

Bitumen and Bitumen Modification

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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. 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. Good crude oils and proper distillation processes can enhance bitumen properties.

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][5][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.

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:

- Asphaltenes
- 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.

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 ^[17].

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. ^[18], 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 ^[19]. 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 ^[20]. [Table 1](#) summarizes the most common types of additives used as bitumen modifiers.

Table 1. Examples of additives used to modify bitumen (reconstructed from ^[20] 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	

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

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.

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][21][22][23][24][25][26][27][28][29][30][31][32][33][34][35]. 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 [36][21][26]. Secondly, some drawbacks have been observed, such as thermal instability and PmB's phase separation problems [37][38]. 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) [39]. 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 [40][41], sulfur (S) [42][43][44][45][46][47][48][49], polyphosphoric acid (PPA) [50][51][52], sulfonic acid [53], carboxylic anhydrides [54][55][56], silanes [57][58], thiourea dioxide [59], nanocomposite-modified bitumen [60][61][62][63][64][65][66][67][68], and reactive polymers [69][70][71][72][73][74][75][76][77][78][79][80][81][82][83]. 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.

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][84][85]. 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 [84]. Although naturally present as constitutive components of all crude oil products [86][87] and studied in the technical literature, where bitumen wax content [88][89][90], crystallization properties [91], chemical structure [92][93], and influences on bitumen and bitumen mixture properties [85][88][94][95][96][97][98][99] 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 [84][88][99]. 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 [84]; 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. [100] 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. [101][102] 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 [103], fatigue characteristics [4], thermo-mechanical properties [104], and viscosity and rheological properties [105]. Rossi et al. [84] 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.

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