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Polymer Modification of Bitumen: Advances and Challenges

Jiqing Zhu *, Björn Birgisson, Niki Kringos

Division of Highway and Railway Engineering, Department of Transport Science, KTH
Royal Institute of Technology, Brinellvägen 23, 100 44 Stockholm, Sweden

* Corresponding author. Tel.: +46 (0)8 - 790 8707

E-mail: jiqing.zhu@abe.kth.se (J. Zhu)

Abstract. Advances and challenges in the field of bitumen polymer modification for road construction during the last 40 years are reviewed in this paper. The history of bitumen polymer modification is described chronologically. Some popular plastomers and thermoplastic elastomers in bitumen modification are discussed regarding their advantages and disadvantages, including polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA), ethylene-butyl acrylate (EBA), styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) and styrene-ethylene/butylene-styrene (SEBS). Although these polymers all improve bitumen properties to some extent, there are still some drawbacks limiting the future development of bitumen polymer modification, such as high cost, low ageing resistance and poor storage stability of polymer modified bitumen (PMB). Researchers attempted various ways to remove these drawbacks. Some technical developments for removing drawbacks are reviewed in this paper, including saturation, sulfur vulcanization, adding antioxidants, using hydrophobic clay minerals, functionalization and application of reactive polymers. The future development of polymers for bitumen modification is analyzed as well. Since it is currently challenging to perfectly achieve all expected PMB properties at the same time, some compromised recommendations are given in this paper, among which greatly enhancing the properties with an acceptably high cost, significantly reducing the cost with relatively poor properties and their combinations. Functionalization is emphasized as a promising way to enhance the properties of currently used polymers and develop new-type polymer modifiers with much greater success in the future. It is also recommended that future research on bitumen polymer modification focuses more on function development towards enhancing: adhesion with aggregates, long-term performance and recyclability.

Keywords: *polymer modified bitumen; advance; challenge; future development*

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1. Introduction

Bitumen is one of the oldest known engineering materials [1]. It has been used for thousands of years [2] in various ways, e.g. as adhesive, sealant, preservative, waterproofing agent and pavement binder. Ancient inhabitants directly used the natural bitumen which is usually in the earth's surface [2]. In the early 1900s, refined bitumen was first produced by refining crude oil in the USA [1]. Since then, the world consumption of bitumen has increased rapidly, most of which was used in road construction. According to a joint publication of Asphalt Institute and Eurobitume in 2011, the current world consumption of bitumen is approximately 102 million tonnes per year, 85% of which is used in various kinds of pavements [3]. In fact, the chemistry composition of produced bitumen is very complex and variable; and the properties of produced bitumen are closely related to the crude oil sources and the refinery processes. By selecting good crude oil or proper refinery processes, some good bitumen properties can be obtained. However, the limited oil resources for producing good-quality bitumen and the lack of effective control actions during refinery, as well as the driving force of earning the maximum economic benefits, made industries pay more attention on bitumen modification [4]. Additionally, pavement industry has developed rapidly all over the world during the last few decades, especially in developing countries. Following the rapid development, increased traffic load, higher traffic volume, and insufficient maintenance led to many severe distresses (e.g. rutting and cracking) of road surfaces. The harsh reality was demanding more on bitumen quality. In order to obtain bitumen with enhanced quality, an increasing number of investigations also began to focus on bitumen modification. Among all attempted or investigated modification methods of bitumen, polymer modification has been one of the most popular approaches.

Polymer modification of bitumen is the incorporation of polymers in bitumen by mechanical mixing or chemical reaction [5]. During the last 40 years, more and more researchers began to concentrate themselves on polymer modification of bitumen and a rapidly increasing number of research articles have been published since 1970s. In these, the various investigated polymers included plastomers (e.g. polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA), ethylene-butyl acrylate (EBA)) and thermoplastic elastomers (e.g. styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), and styrene-ethylene/butylene-styrene (SEBS)) [6-12], although none of these were initially designed for bitumen modification. These polymers were reported to lead to some improved properties of bitumen, such as higher stiffness at high temperatures, higher cracking resistance at low temperatures, better moisture resistance or longer fatigue life [13-18]. In [2], an extensive summary was given that an effective polymer modification results in a thermodynamically unstable but kinetically stable system in which the polymer is partially swollen by the light components of bitumen. Some important factors, including the characteristics of the bitumen and the polymer themselves, the content of polymer and the manufacturing processes, determine the final properties of polymer modified bitumen (PMB) [5, 19]. As polymer content increases, phase inversion may occur in some PMBs: from bitumen being the dominant phase to polymer becoming the dominant phase [20]. However, an ideal microstructure for PMB contains two interlocked continuous phases, which determines the optimum polymer content for bitumen modification [21]. With these two interlocked continuous phases, PMB usually shows better overall performance with respect to mechanical properties, storage stability and cost-effectiveness.

In addition to the reported advantages, researchers also encountered various challenges, including high cost, some PMBs' high temperature sensitivity, low ageing resistance, poor

storage stability and the limited improvement in elasticity. In this, the combination of bitumen oxidation and polymer degradation was reported to cause PMB's ageing propensity [22], which seems especially challenging for some unsaturated polymers, e.g. SBS. The poor storage stability of some PMBs usually results from the poor compatibility between polymer modifiers and bitumen which is controlled by polymers' and bitumen's different properties such as density, molecular weight, polarity and solubility [23]. The chemical structure and reactivity of polymers, however, are also supposed to affect their compatibility with bitumen, which may have a direct relationship with the resulting PMB properties [24]. In order to conquer these challenges, researchers have tried different categories of solutions, such as saturation, sulfur vulcanization, adding antioxidants, using hydrophobic clay minerals, functionalization and application of reactive polymers (which also can be considered as new functionalized products).

Along with technical aspect, economical aspect is of course a huge driving force for the choice of technology. Different kinds of pavements have different demands on performance. From the economic aspect, it is not always better to achieve higher performance for a road. Only when the technology is cost-effective, can people get the maximum benefits from it and can it become popular. As for PMB, the cost is quite relevant with the dosage of the added polymer, while the polymer dosage usually has important influences on the final degree of PMB performance. So before constructing a road, the designers must know what is the needed degree of performance for the road and then decide to use PMB or not, and use how much. Currently, most of the world consumption of bitumen is still base bitumen. As the climate and traffic conditions vary in different countries, the percentage of PMB in all the used bitumen also varies in different countries. Even for a single country, the percentage varies during different years. According to the data released by European Asphalt Pavement Association (EAPA), the percentage of PMB consumption in all the yearly used bitumen for paving is usually less than 20% in most European countries during the last 3 years [25]. The detailed data for each country can be seen in [25]. Regarding the polymer dosage, Eurobitume claimed that a typical SBS polymer content is around 3.5% by weight in the final product, based on an internal industry review relating PMB within Europe [26].

This paper focuses on bitumen polymer modification for road construction, aiming to give a comprehensive overview of the development of bitumen polymer modification over the last 40 years, the challenges people encountered and the solutions researchers came up with as well as their varying success. First, a historical perspective is given in the following with an in-depth discussion on the most popular polymers and their associated technical developments. After this, the potential development of bitumen polymer modification in the future is analyzed. Finally, some conclusions are presented and some recommendations are given.

2. Historical perspective

Bitumen polymer modification has a long history. Even before refined bitumen was produced, people began to modify natural bitumen and some patents were granted for natural rubber modification [1, 27-29]. Synthetic polymers, however, were not widely used until after World War II ended. One well-known early example is neoprene (polychloroprene) latex, which began to be increasingly used for bitumen modification in North America from the 1950s [29].

Plastomers have a longer history of artificial synthesis than thermoplastic elastomers. Most of the currently popular plastomers began to be produced commercially before 1960 [30]. Regarding thermoplastic elastomers, the first commercially acceptable SBS product was developed in the USA in 1965 and the first hydrogenated (or saturated) product, SEBS, was announced in 1972 [31]. In the early years, these commercial polymers were mainly used in packaging, rubber, footwear or adhesive industries.

Bitumen polymer modification was firstly used in the roofing industry, and then the paving industry. In 1965, atactic polypropylene (APP), which is a by-product of isotactic polypropylene (IPP) manufacturing, was firstly used to modify bitumen for roofing in Italy and the first commercial product was marketed in 1967 [32]. SBS, however, was not widely used until the early 1970s in Europe. As for the USA, it was in 1978 that Americans began to widely use modified bitumen in roofing. Around 1980, the first American PMB manufacturer started [32].

Bitumen polymer modification for road construction is a field extensively covered by intellectual property. A patent, relating a bituminous composition with base bitumen and polyisobutylene, was granted as early as 1940 [33]. After that, especially after SBS was introduced to bitumen modification, a large number of patents were applied all over the world. Due to the oil crises of 1973 and 1979, attempts of bitumen polymer modification for road construction began to increase about 40 years ago [34, 35]. During the 1970s, researchers proved that the addition of polymers, including plastomers and thermoplastic elastomers, could improve some properties of paving bitumen, such as reducing temperature sensitivity or increasing the resistance to permanent deformation [35-39]. In 1978, Chaffin et al. [39] reported the potential storage stability problems of bitumen modified with elastomers, but they also wrote that their field test sections constructed in Texas in 1976 were performing well.

During the 1980s, the demand of thin layer for pavement drove more systematic investigations [34, 40-47] to focus on bitumen polymer modification. For example, in 1980, the research carried out by Piazza et al. [40] revealed the features of bitumen respectively modified by plastomers and thermoplastic elastomers. In 1982, Kraus [41] studied the morphology of modified bitumen by elastomers and reported the swelling of polymers in bitumen. In 1983, a binder for pavement wearing courses, which comprises PE modified bitumen, was reported by Denning et al. [42], although it led to phase separation problems and higher manufacturing and compacting temperatures. During the following several years, more investigations [43, 44] on PE modified bitumen were being published. Bowering [45] reviewed the necessity of modifying bitumen with polymers in 1984 and claimed that the relatively high cost of PMB might be outweighed by the effects of reduced layer thickness and extended life of PMB pavements. In 1987, the US Congress established the Strategic Highway Research Program (SHRP) which promoted the popularity of PMB by developing a performance-based specification for both conventional and modified bitumen with an emphasis on rheology. In 1989, Reese et al. [46] reported the good resistance to ageing and cracking of PMB after a two-year field test in California, although they pointed out that further evaluations needed to be performed to be conclusive about the success of the modification.

By the early 1990s, increased interest in research of bitumen polymer modification was observed in many countries [27]. Researchers systematically investigated the mechanical properties, rheology, temperature sensitivity, morphology, thermal behavior, storage stability and ageing of different PMBs [48-63]. Both the advantages and disadvantages of widely

used PMBs were gradually found out. On the one hand, it was concluded that polymer modification resulted in some improved properties of bitumen, such as better elastic recovery, higher cracking resistance at low temperatures and higher rutting resistance at high temperatures of SBS modified bitumen [58-60]. On the other hand, some drawbacks were proven, such as the thermal instability of some polymer modifiers and phase separation problems of some PMBs [48, 61]. In June 1998, a World Road Association (PIARC) International Symposium on polymer modification of bitumen was held in Rome, which gave an overview of the situation at that time and encouraged the publication of a report in 1999 [34]. Furthermore, attempts to remove PMB's drawbacks began from the 1990s. In 1996, Giavarini et al. [7] claimed that PP modified bitumen could be stabilized by adding polyphosphoric acid (PPA) and they believed PPA could help to improve storage stability of PMB by changing the bitumen structure from sol to gel.

After 2000, investigations regarding PMB tended to be divided into two fields: (1) continuing to deeply investigate the mechanism of polymer modification and its failure and (2) attempting to overcome the disadvantages of some PMBs. The first field mainly focused on the microstructure, deformation, cracking, ageing and fatigue of PMB [64-77]. Even now, there are still some academic debates in this field. For example, some researchers believe that bitumen has a heterogeneous colloid structure and PMB should be investigated as a multiphase (polymers/asphaltenes/maltenes) viscoelastic emulsion [78, 79], shown as Figure 1; while some other researchers claim that bitumen is a homogeneous and continuous molecular solution based on their mutual solubility and polymers result in good effects on PMB by their partial solubility in bitumen [80], seen in Figure 2. Another example is some authors think asphaltenes are strongly polar components in bitumen and the polarity of polymer modifiers has a significant influence on their compatibility with bitumen and the final storage stability of the resulting PMBs [2, 78]; but some others believe asphaltenes are typical non-polar molecules from a chemical point of view [81]. As for the attempts to overcome disadvantages in 2000s, various ways were reported to remove PMB's drawbacks, including sulfur vulcanization [82-87], adding antioxidants [22, 88, 89], using hydrophobic clay minerals [90-98] and functionalization (including application of reactive polymers) [10, 99-113]. All these methods will be further discussed in this paper.

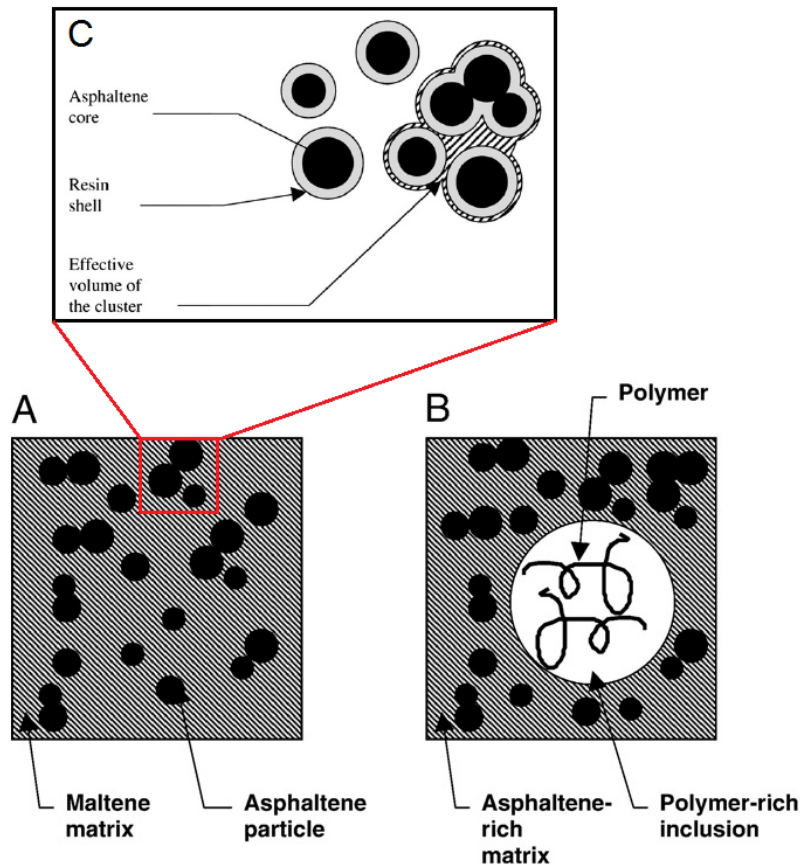


Figure 1. Schematic illustration of the colloidal structure of bitumen and the effect of polymer modification. (A) Base bitumen. (B) The corresponding PMB with increased asphaltenes content in the matrix. (C) Asphaltenes micelles. Adapted from [78] with permission from Elsevier.

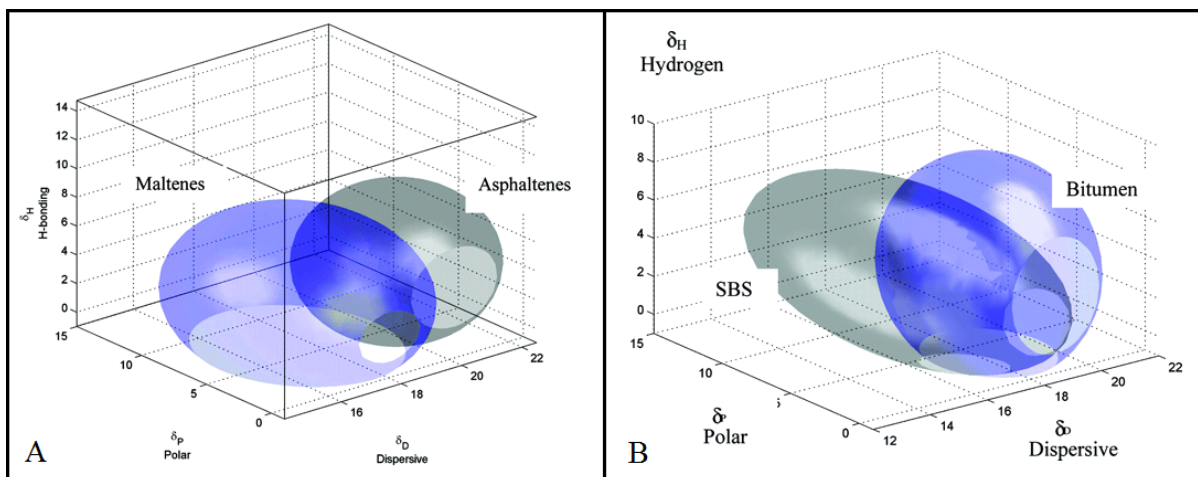


Figure 2. (A) The solubility spheres of maltenes and asphaltenes separated from a Venezuelan bitumen. (B) The Hansen solubility parameters of SBS and the Venezuelan bitumen. Adapted from [80] with permission from American Chemical Society.

3. Popular polymers for bitumen modification

As mentioned in the above, after World War II ended, synthetic polymers began to be used to modify bitumen. Over the years, researchers developed various polymer modifiers. Today, widely used polymers for bitumen modification can be classified into two categories: plastomers and thermoplastic elastomers. As Stroup-Gardiner et al. [114] reported, plastomers have little or no elastic component, usually resulting in their quick early strength

under load and the following permanent deformation or brittle failure. As for thermoplastic elastomers, they soften on heating, harden on cooling [27] and are able to resist permanent deformation by stretching under load and elastically recovering once the load is removed [114], which leads to their greater success than plastomers as bitumen modifiers. Some popular polymers for bitumen modification are listed in Table 1 with their advantages and disadvantages. Among them, SBS attracted the most attention due to its relatively good dispersibility (or appropriate solubility) in bitumen as well as the relatively excellent properties and acceptable cost of SBS modified bitumen [5, 115]. Of course, besides these listed polymers, some others like styrene-butadiene rubber (SBR, random copolymers), styrene-butadiene diblock copolymers (SB) and ethylene-propylene-diene monomer rubber (EPDM) were also popular for bitumen modification [116-118]. In addition, some small-molecule organic materials, such as PPA and paraffin wax, were also widely used as modifiers for bitumen. Since they are not typical polymers, they are not discussed in this paper.

Before reviewing the popular polymer modifiers, it is worth to note that even for a given polymer modifier, selection of base bitumen still has some important effects on the resulting PMB, as each bitumen has its own particular chemical composition and structure. Additionally, base bitumen usually composes over 90% of the PMB by weight, which could introduce overriding influences on the final properties of the PMB. Good-quality base bitumen helps to enhance the effects of polymer modification, while poor-quality one may make the modification futile. Regarding the compatibility between polymer and bitumen, selection of base bitumen is usually completed by laboratory experiments. However, some theoretical trends were also highlighted based on the SARA (saturates, aromatics, resins and asphaltenes) fractions of bitumen: for example, high asphaltenes content may decrease the compatibility between polymer and bitumen and the aromaticity of the maltenes needs to fall between certain values to reach a good level of compatibility [78]. Some other researchers even gave the components distribution of base bitumen with the optimum compatibility with SBS [23].

Table 1. Popular polymers for bitumen modification [2, 4-12, 20, 23, 24, 27-29, 114, 118-125].

Categories	Examples	Advantages	Disadvantages
Plastomers	<ul style="list-style-type: none"> • Polyethylene (PE) • Polypropylene (PP) 	<ul style="list-style-type: none"> • Good high-temperature properties • Relatively low cost 	<ul style="list-style-type: none"> • Limited improvement in elasticity • Phase separation problems
	<ul style="list-style-type: none"> • Ethylene-vinyl acetate (EVA) • Ethylene-butyl acrylate (EBA) 	<ul style="list-style-type: none"> • Relatively good storage stability • High resistance to rutting 	<ul style="list-style-type: none"> • Limited improvement in elastic recovery • Limited enhancement in low-temperature properties
Thermoplastic elastomers	<ul style="list-style-type: none"> • Styrene-butadiene-styrene (SBS) • Styrene-isoprene-styrene (SIS) 	<ul style="list-style-type: none"> • Increased stiffness • Reduced temperature sensitivity • Improved elastic response 	<ul style="list-style-type: none"> • Compatibility problems in some bitumen • Low resistance to heat, oxidation and ultraviolet • Relatively high cost
	<ul style="list-style-type: none"> • Styrene-ethylene/butylene-styrene (SEBS) 	<ul style="list-style-type: none"> • High resistance to heat, oxidation and ultraviolet 	<ul style="list-style-type: none"> • Storage instability problems • Relatively reduced elasticity • High cost

3.1. Plastomers

As an important category of plastomers, polyolefin is one of the earliest used modifiers for bitumen. Various polyolefin materials, including high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), IPP and APP [1, 6,

32, 99, 126, 127], have been studied for application in bitumen modification due to the relatively low cost and the benefits they might bring. Typical Structures of the popular PE and PP are given in Figure 3. After polyolefin materials are added into bitumen, they are usually swollen by the light components of bitumen and a biphasic structure is formed with a polyolefin phase (dispersed phase) in the bitumen matrix (continuous phase) [119]. As the polyolefin concentration increases, phase inversion occurs in the modified bitumen. Two interlocked continuous phases are ideal for polyolefin modified bitumen, which could improve the properties of bitumen to some extent. Those used materials were usually found to result in high stiffness and good rutting resistance of modified bitumen [6], although they are quite different in chemical structure and properties.

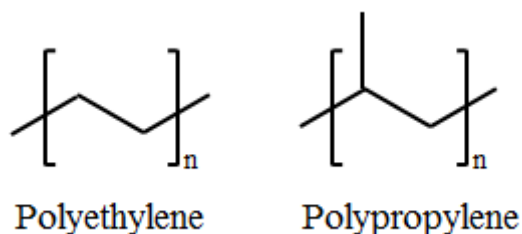


Figure 3. Structures of polyethylene (PE) and polypropylene (PP).

However, those used polyolefin materials failed to significantly improve the elasticity of bitumen [27]. In addition to this, the regular long chains of those polyolefin materials give them the high tendency to pack closely and crystallize, which could lead to a lack of interaction between bitumen and polyolefin and result in the instability of the modified bitumen. Furthermore, some researchers claimed that the compatibility of polyolefin with bitumen is very poor because of the non-polar nature of those used materials [2]. As a result, the limited improvement in elasticity and potential storage stability problems of polyolefin modified bitumen restrict the application of polyolefin materials as a bitumen modifier, whereas they are popular in production of impermeable membranes.

More used plastomers in bitumen modification are ethylene copolymers, such as EVA and EBA [8, 9]. Due to their similar chemical structures, EVA is discussed here as an example of ethylene copolymers. As seen in Figure 4, EVA copolymers are composed of ethylene-vinyl acetate random chains. Compared with PE, the presence of polar acetate groups as short branches in EVA disrupts the closely packed crystalline microstructure of the ethylene-rich segments, reduces the degree of crystallization and increases the polarity of the polymer, which were both believed to be beneficial to improving the storage stability of modified bitumen by some researchers [2]. However, the properties of EVA copolymers are closely related to the vinyl acetate content. When the vinyl acetate content is low, the degree of crystallization is high and the properties of EVA are quite similar to those of LDPE. As the vinyl acetate content increases, EVA tends to present a biphasic microstructure with a stiff PE-like crystalline phase and a rubbery vinyl acetate-rich amorphous phase [1]. The higher the vinyl acetate content, the higher the proportion of amorphous phase. But the degree of crystallization should be controlled carefully when EVA is used as a bitumen modifier, because neither too low (getting easy to be disrupted) nor too high (causing the lack of interactions with bitumen) degree of crystallization is good for bitumen modification [2].

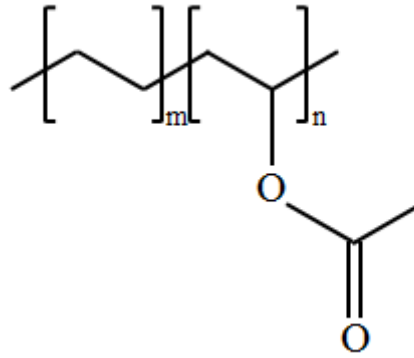


Figure 4. Structure of ethylene-vinyl acetate (EVA).

After EVA copolymers are added into bitumen, the light components of bitumen usually swell the copolymers. At low EVA concentrations, a dispersed EVA-rich phase can be observed within a continuous bitumen-rich phase [103]. As the EVA concentration increases, phase inversion occurs in modified bitumen and the EVA-rich phase becomes a continuous phase. The process of phase inversion in EVA modified bitumen was presented by fluorescent images as Figure 5 [123]. If two interlocked continuous phases form in the modified bitumen, the properties of bitumen could be improved to a large extent. EVA was found to form a tough and rigid network in modified bitumen to resist deformation [9], which means that EVA modified bitumen has an improved resistance to rutting at high temperatures.

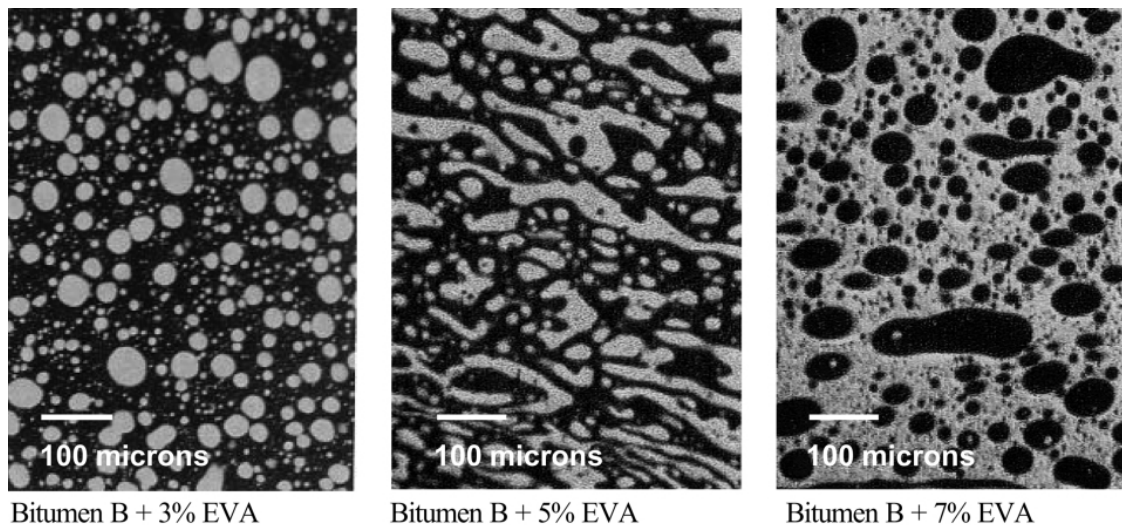


Figure 5. Fluorescent images of EVA modified bitumen with various contents (by weight) of EVA. Reprinted from [123] with permission from Elsevier.

Although some properties of bitumen are enhanced by EVA modification, there are still some problems limiting its application. One large limitation is the fact that EVA cannot much improve the elastic recovery of bitumen due to the elastomer nature of EVA [4, 27]. Furthermore, the glass transition temperature (T_g) of EVA copolymers, which strongly depends on the vinyl acetate content [128], is not low enough to significantly improve the low-temperature properties of bitumen. It was reported that T_g of EVA copolymers with 28.4 wt% of vinyl acetate is $-19.9\text{ }^\circ\text{C}$ [129], which is even quite close to T_g of some base bitumen. As a result, EVA's ability to improve the low-temperature properties of bitumen is rather limited, especially at high EVA concentrations. According to the research by Ameri et al. [121], bitumen's resistance to low-temperature cracking was increased to some extent by

addition of 2 wt% or 4 wt% of EVA, while the resistance to low-temperature cracking was decreased when adding 6 wt%. In contrast, although EBA could cause potential storage instability of modified bitumen [130], its T_g is much lower than that of EVA with the same content of co-monomer (vinyl acetate or butyl acrylate). It was reported that T_g of EBA copolymers with 33.9 wt% of butyl acrylate is $-45.9\text{ }^\circ\text{C}$, which led to the higher cracking resistance of EBA modified bitumen at low temperatures [129]. Additionally, the melting temperature of ethylene-rich segments in EVA copolymers is much lower than the usual preparing temperature of modified bitumen. Those rigid crystalline domains could be partially broken by the applied shear forces during the preparation [2]. In order to prepare the ideally modified bitumen by EVA copolymers, Airey [123] suggested the upper temperature limit as about $55\text{ }^\circ\text{C}$. Even so, those ethylene-rich segments still could melt and be partially broken by shear when EVA modified bitumen is mixed with mineral aggregates before paving, because the usual mixing temperature is also much higher than the melting temperature of ethylene-rich segments.

3.2. Thermoplastic elastomers

Thermoplastic elastomers are usually more effective than plastomers for bitumen modification. The most popular thermoplastic elastomers as bitumen modifiers are SBS copolymers and SIS copolymers. Due to their similar chemical structures, SBS is discussed here as an example of thermoplastic elastomers. SBS copolymers are composed of styrene-butadiene-styrene triblock chains with a biphasic morphology of rigid polystyrene (PS) domains (dispersed phase) in the flexible polybutadiene (PB) matrix (continuous phase) [2, 5], shown as Figure 6A. The chemical linkages between PS and PB blocks can immobilize domains in the matrix. T_g of PS blocks is around $95\text{ }^\circ\text{C}$ and T_g of PB blocks is around $-80\text{ }^\circ\text{C}$ [103]. Under the usual service temperatures of paving bitumen, PS blocks are glassy and contribute to the strength of SBS while PB blocks are rubbery and offer the elasticity [131]. Furthermore, the incompatibility between PS and PB blocks makes it possible to physically crosslink PS blocks as uniformly distributed domains by intermolecular forces at ambient temperatures. This aggregation of PS blocks disappears at high temperatures when the kinetic energy of molecular thermodynamic movements is greater than the energy of intermolecular forces [132]. However, as shown in Figure 6, the physical crosslinking among PS blocks can be reformed and the strength and elasticity of SBS can be restored after cooling, which is very important for SBS to be a popular bitumen modifier.

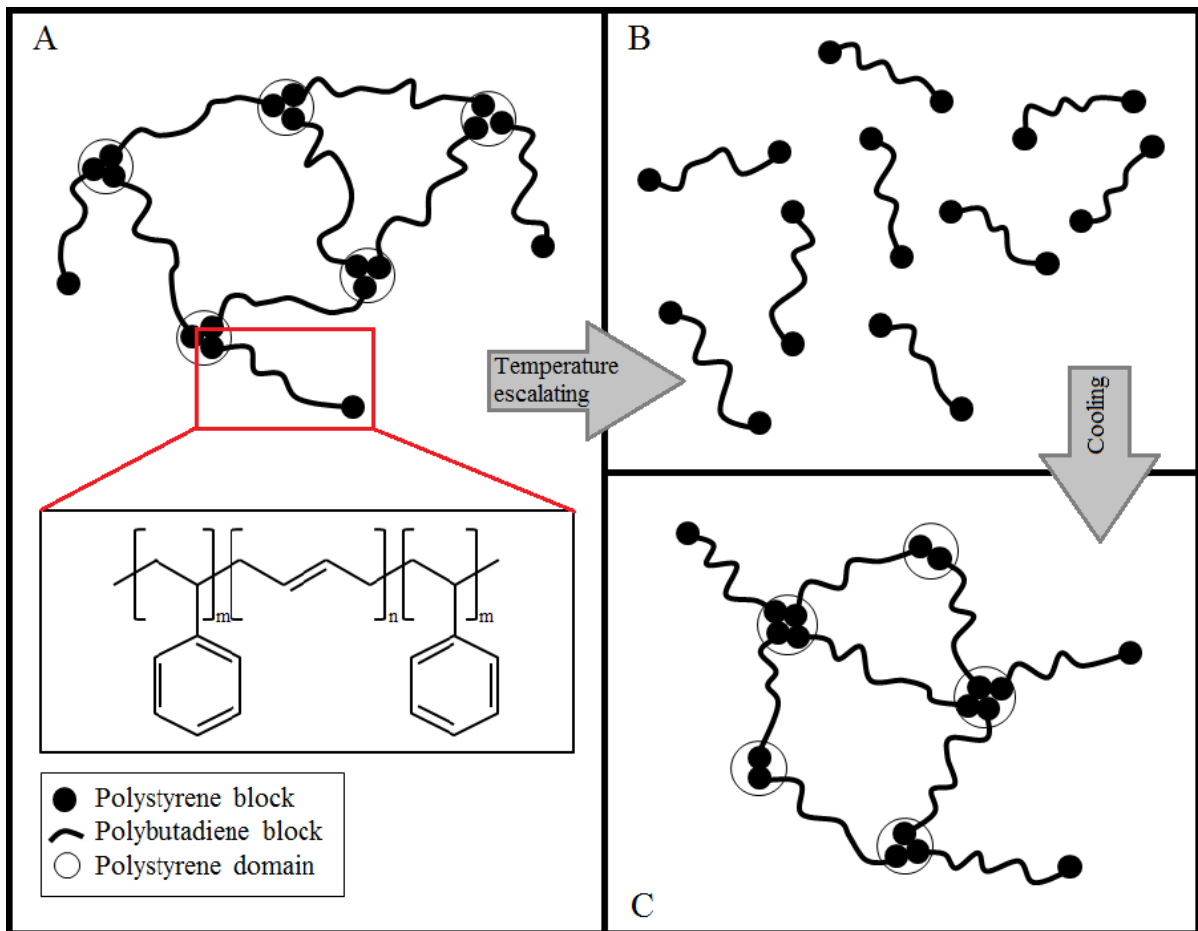


Figure 6. Structure of styrene-butadiene-styrene (SBS) and schematic illustration of reversible crosslinks in SBS.

After SBS copolymers are added into bitumen, some interactions happen between bitumen and SBS. Masson et al. [133] reported that intermolecular interactions between bitumen and the PB blocks are stronger than those with the PS blocks. They believed that PB blocks interact with positively charged groups in bitumen through their π -electrons, whereas PS blocks interact with electron-rich groups in bitumen through their aromatic protons. Mixed with bitumen, PS blocks in SBS copolymers absorb some saturated branches and a few rings in light components of bitumen [115, 124], which leads to the swelling of PS blocks and the hardening of bitumen. When the polymer content is low, SBS is dispersed as a discrete phase in the bitumen [115]. As the SBS concentration increases, phase inversion starts in the modified bitumen. The process of phase inversion in SBS modified bitumen was presented by fluorescent images as Figure 7 [9]. It is ideal to form two interlocked continuous phases: bitumen-rich phase and SBS-rich phase. Within the SBS-rich phase, there are two subphases: swollen PB matrix and essentially pure PS domains [115]. Once the SBS-rich phase forms, a rubbery supporting network is created in the modified bitumen, which results in the increased complex modulus and viscosity, improved elastic response and enhanced cracking resistance at low temperatures of SBS modified bitumen.

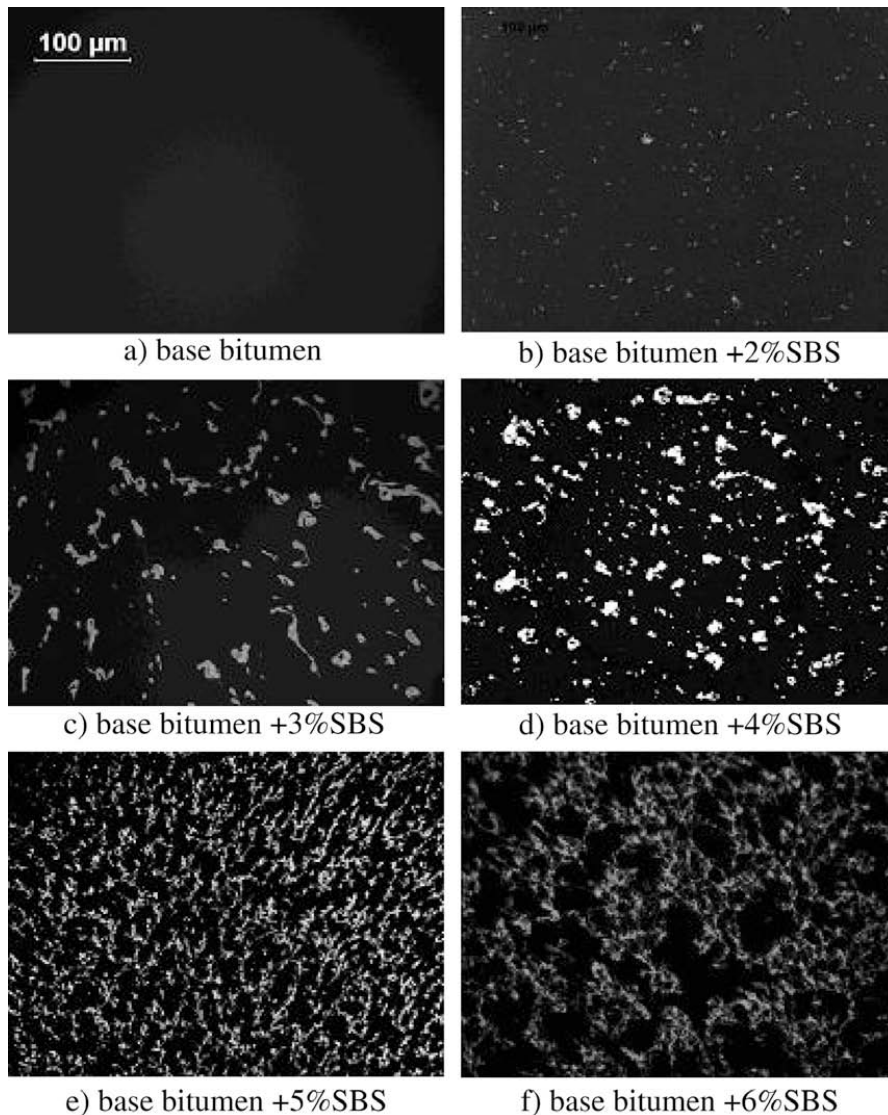


Figure 7. Fluorescent images of SBS modified bitumen with various contents (by weight) of SBS. Reprinted from [9] with permission from Elsevier.

The repeatedly reported excellent properties, relatively good dispersibility (or appropriate solubility) in bitumen and acceptable cost have made SBS popular as a bitumen modifier [5, 115]. However, SBS copolymers are far from perfect. For example, the compatibility between bitumen and SBS is not that good [23, 83, 134]. Storage instability of SBS modified bitumen was reported with images as Figure 8 [83]. Airey [124] claimed that thermoplastic elastomers and asphaltenes compete to absorb the light components of bitumen in SBS-bitumen blends. If these light components are insufficient, phase separation could occur in modified bitumen. It was noted that bitumen with high aromatics content can be helpful in producing a compatible and stable SBS modified bitumen [41] and addition of aromatic oils can improve the compatibility between SBS and some bitumen with low aromatics content [133]. Too high aromatics content in modified bitumen, however, may lead to the swelling and anti-plasticization of some PS blocks [135], which is not good for the resulting properties of the modified bitumen.

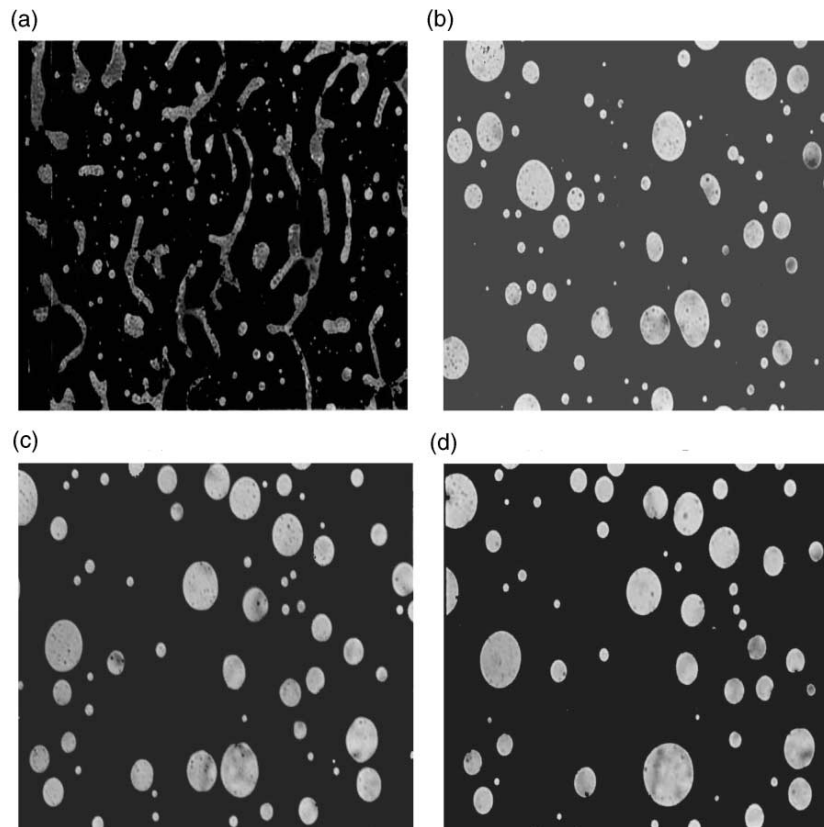


Figure 8. Morphology development with the storage time of a SBS modified bitumen at 160 °C. Reprinted from [83] with permission from Elsevier.

Another problem with SBS modification of bitumen is its low resistance to heat, oxidation and ultraviolet (UV) because of the presence of double bonds and α -H in PB blocks [88, 136]. In fact, the instability of SBS copolymers is mainly due to the high activity of α -H and low bond energy of the π -bond in double bonds. Undesired chemical reactions (e.g. formation of peroxy radicals and hydroperoxides [22]) make them sensitive to heat, oxidation and UV. In order to overcome this disadvantage, researchers firstly paid much attention to saturated thermoplastic elastomers such as SEBS. A representative patent was granted to Gelles et al. of Shell Oil Company [137].

SEBS copolymers, which can be obtained by hydrogenation of SBS, consist of triblock styrene-ethylene/butylene-styrene chains. The chemical saturation makes them highly resistant to heat, oxidation and UV. However, as the double bonds disappear, some researchers claimed that the polarity of the copolymers is considerably reduced [2]. Meanwhile, the ethylene/butylene blocks in SEBS have a trend to crystallize [138]. So the compatibility between SEBS and bitumen was believed to become even worse. According to the research by Polacco et al. [12], stable SEBS modified bitumen can only be prepared at a low polymer content (below about 4 wt% of the total mass) when SEBS acts just as filler and does not improve the viscoelastic properties of bitumen significantly. On the contrary, when SEBS content is high enough to really modify bitumen, the prepared PMB is unstable and tends to phase separate. Additionally, extra cost involved by the hydrogenation process and poorer elastic properties were observed in SEBS modified bitumen [2], which further limits its application as a bitumen modifier.

In order to avoid drawbacks of SEBS modification, researchers from Mexico [138] attempted to use partially saturated SBS copolymers in bitumen modification. They prepared styrene-butadiene-ethylene/butylene-styrene (SBEBS) copolymers with various degrees of

saturation by partial hydrogenation of SBS copolymers and found that SBEBS modified bitumen has better mechanical properties (e.g. higher rutting resistance and better elasticity) than SBS modified bitumen. Although partial hydrogenation may also cause weaker polarity and possible crystallization of the copolymers, it was claimed that SBEBS dispersed better in bitumen and led to improved storage stability of modified bitumen in the research. An explanation for this phenomenon was given in terms of solubility parameters of copolymers in aromatic compounds [138]. However, no further reports on the application of SBEBS are found to support its success in bitumen modification.

Another attempt for enhancing the ageing resistance of SBS modified bitumen was to transfer the double bonds from the backbone to branches, i.e. using high vinyl content SBS copolymers. From 1,3-butadiene, people usually prepare SBS copolymers with the structure as Figure 6A by 1,4-addition mechanism. Some researchers [139] claimed that a novel class of SBS copolymers, called high vinyl content SBS copolymers, can be obtained from 1,3-butadiene by 1,2-addition mechanism with special additives and processing conditions. This SBS copolymer has the double bonds on the branches, which was believed to result in lower viscosity and better compatibility with bitumen [139]. As heat, oxidation and UV preferably attack double bonds on branches, the backbone tends to be left intact. So it was claimed that the ageing resistance of SBS modified bitumen modified could be improved by using high vinyl content SBS copolymers [139]. In addition to this, when employed to modify hard bitumen for base layers, this SBS copolymer was believed to reduce the layer thickness by as much as 40% and material cost by some 25% [139]. A representative patent, which relates high vinyl content diblock copolymers, linear triblock copolymers, multiarm coupled block copolymers and mixtures thereof, was granted to Scholten and Vonk of Kraton Polymers [140]. However, people currently do not have much experience with high vinyl content SBS copolymers. It is still necessary to carry out more research and field tests to find out to what extent they work for bitumen modification, especially in service. Care should still be taken now when introducing high vinyl content SBS copolymers to bitumen modification.

4. Technical developments for removing drawbacks

Although great advances have been achieved in the field of bitumen polymer modification, as discussed in the previous sections, there are still various drawbacks which are limiting its future developments, such as higher costs, some PMBs' low ageing resistance and poor storage stability. Researchers have attempted different ways to remove these drawbacks, including sulfur vulcanization [82-87], adding antioxidants [22, 88, 89], using hydrophobic clay minerals [90-98] and functionalization (including application of reactive polymers) [10, 99-113]. Including saturation [2, 12, 138], which has been discussed above, some attempted measurements for removing PMB's drawbacks are listed in Table 2 with their advantages and disadvantages. In the following these are further explained.

Table 2. Attempted measurements for removing PMB's drawbacks [2, 10, 12, 22, 82-113, 134, 138, 141].

Attempted measurements	Advantages	Disadvantages
Saturation	<ul style="list-style-type: none"> Increased resistance to heat, oxidation and ultraviolet 	<ul style="list-style-type: none"> Phase separation problems High cost
Sulfur vulcanization	<ul style="list-style-type: none"> Improved storage stability Good high-temperature properties 	<ul style="list-style-type: none"> Only applicable for unsaturated polymer modifiers, like SBS High sensitivity to oxidative ageing and dynamic shear Hydrogen sulfide released Poor recyclability
Antioxidants	<ul style="list-style-type: none"> Reduced oxidation 	<ul style="list-style-type: none"> High cost
Hydrophobic clay minerals	<ul style="list-style-type: none"> Improved storage stability Good rutting resistance Increased ageing resistance 	<ul style="list-style-type: none"> Limited improvement in low-temperature properties, ductility and elastic recovery Hard to be ideally exfoliated
Functionalization	<ul style="list-style-type: none"> Improved compatibility More functions not attempted 	<ul style="list-style-type: none"> Uncontrollability in some cases High cost
Reactive polymers	<ul style="list-style-type: none"> Improved compatibility Enhanced high-temperature properties 	<ul style="list-style-type: none"> Limited improvement in low-temperature properties Gelation problems

4.1. Sulfur vulcanization

Sulfur vulcanization, a chemical process widely used in the rubber industry, was found to be able to improve the storage stability of some PMBs with unsaturated polymer modifiers (e.g. SBS modified bitumen) [82-87]. It is believed that sulfur works in two ways: chemically crosslinking the polymer molecules and chemically coupling polymer and bitumen through sulfide and/or polysulfide bonds [83]. These chemical interactions are much stronger than the physical ones (e.g. the aggregation of PS blocks in SBS copolymers) and they do not disappear even at quite high temperatures, which was believed to be very beneficial for improving the storage stability of PMB. The crosslinking of polymer molecules leads to the formation of a stable polymer network in bitumen; while the coupling between polymer and bitumen directly reduces the possibility of separation.

Although the exact reaction mechanism of PMB sulfur vulcanization is still somewhat unclear, research on rubber sulfur vulcanization and sulfur extended bitumen (SEB) may be helpful to understand the chemical reactions during PMB sulfur vulcanization. In the case of SBS modified bitumen, addition to double bonds and substitution of allylic hydrogen atoms could be the main reactions for linking sulfur and SBS copolymers [142, 143]. During this process, the loss of unsaturation, the shift of the double bonds and a molecular isomerization may occur [142, 144]. As for the linkages between sulfur and bitumen, the dehydrogenation of bitumen components and combination of sulfur radicals are possible reactions [145-147]. However, due to the complex composition of PMB and the absence of catalysts (e.g. accelerators and activators) in PMB sulfur vulcanization, all these possible reactions need to be critically proven by further studies.

Since the linking of sulfur with polymer modifiers is based on the chemical reactions with unsaturated bonds in polymer, the application of sulfur vulcanization is limited within PMBs modified by unsaturated polymers, of which SBS is the most widely used one. Sulfur vulcanization of SBS modified bitumen, on which many patents were granted, has been industrially used for more than 30 years. It was proven that sulfur vulcanization led to some improved properties of some PMBs. Besides enhanced storage stability, some researchers [83-85, 148] claimed that sulfur vulcanization could also improve the elasticity, deformation resistance and some rheological properties of the PMB, but other ones [86, 87] found that

sulfur vulcanization made the PMB more susceptible to oxidative ageing and dynamic shear and concluded that it is not a good idea to use sulfur as a sole additional modifier in PMB. Furthermore, hydrogen sulfide, a hazardous gas for both human health and the environment, could be generated during sulfur vulcanization because of the abstraction of hydrogen atoms in both bitumen and polymer modifiers, especially at high temperatures [149-151]. Of course, some researchers might argue that the gaseous emission is relatively small and most manufacturers know how to deal with the risks and dangers associated. Another problem with sulfur vulcanization is the resulting PMB's poor recyclability, which might be caused by the chemical reactions of sulfur during the vulcanization process. All these drawbacks are limiting the application of sulfur vulcanization in PMB.

4.2. Antioxidants

As previously mentioned, some PMBs are sensitive to oxidation, e.g. SBS modified bitumen. In these cases, using antioxidants could be helpful to retard oxidation of the PMB. Various antioxidants, including hindered phenols, phosphites and organic zinc compounds, have been introduced in PMB in the laboratory. They are believed to work by scavenging the free radicals and/or decomposing the hydroperoxides that are generated in the process of oxidation [22, 88, 89]. These intermediates are very reactive and contribute a lot to the oxidation. By controlling them, those antioxidants were proven to retard oxidation of the PMB to some extent in the laboratory, but the real service conditions of a road are quite different with the laboratory conditions. Antioxidants might encounter more problems in service, such as their insufficient mobility in the viscous medium at service temperatures. Authors unfortunately did not find any report on field test sections with antioxidants in PMB. Additionally, the high cost of introducing antioxidants is also a factor limiting their application [141].

4.3. Hydrophobic clay minerals

Hydrophobic clay minerals have been used in both base bitumen and PMB. It is claimed that their use in PMB is mainly for two aims: (1) improving the ageing 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 [134]. As shown in Figure 9A, the commonly used clay minerals in PMB, such as montmorillonite and kaolinite, have a 2:1-type layered structure, which means that layers in their crystal structure are made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide [152]. Every single layer of theirs has a thickness of around 1 nm [94, 95, 97, 134]. These clay minerals' ability to disperse into individual layers at the nanometer level and to fine-tune their hydrophilic surfaces into hydrophobic ones through ion exchange reactions [152] makes it possible to use them in PMB. After mixed, hydrophobic clay minerals disperse in the matrix of PMB. As seen in Figure 9B, the structure of dispersed hydrophobic clay minerals can be intercalated or exfoliated [94, 153]; and the latter one is more effective for using in PMB. By adding a proper content of hydrophobic clay minerals, the improved storage stability, increased viscosity, higher stiffness and better rutting resistance of PMB can be observed [92, 93]. Furthermore, an improvement in ageing resistance can be achieved by clay platelets' hindering the penetration of oxygen in PMB [134], which can be presented with Figure 9C. Excessive clay minerals, however, may destroy the elastic properties of PMB [93]. Additionally, the ideal exfoliated structure of PMB with hydrophobic clay minerals is hard to obtain; and their use only lead to limited improvements in low-temperature properties,

ductility and elastic recovery [93]. These factors may restrict the application of hydrophobic clay minerals in PMB.

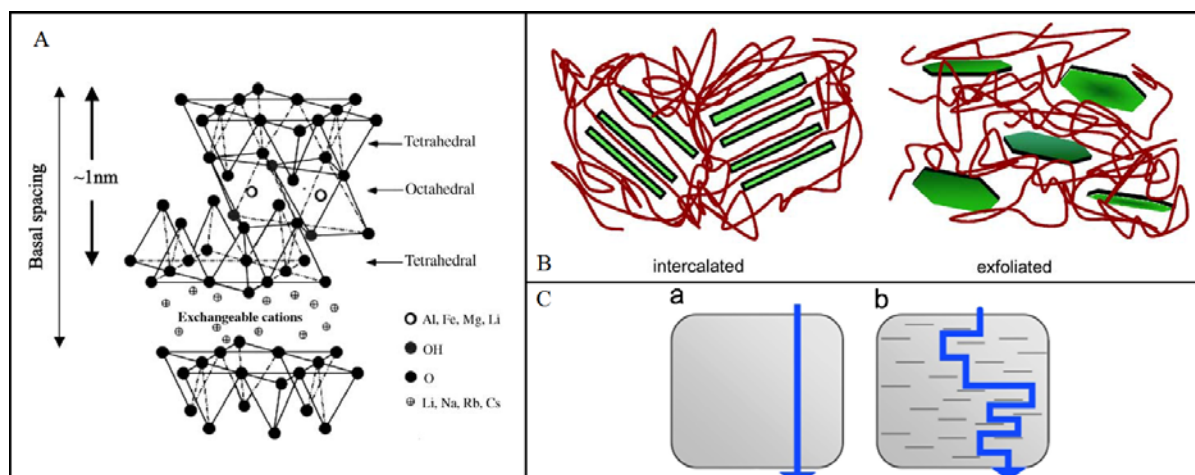


Figure 9. (A) Layered structure of the 2:1-type clay minerals. Reprinted from [152] with permission from Elsevier. (B) Schematic illustration of intercalated and exfoliated clay minerals. Reprinted from [153] with permission from Elsevier. (C) The penetration of oxygen in: (a) SBS modified bitumen; and (b) SBS modified bitumen with hydrophobic clay minerals. Reprinted from [134] with permission from Elsevier.

4.4. Functionalization and reactive polymers

From the view point of bitumen polymer modification, functionalization means the chemical addition of specific functional groups to the polymer for obtaining specific functions of PMB, such as good storage stability, excellent ageing resistance, strong adhesion with aggregates, high stiffness at high temperatures and good cracking resistance at low temperatures. It is a possible way to overcome the disadvantages of currently used polymer modifiers and raise the level of bitumen polymer modification in the future. By functionalization, various new functions of currently available PMBs may be obtained and even some new-type polymer modifiers (other than the currently used ones) could be developed, for instance reactive polymers. In fact, although not typical, saturation also can be considered as a kind of functionalization, adding hydrogen to saturate the polymer.

Although various functions of currently available PMBs may be obtained by functionalization, most reported investigations mainly aim to improve the compatibility of polymer modifiers with bitumen. The added functional groups are usually expected to interact with some components of bitumen in various ways such as forming hydrogen bonds or chemical bonds, which may improve the compatibility to some extent. For instance, Wang et al. [101] prepared functionalized SBS copolymers by respectively adding amino and carboxylic acid groups during synthesis and claimed that these functional groups could improve the compatibility of SBS copolymers with bitumen without significant influences on their other properties. Meanwhile, other researchers functionalized polymer modifiers by grafting. Maleic anhydride (MAH), methacrylic acid and glycidyl methacrylate (GMA), which are structured in Figure 10, were respectively attempted to graft some currently used polymer modifiers and they were all found to be able to improve the storage stability of the PMB even with some other enhanced properties (e.g. higher rutting resistance) [10, 99, 100, 102, 154, 155]. Besides compatibilization, a few attempts [156, 157] were also made towards better adhesion between PMB and aggregates.

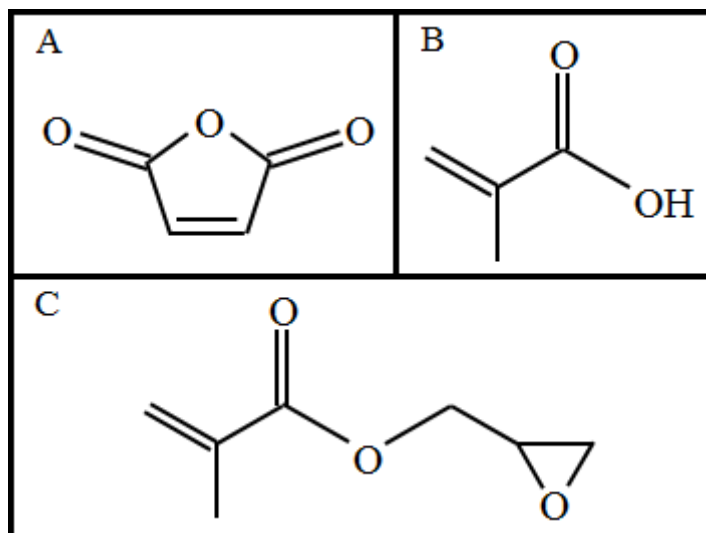


Figure 10. Structures of: (A) maleic anhydride (MAH); (B) methacrylic acid; and (C) glycidyl methacrylate (GMA).

Of course, there are also some issues that can be noted regarding functionalization of currently used polymer modifiers. For example, in the case of improving storage stability, excessive interaction between polymer modifiers and bitumen could destroy the biphasic structure of the PMB and make the products useless [2]. In addition, some researchers claimed that unsaturated polymer (e.g. SBS) is not supposed to be functionalized by grafting because it probably causes the undesired crosslinking [2], although grafted SBS copolymers have been prepared and used in bitumen modification by some other researchers [100, 158, 159].

As for the development of new types of polymer modifiers, reactive polymers are examples that cannot be missed. Reactive polymers used in bitumen modification are those polymer modifiers which are believed to chemically react (rather than physically mix or interact) with some components of bitumen [113], e.g. reactive ethylene polymers and isocyanate-based polymers.

Reactive ethylene polymers are mainly reported as ethylene-based copolymers containing epoxy rings, e.g. ethylene-glycidyl acrylate (EGA) copolymers and random terpolymers of ethylene, GMA and an ester group (usually methyl, ethyl or butyl acrylate) [2, 103, 160]. Some of them even have been used in industry. They are usually claimed to be able to improve the compatibility of polymer with bitumen, as acrylate groups in the molecule are believed to enhance the polymer polarity and the epoxy rings tend to react with some functional groups (e.g. carboxylic acid groups) in bitumen [2]. However, there are also many factors limiting their application. Zanzotto et al. [103] reported that bitumen modification with a lower concentration of EGA copolymers did produce high-temperature properties similar to modification with a higher concentration of other polymer modifiers (e.g. SBS and EVA) but EGA failed to improve the low-temperature properties. According to the research by Polacco et al. [2], when the content of reactive ethylene polymers (actually random terpolymers of ethylene, GMA and an ester group, called reactive ethylene terpolymers, RET) is high enough to be able to really modify bitumen, the prepared PMB is unstable and has a tendency of gelation due to the excessive inter-chain reactions within reactive ethylene polymers. On the contrary, stable modified bitumen with reactive ethylene polymers only can be prepared at a low polymer content (usually 1.5-2.5 wt%) when phase inversion does not occur and mechanical properties of bitumen are not improved significantly. It was believed that reactive ethylene polymers are not suitable for bitumen modification [2].

About isocyanate-based polymers, they are mainly reported as low-molecular-weight polyethylene glycol or polypropylene glycol (PEG or PPG) functionalized with isocyanate groups by reactions with 4,4'-diphenylmethane diisocyanate (MDI) [106-113], an example of which can be seen in Figure 11. They are claimed to be able to enhance some mechanical properties of bitumen by chemical reactions, mainly at high temperatures. Due to the presence of isocyanate groups, these polymers were believed to react with hydroxyl groups in bitumen [112, 113]. When cured with water, they tend to react with each other to modify the bitumen at a higher degree [108, 112, 113]. As a result, isocyanate-based polymers were found to be able to increase the viscosity and improve the storage stability and rutting resistance of bitumen at high temperatures [106, 113]. But they failed to enhance the low-temperature properties as compared with SBS modified bitumen [106]. Furthermore, the reactions between isocyanate-based polymers may also lead to the gelation risks of modified bitumen. Further investigations need to be carried out to solve the potential problems with bitumen modification with isocyanate-based polymers.

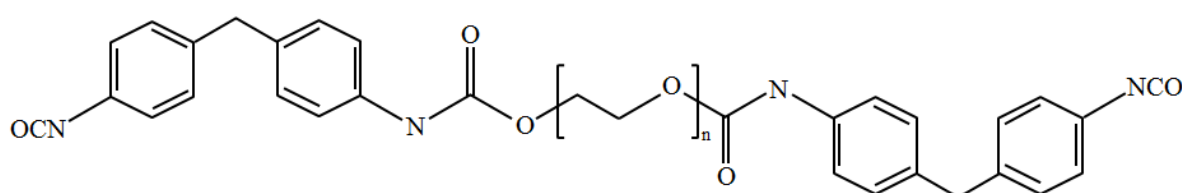


Figure 11. Structure of an isocyanate-based polymer: polyethylene glycol (PEG) functionalized with 4,4'-diphenylmethane diisocyanate (MDI).

5. Future developments

Ideally speaking, the properties of polymer modifiers should be very closely designed with the needed PMB characteristics, seen in Table 3. After mixed with bitumen, polymer modifiers are supposed to physically or chemically interact with bitumen at a proper degree to form a stable biphasic structure with two interlocked continuous phases [53]. As discussed earlier, a low degree of interaction between polymer and bitumen could cause a separation problem; while a high degree may lead to the gelation problem and high costs. The interaction between two polymer molecules also should be neither too low nor too high. The polymers with a biphasic structure of a dispersed rigid phase in a flexible continuous phase may be helpful to obtain better PMB properties. With the modification of these ideal polymers, the bitumen properties will be improved to a large extent.

Table 3. Designed properties of polymer modifiers with needed PMB characteristics.

Needed PMB characteristics	Designed properties of polymer modifiers
To be stiff at high temperatures and soft at low temperatures	Low temperature sensitivity
To be adhesive to aggregates	Outstanding contributions to adhesion of the resulting PMB with aggregates
To be workable	Excellent dispersibility (or appropriate solubility) in bitumen
To be storage-stable	Appropriate compatibility with bitumen
To be durable (ageing- and fatigue-)	High thermal stability and stable in-time response
To be recyclable	Strong responsibility for recyclability of the final products
To be cost-effective	Low cost
To be environment-friendly	Low environmental impact during production and application

In reality, however, it is currently challenging to achieve all the expected properties at the same time. To be practical, compromises will always have to be made and it is therefore important to decide on the dominant characteristics that are most needed, when designing PMB. As shown in Figure 12, compromises can be made in two ways: greatly enhancing the properties with an acceptably high cost or significantly reducing the cost with relatively poor

properties. All previously mentioned efforts for removing PMB’s drawbacks in this paper, actually, focus on the first compromise.

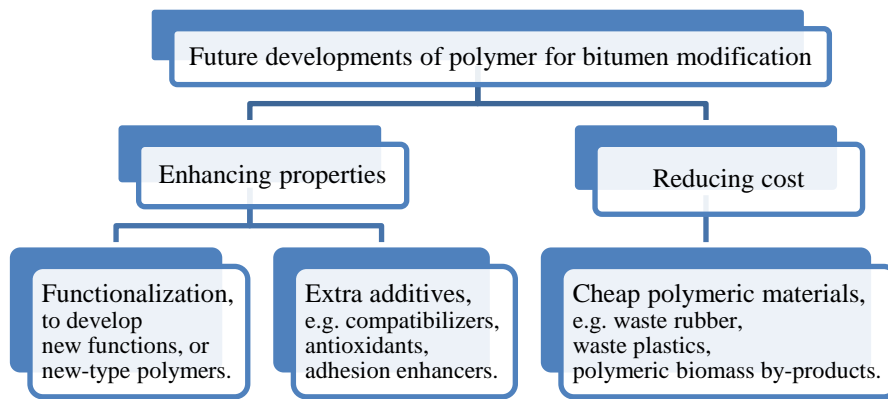


Figure 12. Future developments of polymer for bitumen modification.

For enhancing properties, functionalization and the development of new extra additives are possible directions. Though there are many factors limiting the current application of such functionalized and reactive polymers in bitumen, functionalization does hold a promise for future development. Hereby it is worth noting that enhancing physical interaction seems easier achievable and controllable than chemical interaction when functionalization is aiming at improved polymer-bitumen compatibility or PMB-aggregates adhesion. This is due to the fact that neither bitumen nor aggregates are that chemically reactive after artificial refining under very high temperatures or natural exposure to the environment. Physical interactions are thus much easier to achieve and control in the functionalization process. Of course, if chemical interactions are possible and feasible, they could be more effective for enhancing the adhesion between PMB and aggregates. As for developing new extra additives, more effective compatibilizers, antioxidants and adhesion enhancers could be helpful in improving PMB properties. Regarding compatibilizers, it is valuable to mention that neither too poor nor too great compatibility is good for bitumen modification, because too poor compatibility causes phase separation problems while too great compatibility only leads to very limited improvements [53, 78]. In the case of enhancing properties, the cost will definitely be increased. So allowing the degree of enhancing properties to be high enough to cover the additional cost will result in more cost effective PMB.

For reducing cost, some cheap polymeric materials, especially wastes and by-products (e.g. waste rubber, waste plastics and polymeric biomass by-products), could have potential applications with greater success in the future. The multifold of research focusing on this domain [161-177] further emphasizes this potential. In spite of good environment-friendliness, these wastes or by-products usually make some properties of the PMB relatively poor. So their life costs must be analyzed and proven to be effective before application. Additionally, waste materials usually have their own specific application regimes (e.g. specific climates, specific traffic volume levels) under which they perform better than under others. It is more cost-effective to use them under their own specific application regime, which sounds quite obvious but may be ignored or forgotten in the process.

Furthermore, combinations of the two compromises (i.e. using functionalized wastes or using wastes with extra additives) also could result in acceptable new products. Some research, actually, has started taking this path recently and several articles have been published, summarized in Table 4. Though all of these claimed some improved properties,

care must be taken with these attempts, as they are all isolated research projects and further investigations still need to be performed to find out whether they are feasible or not under generic conditions.

Table 4. Trials towards combining enhancing properties and reducing costs in PMB.

Attempted combinations	Conclusions	Reference No.
Grafting of waste plastics with maleic anhydride (MAH)	MAH grafting significantly improved the storage stability of bitumen modified with waste plastics.	[178]
Combination of polyethylene (PE) packaging wastes with hydrophobic clay minerals	Hydrophobic clay minerals improved the low-temperature properties of modified bitumen without adverse influence on high-temperature properties.	[179, 180]
Grafting of eucommia ulmoides gum (EUG)* with MAH	An appropriate amount of grafted EUG can enhance both the high- and low-temperature properties of styrene-butadiene-styrene (SBS) modified bitumen, in spite of the currently high cost.	[181]
Synthesis of pre-polymers** with castor oil*** and 4,4'-diphenylmethane diisocyanate (MDI)	Modification with the pre-polymers enhanced the rutting resistance of bitumen with much lower producing temperature and higher thermal stability than ordinary polymers.	[182]

Note: * EUG, a natural trans-polyisoprene from eucommia trees.
 ** This attempt synthesized pre-polymers rather than typical polymers.
 *** Castor oil, a natural triglyceride from castor seeds.

Besides the need to compromise between enhanced properties and costs, several additional points can also be taken into consideration in future research on bitumen polymer modification:

- Enhancing adhesion from polymer modifiers. Traditionally anti-stripping agents, such as hydrated lime, cement and amines [183-187], have been added to enhance the adhesion of bitumen with aggregates. Silane coupling agents and sulfur based additives were also used to help anti-stripping [188-190]. Polymers, however, have the advantage of utilizing the desirable properties of different functional groups in the same molecule [191] and have the possibility to help enhancing aggregates adhesion. Although some of the ordinary polymer modifiers (e.g. SBS and EVA) were also reported to lead to improvements in adhesion [15], none of them were specially designed for enhancing adhesion and their capability to help anti-stripping is quite limited. It has long been believed as a promising strategy to use specially designed polymers for enhancing adhesion between bitumen and aggregate [191]. Using extra polymeric adhesion enhancers and combining the function of enhancing adhesion with polymer modifiers are both possible directions, but the latter one is definitely more efficient. In fact, some efforts have been made in this direction. For example, Crossley et al. [157, 192] specially designed and prepared functional polyisoprene modifiers with amino or silane groups at one end of the polymer chain to improve the adhesion of bitumen with aggregates. It was found that high-molecular-weight silane-functional polyisoprene, which was essentially a polymeric silane coupling agent, helped enhancing both the moisture resistance and low-temperature properties of the mixture. More other attempts are supposed to be carried out in this direction.

- Long-term performance of PMB. PMB is expected to perform well in the field over a long time. To evaluate and improve this long-term performance, much research has been performed [51, 114, 193-201]. One focus area in this was testing the actual field performance of newly-developed products by placing and monitoring field test sections [114]. In the late 1980s when the application of PMB started to be promoted by SHRP, many

field test sections with PMB were constructed; and several investigations on the actual long-term performance were conducted in the following years, seen in Table 5, although some of them also paid attention to some other additives. Unfortunately, no consistency was found between these investigations but one: there is not much regularity observed by these field test sections due to the short in-service time and various uncontrollable factors in field. The other main focus area has been the measuring of durability [195-196, 202] by laboratory accelerated tests, such as rolling thin film oven tests (RTFOT) and pressure aging vessel tests (PAV). Fundamental properties of PMB, like stiffness and shear complex modulus, were considered to be more indicative than empirical ones [51]. However, the relationship between these laboratory results and the actual field performance is still not well understood. It could also be argued that the currently performed laboratory oxidative ageing protocols fail to replicate the oxidative aging that occurs in the field, which other researchers have also mentioned [200, 201]. Today, the long-term performance of PMB, both from an economical and environmental perspective, is becoming more important. So in future research, whether investigating currently available PMBs or developing new-type polymer modifiers, the long-term performance of the PMB should be a major consideration.

- **Recyclability of PMB.** Almost 30 years have passed since PMB began to be increasingly used in the late 1980s. Many of the early-constructed PMB pavements have reached the end of their service life and need resurfacing [203]. It complies with the principle of sustainable development to recycle PMB after its service life ends. Researchers tried to investigate the recyclability of PMB, especially the most widely-used SBS modified bitumen [203-209]. Although some of these investigations concluded that it is technically feasible to recycle aged PMB by adding rejuvenators or virgin bitumen [203-206], there is still no widely-accepted PMB recycling technique available today, which also affects the popularization of PMB in turn. Additionally, the mechanism of PMB ageing and rejuvenating is still not well understood. So in the future, more research should be focused in this direction. As for developing new-type polymer modifiers, the concept of sustainable design should be introduced. Many of the current problems with recycling result from the fact that the property of recyclability was not involved when most products were designed. If a modifier is initially designed with recyclability in mind, it will lead to products with better evaluation of life cycle and its popularization will be much easier.

Table 5. Investigations on the actual long-term performance of field test sections with PMB.

Year investigated	Location of sites	Amount of sites	Polymer information	In-service time before investigated	Conclusions	Reference No.
1990	USA, Canada and Austria	More than 30	Various polymers including PE, EVA, SBR and SBS	Less than 5 years	<ul style="list-style-type: none"> No significant difference was observed in performance between most test sections and the control ones. 	[193]
1993	USA	6	Various polymers including EVA, SBR and SBS	Various, no longer than 73 months	<ul style="list-style-type: none"> No distinctive pattern was found between the performance of modified and unmodified bitumen, nor among the performance of the same modified bitumen types, when compared between different sections. 	[51]
1995	USA and Canada	20	Various polymers including LDPE, some unspecified polyolefin, EVA, SBR and SBS	Various, no longer than 9 years	<p>The lack of related information made it different to draw more than a couple of specific observations:</p> <ul style="list-style-type: none"> EVA modification has a tendency for brittle behavior as seen by the reports of premature cracking; and There were no consistent trends in rutting resistance for any of the reported modifiers. 	[114]
2002	USA	1	Various polymers including LDPE, SBR and some styrene-butadiene block copolymers	11 years	<ul style="list-style-type: none"> For most test sections, the use of PMB did improve the field cracking resistance over the unmodified bitumen. However, LDPE increased the brittleness of the bitumen and mixture, leading to extensive cracking. Bitumen modification is not necessary to control rutting. Properly designed and constructed mixture can perform under heavy traffic without rutting. 	[194]
2007	Switzerland	16	Various polymers including PE, EVA, SBS and EPDM	19 years	<ul style="list-style-type: none"> After 14 years, PMBs showed some improved performance. Especially, one section with SBS modified bitumen showed great cracking resistance. However, one section with base bitumen performed as well as some PMBs. After 19 years, the crosslinked polymer modified bitumen showed very good durability. 	[197, 198]
2011	Canada	7	Various polymers including SBS, SB and RET	8 years	<ul style="list-style-type: none"> Bitumen modified with RET and PPA performed as desired, without virtual crack after eight years of service. One of the two SBS modified bitumen sections cracked at a moderate amount, with intermittent full width transverse cracks of moderate severity. The remaining sections all experienced severe and excessive distress, with numerous longitudinal and transverse cracks. 	[199-201]

6. Conclusions and recommendations

This paper reviews the achieved advances and encountered challenges in the field of bitumen polymer modification during the last 40 years. The largely discussed technical developments include the application of some popular plastomers (PE, PP, EVA and EBA) and thermoplastic elastomers (SBS, SIS and SEBS), saturation, sulfur vulcanization, adding antioxidants, using hydrophobic clay minerals and functionalization (including application of reactive polymers). Based on this overview, needed future developments of polymer for bitumen modification were analyzed and the following conclusions and recommendations are drawn:

- (1) Polymer modification has been proven to be an effective way to improve bitumen properties to some extent by many researchers and has been used widely in practice. However, the currently popular polymer modifiers have various disadvantages limiting their application. Some important problems with bitumen polymer modification are still not well understood. More efforts are supposed to be made to promote a further development.
- (2) Researchers tried various solutions to remove drawbacks of currently used polymer modifiers, among which saturation, functionalization (including application of reactive polymers) and using extra additives (sulfur, antioxidants and hydrophobic clay minerals). These solutions do overcome some disadvantages of PMB, but most cause some new problems. So more research needs to be carried out in the future to solve these problems and find new ways to modify bitumen effectively and cheaply.
- (3) Since it is currently challenging to perfectly achieve all expected PMB properties at the same time, some compromised ways might be optional for the future development of bitumen polymer modification: greatly enhancing the properties with an acceptably high cost, significantly reducing the cost with relatively poor properties or their combinations. Functionalization is considered as a promising way to enhance the properties of currently used polymers and develop new-type polymer modifiers with much greater success in the future.
- (4) It is recommended that future research on bitumen polymer modification pay more attention to the following points:
 - Function development of enhancing adhesion with aggregates for polymer modifiers;
 - Long-term performance of PMB; and
 - Recyclability of PMB.

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