constr. Build. Mater.* **2012**, *36*, 1001–1007. [CrossRef]
60. Stroup-Gardiner, M.; Newcomb, D.E. *Polymer Literature Review*; September. Report N°: MN/RC-95/27; Minnesota Department of Transportation: Saint Paul, MN, USA, 1995.
61. Iatridi, Z.; Tsitsilianis, C. Water-Soluble Stimuli Responsive Star-Shaped Segmented Macromolecules. *Polymers* **2011**, *3*, 1911–1933. [CrossRef]
62. Available online: https://www.eastman.com/Markets/Tackifier_Center/Pages/Block_Copolymer.aspx (accessed on 3 July 2018).
63. Chen, J.S.; Liao, M.C.; Shiah, M.S. Asphalt Modified by Styrene-Butadiene-Styrene Triblock Copolymer: Morphology and Model. *J. Mater. Civ. Eng.* **2002**, *14*, 224–229. [CrossRef]
64. Airey, G.D. Rheological Properties of Styrene Butadiene Styrene Polymer Modified Road Bitumens. *Fuel* **2003**, *82*, 1709–1719. [CrossRef]
65. Masson, J.F.; Collins, P.; Robertson, G.; Woods, J.R.; Margeson, J. Thermodynamics Phase Diagrams and Stability of Bitumen-Polymer Blends. *Energy Fuels* **2003**, *17*, 714–724. [CrossRef]
66. Wen, G.; Zhang, Y.; Zhang, Y.; Fan, Y. Rheological Characterization of Storage-Stable SBS-Modified Asphalts. *Polym. Test.* **2002**, *21*, 295–302. [CrossRef]
67. Wang, T.; Yi, T.; Yuzhen, Z. Compatibility of SBS-modified Asphalt. *Pet. Sci. Technol.* **2010**, *28*, 764–772. [CrossRef]
68. Galooyak, S.S.; Dabir, B.; Nazarbeygi, A.E.; Moeini, A. Rheological Properties and Storage Stability of Bitumen/SBS/Montmorillonite Composites. *Constr. Build. Mater.* **2010**, *24*, 300–307. [CrossRef]
69. Krauss, G. Modification of Asphalt by Block Polymers of Butadiene and Styrene. *Rubber Chem. Technol.* **1982**, *55*, 1389–1402. [CrossRef]
70. Wloczysiak, P.; Vidal, A.; Papirer, E.; Gauvin, P. Relationships Between Rheological Properties, Morphological Characteristics and Composition of Bitumen-Styrene Butadiene Styrene Copolymers Mixes. I. A Three Phase System. *J. Appl. Polym. Sci.* **1998**, *65*, 1595–1607. [CrossRef]
71. Lu, X.; Isacsson, U. Compatibility and Storage Stability of Styrene-Butadiene-Styrene Copolymer Modified Bitumens. *Mater. Struct.* **1997**, *30*, 618–626. [CrossRef]
72. Nikolaides, A. *Highway Engineering Pavements, Materials and Control of Quality*, 1st ed.; CRC Press Taylor & Francis: Boca Raton, FL, USA, 2014; ISBN 9781466579972.
73. Pyshyev, S.; Gunka, V.; Grytsenko, Y.; Bratychack, M. Polymer modified bitumen: Review. *Chem. Chem. Technol.* **2016**, *10*, 631–636. [CrossRef]
74. Dinnen, A. Epoxy bitumen binders for critical road conditions. In Proceedings of the 2nd Eurobitume, Cannes, France, 7–9 October 1981; p. 294.
75. Chan, C.H.; Sabu, T.; Pothan, L.A.; Maria, H.J. Composites and Nanocomposites. In *Natural Rubber Materials (Vol. 2)*; Royal Society of Chemistry: Cambridge, UK, 2013; ISBN 978-1-84973-631-2.
76. Kohjiya, S. *Chemistry, Manufacture and Applications of Natural Rubber*, 1st ed.; Woodhead Publishing Limited: Cambridge, UK, 2014; ISBN 9780857096838.
77. Van Krevelen, D.W.; Te Nijenhuis, K. *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*, 4th ed.; Elsevier: Oxford, UK, 2009; ISBN 9780080548197.
78. Mark, J.E. (Ed.) *Physical Properties of Polymers Handbook*, 2nd ed.; Springer-Verlag: New York, NY, USA, 1996; ISBN 978-0-387-31235-4.
79. Studebaker, M.L. Effect of Curing Systems on Selected Physical Properties of Natural Rubber Vulcanizates. *Rubber Chem. Technol.* **1966**, *39*, 1359–1381. [CrossRef]
80. Wen, Y.; Wang, Y.; Zhao, K.; Sumalee, A. The use of natural rubber latex as a renewable and sustainable modifier of asphalt binder. *Int. J. Pavement Eng.* **2017**, *8*, 547–559. [CrossRef]
81. Shaffie, E.; Ahmad, J.; Arshad, A.K.; Kamarudin, F. Stripping Performance and Volumetric Properties Evaluation of Hot Mix Asphalt (HMA) Mix Design Using Natural Rubber Latex Polymer Modified Binder (NRMB). In *INCIEC*; Springer: Singapore, 2014.
82. Saad, A.A.; Yusof, I.B.; Hermadi, M.; Marwan, B.S.; Alfergani, M.B.S. Pavement Performance with Carbon Black and Natural Rubber (Latex). *Int. J. Eng. Adv. Technol.* **2013**, *2*, 124–129.

83. Krishnapriya, M.G. Performance Evaluation of Natural Rubber Modified Bituminous Mixes. *Int. J. Civ. Struct. Environ. Infrastruct. Eng. Res. Dev.* **2015**, *5*, 121–134.
84. Nrachai, T.; Chayatan, P.; Direk, L. The modification of asphalt with natural rubber latex. *Proc. East. Asia Soc. Transp. Stud.* **2005**, *5*, 679–694.
85. Okieimen, F.E.; Akinlabi, A.K. Processing characteristics and physico-mechanical properties of natural rubber and liquid natural rubber blends. *J. Appl. Polym. Sci.* **2002**, *85*, 1070–1076. [CrossRef]
86. Ibeagi, U.M.; Okereke, S.; Okpareke, O.C.; Ukoha, P.O. Studies on the Modifications of Asphalt Binder Using Some Selected Polymers. *Int. J. Chem. Sci.* **2012**, *10*, 2048–2056.
87. Azahar, N.B.M.; Hassan, N.A.; Jaya, R.P.; Mahmud, M.Z.H. An overview on natural rubber application for asphalt modification. *Int. J. Agric. For. Plant.* **2016**, *2*, 212–218.
88. Vural Kök, B.; Çolak, H. Laboratory comparison of crumb rubber and SBS modified bitumen and hot mix asphalt. *Constr. Build. Mater.* **2011**, *25*, 3204–3212.
89. Wang, H.; You, Z.; Mills-Bealeb, J.; Haoa, P. Laboratory evaluation on high temperature viscosity and low temperature stiffness of asphalt binder with high percent scrap tire rubber. *Constr. Build. Mater.* **2012**, *26*, 583–590. [CrossRef]
90. Mashaan, N.S.; Karim, M.R. Waste tyre rubber in asphalt pavement modification. *Mater. Res. Innov.* **2014**, *18* (Suppl. 6), S6–S9. [CrossRef]
91. Grechanovskii, V.A.; Ya Poddubnyi, I.; Ivanova, L.S. Molecular Structure and Macroscopic Properties of Synthetic Cis-Poly(Isoprene). *Rubber Chem. Technol.* **1974**, *47*, 342–356. [CrossRef]
92. Flory, P.J. Effects of Molecular Structure on Physical Properties of Butyl Rubber. *Rubber Chem. Technol.* **1946**, *19*, 552–598. [CrossRef]
93. Olivares, H.F.; Schultz, W.B.; Fernández, A.M.; Moro, B.C. Rubber-modified Hot Mix Asphalt Pavement by Dry Process. *Int. J. Pavement Eng.* **2009**, *10*, 277–288. [CrossRef]
94. Hassan, N.A.; Airey, G.D.; Jaya, R.P.; Mashros, N.; Aziz, M.M. A Review of Crumb Rubber Modification in Dry Mixed Rubberised Asphalt Mixtures. *J. Teknol.* **2014**, *70*, 127–134.
95. Lo Presti, D. Recycled Tyre Rubber Modified Bitumens for road asphalt mixtures: A literature review. *Constr. Build. Mater.* **2013**, *49*, 863–881. [CrossRef]
96. *Standard Specification for Asphalt-Rubber Binder, D 6114–97*; ASTM: West Conshohocken, PA, USA, 2002.
97. Valkering, C.P.; Vonk, W. Thermoplastic rubbers for the modification of bitumens: Improved elastic recovery for high deformation resistance of asphalt mixes. In Proceedings of the 15th Australian Road Research Board (ARRB) Conference, Darwin, Australia, 26–31 August 1999; pp. 1–19.
98. Krutz, N.C.; Siddharthan, R.; Stroup-Gardiner, M. Investigation of rutting potential using static creep testing on polymer-modified asphalt concrete mixtures. *Transp. Res. Rec.* **1991**, *1317*, 100–118.
99. Collins, J.H.; Bouldin, M.G.; Gelles, R.; Berker, A. Improved performance of paving asphalts by polymer modification (with discussion). In Proceedings of the Association of Asphalt Paving Technologists Technical Sessions, Seattle, DC, USA, 4–6 March 1991; pp. 43–79.
100. Bouldin, M.G.; Collins, J.H.; Berker, A. Rheology and microstructure of polymer/asphalt blends. *Rubber Chem. Technol.* **1991**, *64*, 577–600. [CrossRef]
101. Wardlaw, K.R.; Shuler, S. (Eds.) *Polymer Modified Asphalt Binders*; ASTM: West Conshohocken, PA, USA, 1992; ISBN 0-8031-1413-3.
102. Stock, A.F.; Arand, W. Low temperature cracking in polymer modified binders. In Proceedings of the Asphalt Paving Technology, Austin, TX, USA, 22–24 March 1993; pp. 23–53.
103. Aglan, H. Polymeric additives and their role in asphaltic pavements. Part I: Effect of additive type on the fracture and fatigue behavior. *J. Elastomers Plast.* **1993**, *25*, 307–321. [CrossRef]
104. Bahia, H.U.; Anderson, D.A. Glass transition behavior and physical hardening of asphalt binders (with discussion). In Proceedings of the Asphalt Paving Technology, Austin, TX, USA, 22–24 March 1993; pp. 93–129.
105. Elmore, W.E.; Thomas, W.K.; Mansour, S.; Bolzan, P. *Long-Term Performance Evaluation of Polymer-Modified Asphalt Concrete Pavements*; Report No.: FHWA-TX-94+1306-1F; Federal Highway Administration: Washington, DC, USA, 1993.
106. Bonemazzi, F.; Braga, V.; Corrieri, R.; Giavarini, C. Characteristics of polymers and polymer-modified binders. *Transp. Res. Rec.* **1996**, *1535*, 36–47. [CrossRef]

107. Brulè, B. Polymer-modified asphalt cements used in the road construction industry: Basic principles. *Transp. Res. Rec.* **1996**, *1535*, 48–53. [CrossRef]
108. Adedeji, A.; Grünfelder, T.; Bates, F.S.; Macosko, C.W.; Stroup-Gardiner, M.; Newcomb, D.E. Asphalt modified by SBS triblock copolymer: Structures and properties. *Polym. Eng. Sci.* **1996**, *36*, 1707–1723. [CrossRef]
109. Shin, E.E.; Bhurke, A.; Edward, S.; Rozeveld, S.; Drzal, L.T. Microstructure, morphology, and failure modes of polymer-modified asphalts. *Transp. Res. Rec.* **1996**, *1535*, 61–73. [CrossRef]
110. Loeber, L.; Durand, A.; Muller, G.; Morel, J.; Sutton, O.; Bargiacchi, M. New investigations on the mechanism of polymer–bitumen interaction and their practical application for binder formulation. In Proceedings of the 1st Eurasphalt & Eurobitume Congress, Congress Paper No. 5115, Strasbourg, France, 7–10 May 1996.
111. Gahvari, F. Effects of thermoplastic block copolymers on rheology of asphalt. *J. Mater. Civ. Eng.* **1997**, *9*, 111–116. [CrossRef]
112. Giavarini, C.; De Filippis, P.; Santarelli, M.L.; Scarsella, M. Production of stable polypropylene-modified bitumens. *Fuel* **1996**, *75*, 681–686. [CrossRef]
113. Rojo, E.; Fernàndez, M.; Peña, J.J.; Peña, B. Rheological aspects of blends of metallocene-catalysed atactic polypropylenes with bitumen. *Polym. Eng. Sci.* **2004**, *44*, 1792–1799. [CrossRef]
114. González, O.; Muñoz, M.E.; Santamaría, A. Bitumen/polyethylene blends: Using m-LLDPEs to improve stability and viscoelastic properties. *Rheol. Acta* **2006**, *45*, 603–610. [CrossRef]
115. Henderson, G. Bituminous Binders and Process of Making Same from Coal-Tar Pitch. U.S. Patent 1264932, 30 July 1917.
116. Gagle, D.W.; Draper, H.L. High Ductility Asphalt. U.S. Patent 4130516, 12 April 1976.
117. Wen, G.; Zhang, Y.; Zhang, Y.; Sun, K.; Chen, Z. Vulcanization characteristics of asphalt/SBS blends in the presence of sulphur. *J. Appl. Polym. Sci.* **2001**, *82*, 989–996. [CrossRef]
118. Wen, G.; Zhang, Y.; Zhang, Y.; Sun, K. Improved properties of SBS modified asphalt with dynamic vulcanization. *Polym. Eng. Sci.* **2002**, *42*, 1070–1081. [CrossRef]
119. Chen, J.S.; Huang, C.C. Fundamental characterization of SBS-modified asphalt mixed with sulphur. *J. Appl. Polym. Sci.* **2006**, *103*, 2817–2825. [CrossRef]
120. Zhang, F.; Yu, J.; Wu, S. Effect of ageing on rheological properties of storage-stable SBS/sulphur-modified asphalts. *J. Hazard Mater.* **2010**, *182*, 507–517. [CrossRef] [PubMed]
121. Zhang, F.; Yu, J.; Han, J. Effects of thermal oxidative ageing on dynamic viscosity, TG/DTG, DTA and FTIR of SBS-and SBS/sulphur-modified asphalts. *Constr. Build. Mater.* **2011**, *25*, 129–137. [CrossRef]
122. Masson, J.-F.; Gagné, M. Polyphosphoric Acid (PPA)-Modified Bitumen: Disruption of the Asphaltenes Network Based on the Reaction of Non-basic Nitrogen with PPA. *Energy Fuels* **2008**, *22*, 3402–3406. [CrossRef]
123. Miknis, F.P.; Thomas, K.P. NMR Analysis of Polyphosphoric Acid-modified Bitumens. *Road Mater. Pavement Des.* **2008**, *9*, 59–72. [CrossRef]
124. Jaroszek, H. Polyphosphoric acid (PPA) in road asphalts modification. *CHEMIK* **2012**, *66*, 1340–1345.
125. García-Morales, M. Dodecylbenzenesulfonic Acid as a Bitumen Modifier: A Novel Approach to Enhance Rheological Properties of Bitumen. *Energy Fuels* **2017**, *31*, 5003–5010.
126. Herrington, P.R.; Wu, Y.; Forbes, M.C. Rheological modification of bitumen with maleic anhydride and dicarboxylic acids. *Fuel* **1999**, *78*, 101–110. [CrossRef]
127. Kang, Y.; Wang, F.; Chen, Z. Reaction of asphalt and maleic anhydride: Kinetics and mechanism. *Chem. Eng. J.* **2010**, *164*, 230–237. [CrossRef]
128. Cong, P.; Chen, S.; Chen, H. Preparation and properties of bitumen modified with the maleic anhydride grafted styrene-butadiene-styrene triblock copolymer. *Polym. Eng. Sci.* **2011**, *51*, 1273–1279. [CrossRef]
129. Marzocchi, A.; Roberts, M.G.; Bolen, C.E. Asphalt Compositions Modified with Organo-Silane Compounds. U.S. Patent US4292371A, 24 March 1980.
130. Peng, C.; Chen, P.; You, Z.; Lv, S.; Zhang, R.; Xu, F.; Zhang, H.; Chen, H. Effect of silane coupling agent on improving the adhesive properties between asphalt binder and aggregates. *Constr. Build. Mater.* **2018**, *169*, 591–600. [CrossRef]
131. Cuadri, A.A.; Partal, P.; Navarro, F.J.; García-Morales, M.; Gallegos, C. Bitumen chemical modification by thiourea dioxide. *Fuel* **2011**, *90*, 2294–2300. [CrossRef]

132. Ouyang, C.; Wang, S.; Zhang, Y.; Zhang, Y. Preparation and properties of styrene–butadiene–styrene copolymer/kaolinite clay compound and asphalt modified with the compound. *Polym. Degrad. Stab.* **2005**, *87*, 309–317. [CrossRef]
133. Ouyang, C.; Wang, S.; Zhang, Y.; Zhang, Y. Thermo-rheological properties and storage stability of SEBS/kaolinite clay compound modified asphalts. *Eur. Polym. J.* **2006**, *42*, 446–457. [CrossRef]
134. Ouyang, C.; Wang, S.; Zhang, Y.; Zhang, Y. Low-density polyethylene/silica compound modified asphalts with high-temperature storage stability. *J. Appl. Polym. Sci.* **2006**, *101*, 472–479. [CrossRef]
135. Yu, J.; Wang, L.; Zeng, X.; Wu, S.; Li, B. Effect of montmorillonite on properties of styrene–butadiene–styrene copolymer modified bitumen. *Polym. Eng. Sci.* **2007**, *47*, 1289–1295. [CrossRef]
136. Polacco, G.; Kříž, P.; Filippi, S.; Stastna, J.; Biondi, D.; Zanzotto, L. Rheological properties of asphalt/SBS/clay blends. *Eur. Polym. J.* **2008**, *44*, 3512–3521. [CrossRef]
137. Zhang, B.; Xi, M.; Zhang, D.; Zhang, H.; Zhang, B. The effect of styrene-butadiene-rubber/montmorillonite modification on the characteristics and properties of asphalt. *Constr. Build. Mater.* **2009**, *23*, 3112–3117. [CrossRef]
138. Golestani, B.; Nejad, F.M.; Galooyak, S.S. Performance evaluation of linear and nonlinear nanocomposite modified asphalts. *Constr. Build. Mater.* **2012**, *35*, 197–203. [CrossRef]
139. Jasso, M.; Bakos, D.; MacLeod, D.; Zanzotto, L. Preparation and properties of conventional asphalt modified by physical mixtures of linear SBS and montmorillonite clay. *Constr. Build. Mater.* **2013**, *38*, 759–765. [CrossRef]
140. Zhang, H.; Yu, J.; Wang, H.; Xue, L. Investigation of microstructures and ultraviolet aging properties of organo-montmorillonite/SBS modified bitumen. *Mater. Chem. Phys.* **2011**, *129*, 769–776. [CrossRef]
141. Zanzotto, L.; Stastna, J.; Vacin, O. Thermomechanical properties of several polymer modified asphalts. *Appl. Rheol.* **2000**, *10*, 134–144.
142. Hesp, S.; Hoare, T.R.; Roy, S.D. Low-temperature fracture in reactive ethylene-terpolymer-modified asphalt binders. *Int. J. Pavement Eng.* **2002**, *3*, 153–159. [CrossRef]
143. Polacco, G.; Stastna, J.; Biondi, D.; Antonelli, F.; Vlachovicova, Z.; Zanzotto, L. Rheology of asphalts modified with glycidylmethacrylate functionalized polymers. *J. Colloid Interface Sci.* **2004**, *280*, 366–373. [CrossRef] [PubMed]
144. Yeh, P.H.; Nien, Y.-H.; Chen, J.-H.; Chen, W.-C.; Chen, J.-S. Thermal and rheological properties of maleated polypropylene modified asphalt. *Polym. Eng. Sci.* **2005**, *45*, 1152–1158. [CrossRef]
145. Fu, H.; Xie, L.; Dou, D.; Li, L.; Yu, M.; Yao, S. Storage stability and compatibility of asphalt binder modified by SBS graft copolymer. *Constr. Build. Mater.* **2007**, *21*, 1528–1533. [CrossRef]
146. Wang, Q.; Liao, M.; Wang, Y.; Ren, Y. Characterization of end functionalized styrene butadiene–styrene copolymers and their application in modified asphalt. *J. Appl. Polym. Sci.* **2007**, *103*, 8–16. [CrossRef]
147. Navarro, F.J.; Partal, P.; García-Morales, M.; Martinez-Boza, F.J.; Gallegos, C. Bitumen modification with a low-molecular-weight reactive isocyanate-terminated polymer. *Fuel* **2007**, *86*, 2291–2299. [CrossRef]
148. Li, J.; Zhang, Y.; Zhang, Y. The research of GMA-g-LDPE modified Qinhuangdao bitumen. *Constr. Build. Mater.* **2008**, *22*, 1067–1073.
149. Martin-Alfonso, M.J.; Partal, P.; Navarro, F.J.; García-Morales, M.; Gallegos, C. Use of an MDI functionalized reactive polymer for the manufacture of modified bitumen with enhanced properties for roofing applications. *Eur. Polym. J.* **2008**, *44*, 1451–1461. [CrossRef]
150. Martin-Alfonso, M.J.; Partal, P.; Navarro, F.J.; García-Morales, M.; Gallegos, C. Role of water in the development of new isocyanate-based bituminous products. *Ind. Eng. Chem. Res.* **2008**, *47*, 6933–6940. [CrossRef]
151. Martin-Alfonso, M.J.; Partal, P.; Navarro, F.J.; García-Morales, M.; Bordado, J.C.M.; Diogo, A.C. Effect of processing temperature on the bitumen/ MDI–PEG reactivity. *Fuel Process. Technol.* **2009**, *90*, 525–530. [CrossRef]
152. Navarro, F.J.; Partal, P.; García-Morales, M.; Martín-Alfonso, M.J.; Martínez-Boza, F.; Gallegos, C.; Bordado, J.C.M.; Diogo, A.C. Bitumen modification with reactive and non-reactive (virgin and recycled) polymers: A comparative analysis. *J. Ind. Eng. Chem.* **2009**, *15*, 458–464. [CrossRef]
153. Carrera, V.; Partal, P.; García-Morales, M.; Gallegos, C.; Páez, A. Influence of bitumen colloidal nature on the design of isocyanate-based bituminous products with enhanced rheological properties. *Ind. Eng. Chem. Res.* **2009**, *48*, 8464–8470. [CrossRef]

154. Carrera, V.; Garcia-Morales, M.; Partal, P.; Gallegos, C. Novel bitumen/isocyanate-based reactive polymer formulations for the paving industry. *Rheol. Acta* **2010**, *49*, 563–572. [CrossRef]
155. Shivokhin, M.; Garcia-Morales, M.; Partal, P.; Cuadri, A.A. Rheological behaviour of polymer-modified bituminous mastics: A comparative analysis between physical and chemical modification. *Constr. Build. Mater.* **2012**, *27*, 234–240. [CrossRef]
156. Syroezhko, A.M.; Begak, O.Y.; Fedorov, V.V.; Gusarova, E.N. Modification of paving asphalts with sulphur. *Russ. J. Appl. Chem.* **2003**, *76*, 491–496. [CrossRef]
157. Petrossi, U. Modifizierte Bitumen und Verahren zu Ihrer Herstellung. U.S. Patent 3803066, 22 February 1971.
158. Maldonado, P.; Mas, J.; Phung, T.K. Process for Preparing Bitumen-Polymer Compositions. U.S. Patent 4145322, 20 March 1979.
159. Martınez-Estrada, A.; Chávez-Castellanos, A.E.; Herrera-Alonso, M.; Herrera-Najera, R. Comparative study of the effect of sulphur on the morphology and rheological properties of SB- and SBS-modified asphalt. *J. Appl. Polym. Sci.* **2010**, *115*, 3409–3422. [CrossRef]
160. Chevillard, C.; Buras, P.; Kelly, K.P.; Butler, J.R. Method for Preparation of Stable Bitumen Polymer Compositions. U.S. Patent 6441065, 27 July 2004.
161. Ho, S.; MacLeod, D.; Brown, J.; Gee, L.; Zanzotto, L. Process of Polymer Modified Asphalt Preparation. U.S. Patent 0118395 A1, 14 January 2014.
162. Sun, D.; Ye, F.; Shi, F.; Lu, W. Storage stability of SBS-modified road asphalt: Preparation, morphology, and rheological properties. *Pet. Sci. Technol.* **2006**, *24*, 1067–1077. [CrossRef]
163. Gedik, A.; Lav, A.H. Analytical, morphological, and rheological behavior of sulfur-extended-binder. *Can. J. Civ. Eng.* **2016**, *43*, 532–541. [CrossRef]
164. Hagenbach, G.; Maldonado, P.; Maurice, J. Process for Preparing Bitumen-Polymer Compositions, Application to These Compositions of the Obtention of Coverings and Mother Solution of Polymers Usable for the Obtention of the Said Compositions. U.S. Patent 4554313A, 9 June 1983.
165. Lee, D. Modification of asphalt and asphalt paving mixtures by sulfur additives. *Ind. Eng. Chem. Prod. Res. Dev.* **1975**, *14*, 171–177. [CrossRef]
166. De Filippis, P.; Giavarini, C.; Santarelli, M.L. Reaction of visbreaker bitumens with sulfur. *Pet. Sci. Technol.* **1997**, *15*, 743–753. [CrossRef]
167. De Filippis, P.; Giavarini, C.; Santarelli, M.L. Sulphur-extended asphalt: Reaction kinetics of H_2S evolution. *Fuel* **1998**, *77*, 459–463. [CrossRef]
168. Kelly, K.P.; Butler, J.R. Method for Preparation of Stable Bitumen Polymer Compositions. U.S. Patent 6180697 Bl, 5 July 2002.
169. Butler, J.R.; Kelly, K.P. Method for Preparing Asphalt and Polymer Compositions Incorporating Multi-Component Crosslinking Agents. U.S. Patent 6,407,152 Bl, 28 November 2000.
170. Butler, J.R.; Kelly, K.P.; Buras, P. Method for Preparation of Stable Bitumen Polymer Compositions. U.S. Patent 0073761A1, 4 September 1999.
171. Schermer, W.E.M.; Steernberg, K. Preparation Process for Polymer-Modified Bitumen. U.S. Patent 5719216A, 21 September 1996.
172. Kodrat, I.; Sohn, D.; Hesp, S.A.M. Comparison of polyphosphoric acid-modified asphalt binders with straight and polymer-modified materials. *Transp. Res. Rec.* **2007**, *1998*, 47–55. [CrossRef]
173. Ashry, E.S.H.; Awad, L.; El Zaher, M.A.; Elkharashe, E.; Bkheat, A.A. Modification of asphalt properties. *Prog. Rubber Plast. Recycl. Technol.* **2008**, *24*, 273–285. [CrossRef]
174. Huang, S.C.; Turner, T.; Miknis, F.; Thomas, K. Long-term aging characteristics of polyphosphoric acid-modified asphalts. *Transp. Res. Rec.* **2008**, *2051*, 1–7. [CrossRef]
175. Masson, J.F.; Collins, P.; Woods, J.R.; Bundalo-Perc, S.; Margeson, J. Chemistry and effects of polyphosphoric acid on the microstructure, molecular mass, glass transition temperatures and performance grades of asphalts. *J. Assoc. Asph. Paving Technol.* **2009**, *78*, 403–430.
176. Baumgardner, G.L. Why and how of polyphosphoric acid modification—An industry perspective. *J. Assoc. Asph. Paving Technol.* **2010**, *79*, 663–678.
177. Bennert, T.; Martin, J.V. Polyphosphoric acid in combination with styrene butadiene styrene block copolymer-laboratory mixture evaluation. *J. Assoc. Asph. Paving Technol.* **2010**, *79*, 773–791.
178. D'Angelo, J.A. Effect of poly phosphoric acid on asphalt binder properties. *J. Assoc. Asph. Paving Technol.* **2010**, *79*, 679–693.

179. McGennis, R.B. Case study: Implementation of polyphosphoric acid modification of asphalt binders and related experience. *J. Assoc. Asph. Paving Technol.* **2010**, *79*, 793–816.
180. Romagosa, E.E.; Maldonado, R.; Fee, D.; Dongre, R. Polyphosphoric acid binder modification. *J. Assoc. Asph. Paving Technol.* **2010**, *79*, 743–771.
181. Li, X.; Clyne, T.; Reinke, G.; Johnson, E.N. Laboratory evaluation of asphalt binders and mixtures containing polyphosphoric acid. *Transp. Res. Rec.* **2011**, *2210*, 47–56. [CrossRef]
182. Huang, S.C.; Miknis, F.P.; Schuster, W.; Salmans, S.; Farrar, M.; Boysen, R. Rheological and chemical properties of hydrated lime and polyphosphoric acid-modified asphalts with long-term aging. *J. Mater. Civ. Eng.* **2011**, *23*, 628–637. [CrossRef]
183. De Fatima, A.A.M.; de Freitas, V.C.L.; Pasa, V.M.D.; Leite, L.F.M. Weathering aging of modified asphalt binders. *Fuel Process. Technol.* **2013**, *115*, 19–25.
184. Zhang, F.; Hu, C. Influence of aging on thermal behaviour and characterization of SBR compound-modified asphalt. *J. Anal. Calorim.* **2014**, *115*, 1211–1218. [CrossRef]
185. Orange, G.; Jean-Valery, M.; Menapace, A.; Hemsley, M.; Baumgardner, G.L. Rutting and moisture resistance of asphalt mixtures containing polymer and polyphosphoric acid modified bitumen. *Road Mater. Pavement Des.* **2004**, *5*, 323–354. [CrossRef]
186. Baumgardner, G.L.; Masson, J.-F.; Hardee, J.R.; Menapace, A.M.; William, A.G. Polyphosphoric acid modified asphalt: Proposed mechanisms. *J. Assoc. Asph. Paving Technol.* **2005**, *74*, 283–305.
187. Thomas, K.P.; Turner, T.F. Polyphosphoric-acid modification of asphalt binders—Impact on rheological and thermal properties. *Road Mater. Pavement Des.* **2008**, *9*, 181–205. [CrossRef]
188. Oliviero Rossi, C.; Spadafora, A.; Teltayev, B.; Izmailova, G.; Amerbayev, Y.; Bortolotti, V. Polymer modified bitumen: Rheological properties and structural characterization. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *480*, 390–397. [CrossRef]
189. Zhang, F.; Hu, C. The research for SBS and SBR compound modified asphalts with polyphosphoric acid and sulphur. *Constr. Build. Mater.* **2013**, *43*, 461–468. [CrossRef]
190. Selvavathi, V.; Sekar, V.A.V.; Sriram, V.; Sairam, B. Modifications of bitumen by elastomer and reactive polymer—A comparative study. *Pet. Sci. Technol.* **2002**, *20*, 535–547. [CrossRef]
191. Pérez-Lepe, A.; Martınez-Boza, F.J.; Attane, P.; Gallegos, C. Destabilization mechanism of polyethylene-modified bitumen. *J. Appl. Polym. Sci.* **2006**, *100*, 260–267. [CrossRef]
192. Bulatović, V.O.; Rek, V.; Markovic, J. Rheological properties of bitumen modified with ethylene butylacrylate glycidylmethacrylate. *Polym. Eng. Sci.* **2014**, *54*, 1056–1065. [CrossRef]
193. Perez-Lepe, A.; Martínez-Boza, F.J.; Gallegos, C. High temperature stability of different polymer-modified bitumens: A rheological evaluation. *J. Appl. Polym. Sci.* **2007**, *103*, 1166–1174. [CrossRef]
194. Kawakami, A.; Ando, K. Curable Composition. U.S. Patent 7452930B2, 24 October 2006.
195. Duty, R.C.; Liu, H.F. Study of the reaction of maleic anhydride with Illinois bituminous coal. *Fuel* **1980**, *59*, 546–550. [CrossRef]
196. Zher'akova, G.; Kochkan'an, R. Reactivity and structure investigation of coals in reaction with dienophiles. *Fuel* **1990**, *69*, 898–901. [CrossRef]
197. Nadkarni, V.M.; Shenoy, A.V.; Mathew, J. Thermomechanical behaviour of modified asphalts. *J. Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 478–484. [CrossRef]
198. Becker, Y.M.; Muller, A.J.; Rodriguez, Y. Use of rheological compatibility criteria to study SBS modified asphalts. *J. Appl. Polym. Sci.* **2003**, *90*, 1772–1782.
199. Ray, S.S.; Okamoto, M. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Prog. Polym. Sci.* **2003**, *28*, 1539–1641.
200. Alexandre, M.; Dubois, P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater. Sci. Eng.* **2000**, *28*, 1–63. [CrossRef]
201. Paul, D.R.; Robeson, L.M. Polymer nanotechnology: Nanocomposites. *Polymer* **2008**, *49*, 3187–3204. [CrossRef]
202. Blumstein, A. Polymerization of adsorbed monolayers: II. Thermal degradation of the inserted polymers. *J. Polym. Sci. A* **1965**, *3*, 2665–2673. [CrossRef]
203. Krishnamoorti, R.; Vaia, R.A.; Giannelis, E.P. Structure and dynamics of polymer-layered silicate nanocomposites. *Chem. Mater.* **1996**, *8*, 1728–1734. [CrossRef]

204. Liu, X.; Wu, Q.; Berglund, L.; Jiaqi, F. Polyamide 6-clay nanocomposites/polypropylene-grafted-maleic anhydride alloys. *Polymer* **2001**, *42*, 8235–8239. [CrossRef]
205. Tjong, S.C.; Bao, S.P. Impact fracture toughness of polyamide-6/montmorillonite nanocomposites toughened with a maleated styrene/ethylene butylene/styrene elastomer. *J. Polym. Sci. Part B Polym. Phys.* **2005**, *43*, 585–595. [CrossRef]
206. González, I.; Eguiazábal, J.I.; Nazábal, J. Nanocomposites based on a polyamide 6/maleated styrene-butylene-co-ethylene-styrene blend: Effects of clay loading on morphology and mechanical properties. *Eur. Polym. J.* **2006**, *42*, 2905–2913. [CrossRef]
207. Wang, H.; Zeng, C.; Elkovitch, M.; Lee, L.J.; Koelling, K.W. Processing and properties of polymeric nano-composites. *Polym. Eng. Sci.* **2001**, *41*, 2036–2046. [CrossRef]
208. Yurekli, K.; Karim, A.; Amis, E.J.; Krishnamoorti, R. Influence of layered silicates on the phase-separated morphology of PS—PVME Blends. *Macromolecules* **2003**, *36*, 7256–7267. [CrossRef]
209. Si, M.; Araki, T.; Ade, H.; Kilcoyne, A.L.D.; Fisher, R.; Sokolov, J.C.; Rafailovich, M.H. Compatibilizing bulk polymer blends by using organoclays. *Macromolecules* **2006**, *39*, 4793–47801. [CrossRef]
210. Vo, L.T.; Giannelis, E.P. Compatibilizing poly(vinylidene fluoride)/Nylon-6 blends with nanoclay. *Macromolecules* **2007**, *40*, 8271–8276. [CrossRef]
211. Chow, W.S.; MohdIshak, Z.A.; Karger-Kocsis, J. Morphological and rheological properties of polyamide 6/poly(propylene)/organoclay nanocomposites. *Macromol. Mater. Eng.* **2005**, *290*, 122–127. [CrossRef]
212. Fang, Z.; Xu, Y.; Tong, L. Free-volume hole properties of two kinds thermoplastic nanocomposites based on polymer blends probed by positron annihilation lifetime spectroscopy. *J. Appl. Polym. Sci.* **2006**, *102*, 2463–2469. [CrossRef]
213. Filippi, S. Effects of organoclay on morphology and properties of nanocomposites based on LDPE/PA-6 Blends without and with SEBS-g-MA compatibilizer. *Polym. Eng. Sci.* **2009**, *49*, 1187–1197. [CrossRef]
214. Wang, Y.P.; Liu, D.J.; Li, Y.F.; Gao, J.M. Preparation and properties of asphalts modified with SBS/organobentonite blends. *Polym. Polym. Compos.* **2006**, *14*, 403–411. [CrossRef]
215. Merusi, F.; Giuliani, F.; Filippi, S.; Polacco, G. A model combining structure and properties of a 160/220 bituminous binder modified with polymer/clay nanocomposites. A rheological and morphological study. *Mater. Struct.* **2013**, *47*, 819–838. [CrossRef]
216. Zhang, J.; Wang, J.; Wu, Y.; Sun, W.; Wang, Y. Investigation on thermo-rheological properties and stability of SBR modified asphalts containing palygorskite clay. *J. Appl. Polym. Sci.* **2009**, *113*, 2524–2535. [CrossRef]
217. Sureshkumar, M.S.; Filippi, S.; Polacco, G.; Kazatchkov, I.; Stastna, J.; Zanzotto, L. Internal structure and linear viscoelastic properties of EVA/asphalt nanocomposites. *Eur. Polym. J.* **2010**, *46*, 621–633. [CrossRef]
218. Sureshkumar, M.S.; Stastna, J.; Polacco, G.; Filippi, S.; Kazatchkov, I.; Zanzotto, L. Rheology of bitumen modified by EVA—Organoclay nanocomposites. *J. Appl. Polym. Sci.* **2010**, *118*, 557–565.
219. Rossi, D.; Filippi, S.; Merusi, F.; Giuliani, F.; Polacco, G. Internal Structure of Bitumen/Polymer/Wax Ternary Mixtures for Warm Mix Asphalt. *J. Appl. Polym. Sci.* **2013**, *129*, 3341–3354. [CrossRef]
220. Edwards, Y.; Redelius, P. Rheological Effects of Waxes in Bitumen. *Energy Fuels* **2003**, *17*, 511–520. [CrossRef]
221. Warth, A.B. *The Chemistry and Technology of Waxes*; Reinhold: Waldwick, NJ, USA, 1956.
222. Thanh, N.X.; Hsieh, M.; Philip, R.P. Waxes and Asphaltenes in Crude Oils. *Org. Geochem.* **1999**, *30*, 119–132. [CrossRef]
223. Edwards, Y.; Isacsson, U. Wax in Bitumen, Part 1-Classifications and General Aspects. *Road Mater. Pavement Des.* **2005**, *6*, 281–309. [CrossRef]
224. Edwards, Y.; Isacsson, U. Wax in Bitumen, Part 2-Characterization and Effects. *Road Mater. Pavement Des.* **2005**, *6*, 439–468. [CrossRef]
225. Lu, X.; Kalman, B.; Redelius, P. A New Test Method for Determination of Wax Content in Crude Oils, Residues and Bitumen. *Fuel* **2008**, *87*, 1543–1551. [CrossRef]
226. Lu, X.; Langton, M.; Olofsson, P.; Redelius, P. Wax Morphology in Bitumen. *J. Mater. Sci.* **2005**, *40*, 1893–1900. [CrossRef]
227. Michon, L.C.; Netzel, D.A.T.; Turner, F.; Martin, D.; Planche, J.P. A ^{13}C NMR and DSC Study of the Amorphous and Crystalline Phases in Asphalts. *Energy Fuels* **1999**, *13*, 603–610. [CrossRef]
228. Lu, X.; Redelius, P. Compositional and Structural Characterization of Waxes Isolated from Bitumens. *Energy Fuels* **2006**, *20*, 653–660. [CrossRef]

229. Lu, X.; Redelius, P. Effect of Bitumen Wax on Asphalt Mixture Performance. *Constr. Build. Mater.* **2007**, *21*, 1961–1970. [CrossRef]
230. Lee, H.; Wong, W. Effect of wax on basic and rheological properties of bitumen with similar Penetration-grades. *Constr. Build Mater.* **2009**, *23*, 507–514. [CrossRef]
231. Wong, W.; Li, G. Analysis of the effect of wax content on bitumen under performance grade classification. *Constr. Build. Mater.* **2009**, *23*, 2504–2510. [CrossRef]
232. Giuliani, F.; Merusi, F. Flow Characteristics and Viscosity Functions in Asphalt Binders Modified by Wax. *Int. J. Pavement Res. Technol.* **2009**, *2*, 51–60.
233. Merusi, F.; Caruso, A.; Roncella, R.; Giuliani, F. Moisture Susceptibility and Stripping Resistance of Asphalt Mixture Modified with Different Synthetic Waxes. *Transp. Res. Rec.* **2010**, *2180*, 110–120. [CrossRef]
234. Merusi, F.; Giuliani, F. Rheological Characterization of Wax-Modified Asphalt Binders at High Service Temperatures. *Mater. Struct.* **2011**, *44*, 1809–1820. [CrossRef]
235. Edwards, Y.; Tasdemir, Y.; Butt, A. An Energy Saving and Environmental Friendly Wax Concept for Polymer Modified Mastic Asphalt. *Mater. Struct.* **2010**, *43*, 123–131. [CrossRef]
236. Kim, H.; Lee, S.J.; Amirkhasian, S.N. Effects of Warm Mix Asphalts Additives on Performance Properties of Polymer Modified Asphalt Binders. *Can. J. Civ. Eng.* **2010**, *37*, 17–24. [CrossRef]
237. Kim, H.; Lee, S.J.; Amirkhasian, S.N. Performance Evaluation of Recycled PMA Binders Containing Warm Mix Asphalt Additives. *J. Test. Eval.* **2011**, *39*, 728–734.
238. Akisetty, C.K.; Lee, S.J.; Amirkhanian, S.N. Laboratory Investigation of the Influence of Warm Asphalt Additives on Long-Term Performance Properties of CRM Binders. *Int. J. Pavement Eng.* **2011**, *11*, 153–160. [CrossRef]
239. Gonzalez, V.; Martinez-Boza, F.J.; Navarro, F.J.; Gallegos, C.; Perez-Lepe, A.; Paez, A. Thermomechanical Properties of Bitumen Modified with Crumb Rubber and Polymeric Additives. *Fuel Process. Technol.* **2010**, *91*, 1033–1039. [CrossRef]
240. Akisetty, C.K.; Gandhi, T.; Lee, S.J.; Amirkhanian, S.N. Analysis of Rheological Properties of Rubberized Binders Containing Warm Asphalt Additives. *Can. J. Civ. Eng.* **2010**, *37*, 763–771. [CrossRef]