




A review on polymers additives in flexible pavement

Supriya Mahida^{1,*} , Yogesh U. Shah¹, Sangita Sharma², and Prakash Mehta³

¹Department of Civil Engineering, Institute of Infrastructure Technology Research and Management, Ahmedabad, Gujarat, India

²CSIR-Central Road Research Institute, New Delhi, India

³Tawata Technologies, Ahmedabad, India

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ABSTRACT

Globally, the plastic manufacture developed plastic from many years due to the extensive utilization of the plastics in various sectors. The constant interest of the use of plastic creates huge plastic wastes which need a proper solution to dispose the plastic wastes which indirectly or directly participate to the environment problems. Taking into the account sustainability and eco-friendly aspects, there has been an increase in the importance in the utilization of the plastic wastes in the construction industries. Many researchers are focused on the use of polymer-modified bitumen since from decades. Earlier, mixing of virgin polymer was added in bitumen to enhance its properties for road construction in addition to a high temperature was considered but adding recycled polymer in bitumen almost possesses similar improved results for the performance of the pavement with respect to pure polymers. This paper is state of art about the application of polymers in bitumen pavement. In this review paper, a significant study on the benefits and history of utilizing pure and waste polymer in bitumen is conferred by survey of application of polymer in bitumen to enhance the characteristics of bitumen pavement.

Introduction

With the help of economic development, the standard of living has been improved. Thus, both economic growth and the environmental management are the essential responsibilities of twenty-first century. Simultaneously, both require an effective support and suitable applications, so that they are not only

compatible but also remain supportive. At the global level, the increase in waste management problems has become a serious issue which is due to the rapid growth of population, industrialization and urbanization [1, 2]. Lack or inadequate environmental management at the foundation level is the real problem. To minimize the environmental degradation, the basic need is to focus toward the development in the technology to find best alternatives.

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Address correspondence to E-mail: supriyamahida@gmail.com

Plastic is a synthetic or semi-synthetic polymer which is commonly derived from petrochemicals having higher molecular weight. The uses of various plastic forms are increasing constantly throughout the world [3–6]. The statistics of worldwide consumption of plastics in 2005 and 2015 are shown in Fig. 1 [7]. It shows that in 2015 the worldwide plastic usage was 45 kg/person, with the highest usage of 136 kg/person in North America. Numbers of plastics are thrown away after single-use which results in waste generation and serious environmental problems. Every year around 3% plastic wastes ended in ocean which creates problems to wildlife and nature [7]. Plastic is an essential component of modern culture, which resulted in increase in the worldwide production 380 [8–10] to 359 [11] million tons from 2015 to 2018, respectively. Figure 2 shows the production of plastic in 2015 by commercial sector [9]. Based on the estimated data, about 36% of the generated plastic is utilized for packaging. These plastic types are polypropylene (PP), polyethylene terephthalate (PET), polyethylene (PE), polyvinyl chloride (PVC), polyurethane (PUR), and polystyrene (PS) [12].

Plastics have been improved continuously with time, strength and durability, and hence, similar types of materials are now considered as a synonym for materials being resistant to many environmental constraints [13]. It is a key of innovation for many products in various sectors such as healthcare, construction, electronic, automotive, packaging, and others [14]. The different properties of plastic like resistance to chemicals and corrosion, electrically and

thermally insulating, lightweight with a high-strength-to-weight ratio, existence of different types of colors and transparent forms, shock resistant, excellent durability, affordable, effortless manufacture, water resistivity and less toxicity make a plastic as a unique and essential material in every aspects of life. Different group of chemically complex compounds linked together forms a plastic which raises a question in collection, separation and recycling. The production and reuse process of the plastics are harmful to the environment [15–19]. Naturally, the degradation of the plastics generally takes billions of years, so the possible choice needs to be followed to reuse or recycle the plastics. In many aspects, the life in 2030 will be unidentifiable correlated with the present life. Throughout this period, increase in the plastics will further play an important role in our living standards. Currently, the plastics are getting smart and probably assist various significant parts in future lives along with human being, technology depends on plastic accumulator, recyclable electronic graphics for magazines or articles and intelligent wrapping that tracks food matter regularly for deterioration signs [20]. In attention to the environment friendly and sustainably development, there is more focus on the usage of plastics in bitumen pavement. The efficiency of the pavement surface are improved by modifying the bitumen [21–29] which results in more resistance to rut and thermal cracking and reduces to damage against fatigue, temperature and stripping susceptibility [30]. High stress locations like busy streets interactions, vehicles weigh stations, airports and race tracks show success of using

Figure 1 Worldwide consumption of plastic [7].

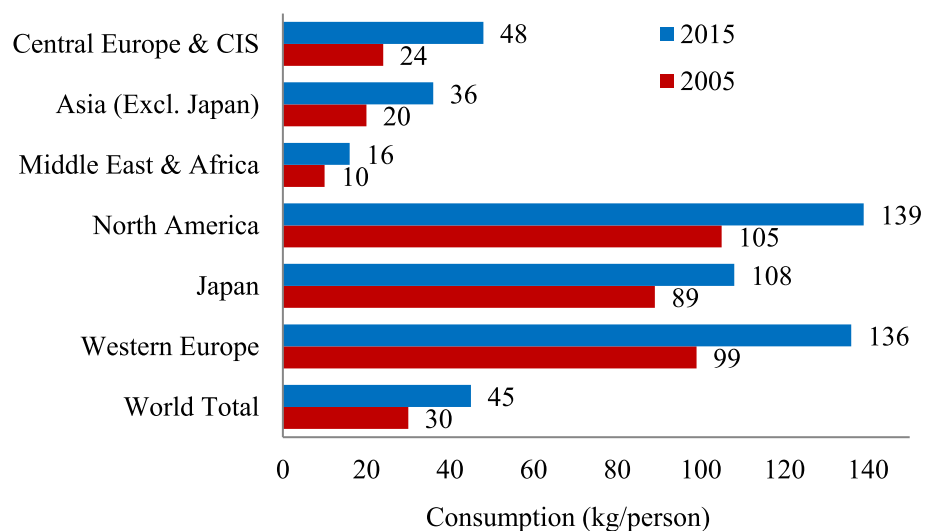
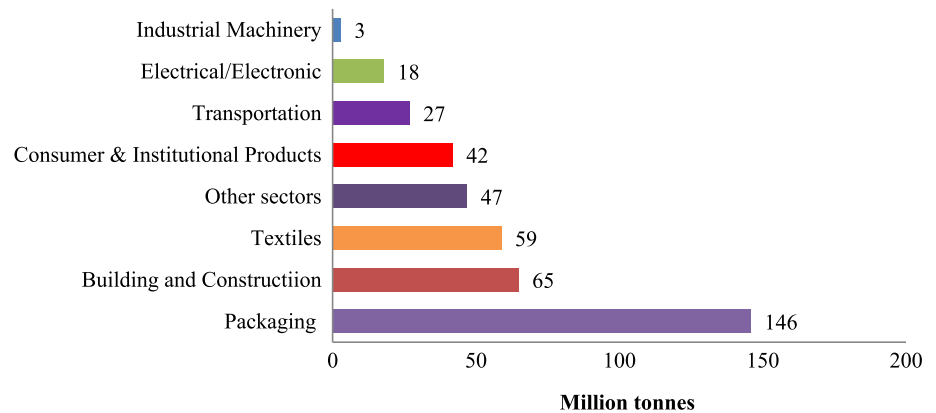


Figure 2 Production of plastic by commercial sector by 2015 [9].



polymer-modified bitumen [31]. Styrene-butadiene styrene (SBS), Elvaloy, styrene butadiene rubber (SBR), ethylene vinyl acetate (EVA), PP, PE and other polymers are used to modify the bitumen which results in higher softening point and viscosity, ductility and elastic recovery. There are plenty of modifiers used to modify the bitumen which results in better performance of surfaces of the roads, but many of them are pure polymers which are complex to identify and are expensive to use as a modifier [32]. To overcome the use of expensive virgin polymer, wastes polymer for the bitumen modification can be used in road construction which helps to reduce the wastage of polymer plastic and shows better performance of the pavement surfaces simultaneously [33–38] which results in both environmentally and economically sustainable solutions [39]. Polymer-modified bitumen determines their technical and theoretical root from the urgency to enhance the durability and efficiency of the bitumen pavement. The modified bitumen is also commercially available modified with different polymers.

This review paper mainly describes about the history, advantages, applications, developments and challenges of the polymer-modified bitumen technologies. Moreover, it also investigates the feasible solutions to resolve the problems against the use of virgin and waste polymer in bitumen modification.

History of polymer-modified bitumen

Bitumen is an oldest known engineering material [40]. In ancient days, natural bitumen was directly used from the earth's surface [41] and modifying bitumen with polymer has a long history. In early

1843, the process of bitumen modification using both natural and synthetic polymers patents was granted [40, 42–46]. In Europe, 1930s the tests projects were ongoing whereas the North America started to utilize the rubber latex in 1950s. Back 1970s, Europe was leading against the United States in using modified bitumen which was limited due to high cost of polymer-modified bitumen [45, 46]. US started using recent developed polymers and technologies of Europe in the mid of 1980s. The polymer-modified bitumen was recorded in the guidelines and provisions of National Asphalt Specifications by Australia [46]. Research and development in polymer-modified bitumen were majorly done by US, France, China and Italy; moreover, some of the promising works also done by Canada, Japan, Russia, Germany and Great Britain [47].

Advantages of polymer-modified bitumen

Bitumen contributions were greatly in the performance of pavement as it has deformation and viscoelastic properties [47]. Bitumen has been in use for roofing and paving aims because of its excellent adhesion and cohesion property with aggregates [41, 47–51]. Stability and flow are the two main properties for the bituminous mixture. To control the traffic demands, optimum stability and minimum flow should be achieved. Shoving and flow on the pavement surface caused due to the lower stability than the traffic demand [52]. To minimize the cause of rutting on the pavement, the flow should be lower. The increase in the flow causes reduction in the stability [53]. In hot-warm environment rutting and in cold environment fatigue cracking are related to the

sensitivity of the bitumen pavement to the temperature difference and the traffic load [54]. High-performance pavement needed when the traffic volume, tire pressure and heavy vehicles increase which requires bitumen as less susceptible to temperature and better adhesion to aggregates. Bitumen properties can be achieved successfully by selecting proper initial crude or the refining process for the production of bitumen. Very few crudes produce good bitumen dealing with limited refining process for the bitumen [47]. Furthermore, industry steps in to modify the bitumen. Air blown process produces hard bitumen [55–57]. For the soft bitumen, fluxing agents or diluents oil is used in the bitumen. Other way to improve the quality of bitumen is by adding polymer in bitumen [47]. Polyphosphoric acid (PPA) used as a modifier in the bitumen without air blowing firstly produced by the Oil Shale Company (TOSCO). Many polymers like SBS, acrylonitrile butadiene styrene (ABS), EVA, styrene-isoprene block copolymers (SIS) and PE were used along with PPA. Both synthetic and natural polymers used for bitumen modification show better performance in the bituminous pavement [51], and bitumen modification is done by the method of blending [49]. Many studies have been conducted on polymer-modified bitumen mixtures from the past two decades. Modifying the bitumen by adding polymers aiming to improve its properties at different temperature ranges in road applications was deliberated in olden days [58]. The use of polymer in bitumen significantly shows an improvement in the performance of the bitumen pavement at low, intermediate and high temperatures. It increases the permanent deformation resistivity, thermal and fatigue cracking at lower temperature and shear modulus at higher temperature of the mixture [49, 54]. The study shows that even adding small amount of polymers to modify the bitumen increases the life span of road pavement [59]. Improvement in the engineering properties involving rut resistance, fatigue cracking, stripping and temperature susceptibility has led the use of polymer-modified bitumen in paving and maintenance operation which results in the reduction of life cycle costs [47]. Table 1 shows the characteristics of different polymers with respect to its advantages, disadvantages and use [40, 42, 60–66]. Each polymer type associates with various positive and negative challenges as a bitumen modifier.

Application of waste polymer alternative to virgin polymer

Initially, it was known to use the virgin polymer to enhance the characteristics of modified bitumen; however, some of the interest's shows to replace virgin polymer with recycled polymer [49]. The important role of the polymer-modified bitumen is to improve the resistance of bitumen mixtures in contrast to cracking at high temperature, without any negative impacts on the low temperature characteristics. The importance of the polymer-modified bitumen is expanded with the improvement in technology because of the demand of a new binder and acceptable for heavy traffic load [67]. The cost of virgin polymer used to enhance the road performance should be overall economic and cost effective but found to be expensive. Recycled polymer shows similar results compared with virgin polymer for better performance of the road. Utilizing the waste polymer as a modifier is valuable, economically and environmentally free as it helps to enhance the pavement performance and providing better characteristics of the roads and also resolve the issues of waste dumping [49]. The characteristics of different polymers used to modify the bitumen are shown in Table 1 which explain the outline of polymers and their applications with advantages and disadvantages as bitumen modifiers [47]. The better quality and longer life of the polymer-modified bitumen pavements often lead to economic aspects compared with conventional unmodified bitumen [68]. According to the use of polymer in bitumen modification, the polymer can be divided as thermoplastic elastomers and plastomers polymers. Generally, elastomers increase the elastic behavior in bitumen and plastomers increase the stiffness and binder viscosity. Ethylene vinyl acetate (EVA) and polyethylene (PE)-based compounds are types of plastomers [69–72]. These polymers can enhance the stiffness of the bitumen and produce a blend of higher viscosity at room temperature. Typically based on different types, polymer requires high shear mixing [69].

Incorporation of polymer in bitumen

Typically, mixing of bitumen and polymer produces polymer-modified bitumen and was broaden because of the conventional bitumen pavement which turn

Table 1 Characteristics of polymer as a bitumen modifier [40, 42, 60–66]

Polymer	Advantages	Disadvantages	Uses
Polyethylene (PE)	High temperature resistance High modulus	Hard to disperse in the bitumen High polymer contents are required to achieve better properties	Industrial use Few road applications
Polyvinyl chloride (PVC)	Aging resistance Low cost Lower cracking PVC disposal	Instability problems No elastic recovery Acts mostly as filler	Not commercially applied
Ethylene-vinyl-acetate (EVA)	Outstanding compatibility in some cases	No improvement in elastic recovery	Paving and roofing
Polypropylene (PP)	No important viscosity increase even though high amounts of polymer are necessary (ease of handling and layout)	Separation problems	Isotactic PP is not commercially applied
	High R and B	No improvement in elasticity or mechanical properties	
	Low penetration	Low thermal fatigue cracking resistance	Atactic PP is used for roofing
	Widens the plasticity range and improves the binder's load resistance		
Styrene-butadiene block copolymer (SBS)	Higher flexibility at low temperatures	High cost	Paving and roofing
Styrene-isoprene block copolymer (SIS)	Better flow and deformation resistance at high temperatures Strength and very good elasticity Increase in rutting resistance	Reduced penetration resistance Higher viscosity at layout temperatures Resistance to heat and to oxidation is lower than that of polyolefins (due to the presence of double bonds in the main chain)	
	Higher aging resistance	Asphalts suitable for SBS blends, need an asphalt with a high aromatic and a low asphaltene content	
	Better asphalt aggregate adhesivity Good blend stability, when used in low proportion		

into incompetent from the last few years due to heavy traffic and increase in load which leads to reduction in the pavement service life. Generally, simple mechanical stirrer under high shear is adopted for dispersion of the polymer in bitumen to produce polymer-modified bitumen. Almost 75% of elastomeric modifiers, 15% of plastomeric modifiers and the other remaining 10% are followed in other

categories [73]. Report suggests that by adding waste plastic in bitumen about 5–10% by weight proportions increases the durability and strength properties of the pavement [74]. In general there are two common methods to mix the polymer in bitumen are dry and wet method. In wet method, latex polymer added in bitumen, whereas in dry method, solid polymers are added in bitumen. Wet method is

generally easy and straightforward. When polymer is directly added in the aggregates and then bitumen is called as dry method. It requires adequate mixing and shearing for the uniform dispersion of polymers. Study showed the use of dry method with high- and low-density polyethylene (HDPE & LDPE) [69]. The solid polymers at high temperature were blend with bitumen since the modified bitumen utilized for road mix. The time of mixing and temperature depends on the bitumen and polymer type. Such as, Naskar et al. [75] reviewed the issues of plastic wastes as a modifier on degradation kinetics and thermal stability of bitumen/waste plastics blend. They used various types of plastic wastes and mixed with penetration-grade bitumen of 60/70 at 180 °C for 45 min. Garcia-Morales et al. [76] studied on four different classes of polymer wastes and mixed with penetration-grade bitumen of 60/70 at 180 °C for 6 h. Report by Shell [40] indicated that the temperature of mixing should be within 185 °C to avoid burning of bitumen and the mixing time should be enough to produce a homogenous mixture of polymer-modified bitumen. Typically, dry method requires significant shearing and mixing for uniformly distribution of the polymer in bitumen. In this method, polymer in a form of a solid like chips or granules was mixed with aggregates and then combined with bitumen. Awwad and Shbeeb [69] studied two different types of polymer by adopting dry method, namely LDPE and HDPE. Mahida et al. showed the uniformly dispersion of 3% PS in VG 30 conventional bitumen by using SEM image as shown in Fig. 3 [77].

Factors affecting polymer-modified bitumen properties

Characteristics of polymer

Polymer gives the most productive mixture when polymer mixed with bitumen to enhance the rut resistance at higher temperature apart from having it more viscous while mixing or extremely brittle at lower temperatures. The modifier supposed to be enough compatible with bitumen to prevent it from phase separation during storage and for further applications. Adding of polymer in bitumen starts from the dosage range from 2 to 10% by weight of bitumen, but most of them adopt 5 to 6%. From last few years, 2–3% polymer content has been chosen. Currently, the uses of waste materials to modify the bitumen are preferred as it lowers the overall cost and also mixed at higher percentages. Many criteria, namely average molecular weight, crystallinity, structure, polymer content, and chemical composition, of the polymer can alter the process of polymer modification [40, 78]. Figure 4 shows the structural formula for some of the polymer modifiers [79]. At lower temperature, the conventional bitumen influences the mechanical characteristics of mixtures; at the same time, mixing modifiers do not show any results on stiffness at lower temperature. Hence, addition of modifiers can absolutely enhance the bitumen temperature susceptibility [80].

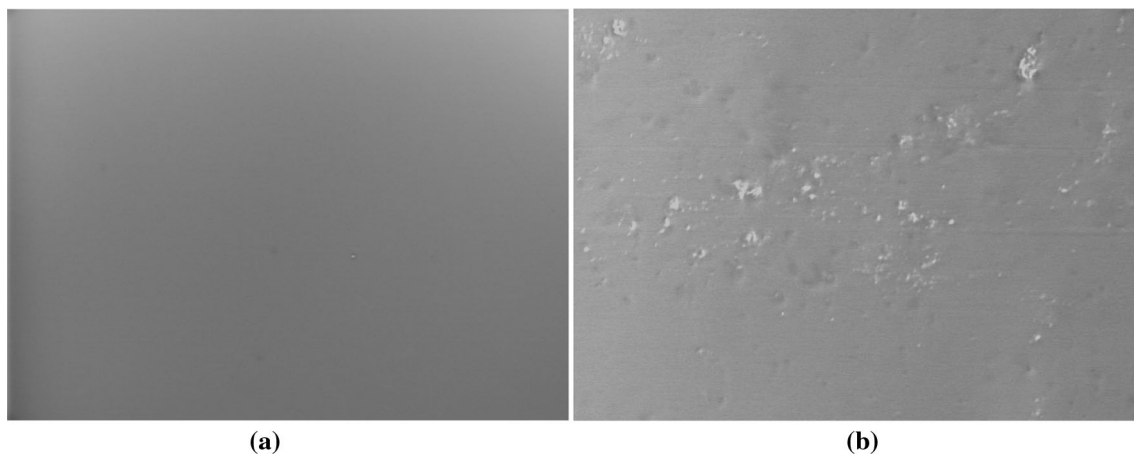


Figure 3 Dispersion of **a** VG 30 and **b** 3% of polystyrene waste by SEM image [77].

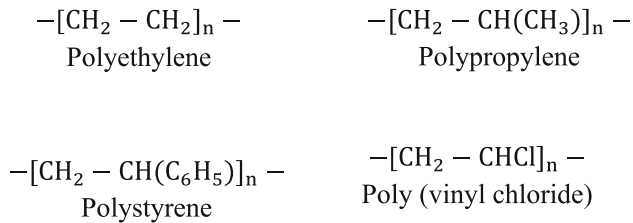


Figure 4 Structural formula of polymer modifiers [79].

Characteristics of bitumen

Bitumen can be natural or industrial type which consists of extensive type of complex organic elements from various origins, structures and industrial applications. The nature of the bitumen is affected by the mechanical properties, stability and micro-morphology. As already mentioned previously, the polymer should be enough compatible with the bitumen and control the compatibility at the time of storage and its applications. Compatibility of the polymer with bitumen is a big challenge because of variations in the viscosity, molecular weight, density and structure of the polymer-modified bitumen components [78]. Additionally, the difference in the bitumen does not simple rely on the base crude composition but also on the method of the production of bitumen [81]. The common outcome from the research on the bitumen nature suggests that the bitumen should consist of sufficient oil content to disperse and widen the polymer. Additionally, it should also include the higher aromatic hydrocarbons which blend sufficiently with polar aromatic polymers. The polymer-modified bitumen blends with high aromatic hydrocarbon in the bitumen are acceptable [82]. Polymer having less polymer content with continuous bitumen phase are enriched with asphaltenes and resins and hence leads to enhance in the properties of elasticity and consistency of the bitumen. Typically, thermoplastic polymer-modified bitumen is two-phase system; a physical blending of the components without chemical interactions. One is a swollen polymer phase, and another is a bitumen phase. The bitumen properties will change with increase in the polymer contents which results in increase in the elastic properties and tensile strength, and reduction in temperature susceptibility [47]. The thermoplastic rubber except the asphaltenes can absorb nearly all the components of bitumen [40]. Thus, high asphaltenes content in the bitumen results in gelation or its precipitation which results in phase

separation and makes blend ineffective. Alternatively, low asphaltenes content gains a single-phase blend. The acceptable degree of the asphaltenes content is determined by polymer molecular weight, aromaticity, asphaltenes molecular content and polymer content. It is important to balance the aromatic content to have a stable bitumen blend and known as compatible blends [40].

Blending requirements

The blending procedure depends on the various factors such as:

Behavior and type of the bitumen

Viscosity and composition of the bitumen influence the process of blending to a greater extent. In mainly, to expand and dissolve the polymer, bitumen should have sufficient fraction. It also expects to have a condensed component that allows ensuring the endurance of polymer-modified bitumen blends. On the other side, lower viscosity bitumen can pre-melt the polymer by itself and afterward rapid the swelling and penetration of the polymer molecules. The bitumen with lower viscosity at the temperature of blending can make better polymer dissolution at the mill which shows rapid decrease in the particle size [40].

Structure and physical behavior of the polymer

The time required for mixing of the polymer and bitumen to achieve a homogenous mixture depends on the chemical composition, its molecular weight and the type of polymer. A polymer with high molecular weight generally takes long duration for a homogenous mixture with bitumen and contrariwise. Particle with small size has large surface area per unit mass of polymer. Therefore, polymer swelling is easy and the bitumen penetration is furthered. It suggests further speedy dissolution is achieved. Therefore, pulverized polymers will dissolve and disperse very quickly than porous pellets [40].

Time-temperature of the mixing

The time and temperature of the blending depend on the bitumen type, necessity to produce its flexibility and polymer swelling. For example, the temperature

should keep below 190 °C to reduce the thermal effects during the SBS mixing process [47]. Though, the ideal blending practice should have minimum temperature for the minimum time to complete the polymer mixing in bitumen both economically perspective and to avoid the cause of thermal on the polymer. Polymer-modified bitumen characteristics and its structure are role of mixing circumstances. It represents the finer microstructure for long-time mixing and rapid completion of the process at higher temperature [47].

Different types of mixing procedure

There are two different mixing procedures of polymer in bitumen, namely low and high shear mixing. Low shear mixing is an ordinary mixing vessel with paddle-stirrer used with powdery type modifier, the process has been restricted to the dissolving and swelling by the bitumen. The mixer should sustain the homogeneity and consistency with respect to temperature. The size of polymer particle is reduced by the hydrodynamic and mechanical shear in high shear mixing. To achieve a homogenous blend, temperature should be increased during mixing to dissolve the polymer in bitumen.

Compatibility and stability

The major problem of polymer-modified bitumen is poor compatibility between bitumen and polymer which is exhibited by the tendency to separate during transportation or at high temperature static storage [68]. In unfavorable conditions, poor compatibility and stability leads to macroscopic segregation of polymer-rich and bitumen-rich phase results in handling related issues and possessed high viscosity. Therefore, paving should be implemented before the thermodynamically unstable polymer/bitumen blends produced with high shear process/high temperature can split. Approximately, all polymer-modified bitumen leads to uncertainty whether they cause separation or not is fundamentally a kinetic difficulty. Therefore, the first demand of polymer-modified bitumen for every researcher is to focus on these problems. A polymer with bitumen can be compatible, slightly compatible or incompatible.

Compatible polymers

Generally, compatible polymers provide substantially stable mixture of polymer-modified bitumen by adopting conventional mixing methods which may or may not enhance the physical characteristics of bitumen. The polymer-modified bitumen should be enough compatible to prevent from phase separation while storing and its bitumen application and to gain the required pavement characteristics. Polymer-modified bitumen having poor storage stability is not recommended for the application of paving, roofing and other industrial works. The compatibility of polymer-modified bitumen depends on the sizes of asphaltenes, polymer molecules and aromaticity. The stability and compatibility of the polymer-modified bitumen blends can be enhanced significantly through various compatibility methods. For example, bitumen and polymer are connected with groups of sulfonic acid or sulfonate and further mixed by Exxon Research and Engineering Co. [47]. For the purposes of better compatibility of the mixer, ButaphaltTM used as an additive which deal with inclusion of an acid after the mixing of the polymer in bitumen by TexPar Energy, Inc. [47]. Ergon Incorporated reported that if an acid is mixed to the bitumen prior to the polymer can enhance the storage stability of the bitumen. It is also well-known that the cross-linking agents like sulfur further enhance the storage stability of the polymer-bitumen structure. It is expected that the polysulfide bonds or sulfide chemically combines the bitumen and the polymer through sulfur. However, bitumen itself includes different types of base sulfur, and the adding of supplementary sulfur is significant to enhance the stability. The blends are completely compatible and homogenous when the polymer is completely dissolved in bitumen. UV microscopy explains the compatibility and homogeneity of the polymer-modified bitumen. Figure 5 and 6 [40] are the fluorescence micrograph that shows the compatible and incompatible system with 4% SBS, respectively. The images were captured every 1 h and observed with the help of fluorescence microscope to check its degree of polymer included in the bitumen. As shown in Fig. 5, the polymer grains are finely dispersed in bitumen and form a homogenous mixture which is considered as compatible system whereas Fig. 6 considers as incompatible system as the mixture fails to appear as homogenous. To find out the



Figure 5 Compatible system with 4% SBS [40].

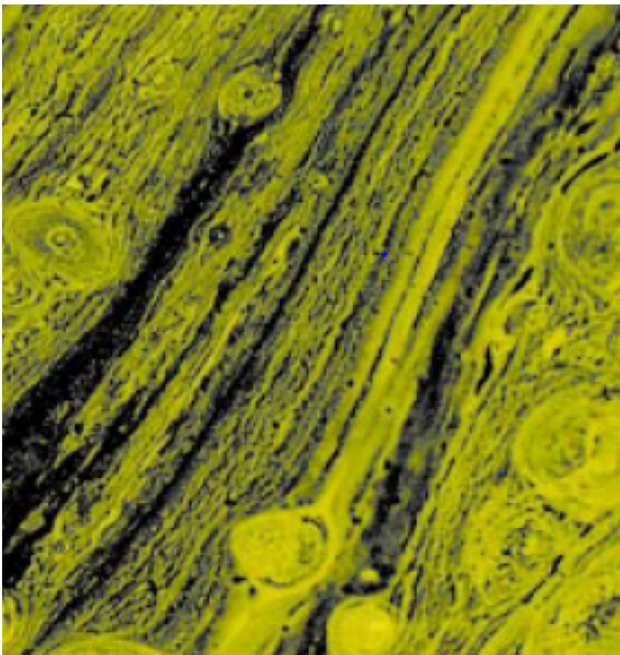


Figure 6 Incompatible system with 4% SBS [40].

compatibility of the polymer-modified bitumen, various methods were approved such as difference in rheological changes, softening point and phase compatibility. About 50 g of polymer-modified bitumen sample is poured in aluminum tube of diameter by 125–140 mm length. At 163 ± 5 °C for 48 ± 1 h, the aluminum tube kept vertically in sealed condition.

The aluminum tube was removed from the oven after the end of conditioning period and placed it immediately in the freezer at -10 ± 10 °C for 4 h minimum, so the sample gets solidified completely. Take out the aluminum tube from the freezer and slice it into three equal parts. Melt the part of top and bottom of the aluminum tube into separate covered 100 ± 20 ml beaker for performing softening test and discard the center part. The difference in test results between top and bottom indicates that there is a degree of incompatibility between the bitumen and polymer. The sample shows high storage stability or compatible system when the softening point difference of the top and bottom is lower than 3 °C. The sample which are unstable or incompatible system results in phase separation when the softening point difference of the top and bottom is more than 3 °C. The microstructure of the top and bottom samples can be observed through fluorescence microscopy to examine its compatibility. The top and bottom samples appear same continuous phase showing true stability of the samples.

Slightly compatible polymer

A slightly compatible polymer needs specialized thermal, mechanical or chemical processes to successfully enhance the properties of bitumen. For example, slightly compatible polymer requires high shear mixing with suitable high temperature to produce a homogenous mixture with bitumen.

Incompatible polymers

Incompatible polymer produces a heterogeneous mixture when mixed with bitumen. In this situation, the polymer changes the chemical stability of the bitumen, and as a result, the mixture possesses inadequate ductility and cohesion. All trading polymer-modified bitumen is heterogeneous at micron scale [83, 84, 85].

Literature review on polymer-modified bitumen (highlights)

From the past, many researchers have concentrated on the utilization of polymers in the bitumen. There are various types of polymers that are available globally and many of them can be easily recycled in

bitumen [86, 87] such as LDPE used extensively in mineral water bottles and soft drink [88]; HDPE used in packaging and plastic bottles; PVC used in plumbing and fittings pipes; PP used in wrapping

industries and straws; acrylonitrile butadiene styrene (ABS) used in laptop, mobile phones and other electronic devices and PET widely used in water bottles and soft drinks. Table 2 shows different types of

Table 2 Examples of different types of modifiers [89]

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
	Thermoplastic polymers	Ethylene–vinyl acetate
Ethylene–methyl acrylate		EMA
Ethylene–butyl acrylate		EBA
Atactic polypropylene		APP
Polyethylene		PE
Polypropylene		PP
Polyvinyl chloride		PVC
Polystyrene		PS
Thermosetting polymers	Epoxy resin	PU
	Polyurethane resin	
	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	
	Latex	Natural rubber
Recycled materials	Crumb rubber, plastics	
	Fibers	
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 asphalt	Trinidad Lake Asphalt	LA
	Gilsonite	
	Rock asphalt	

modifiers used to modify the bitumen [89]. Based on the suitability and availability of the polymers, the bitumen is modified for the road construction [90].

Thermoplastic elastomers

Thermoplastic elastomers recover its elasticity after removal of load and also withstand permanent deformation under stretching [47]. Commonly, mono- or di-olefins of block copolymers are used as thermoplastic elastomers modifiers. Generally, styrene molecule as mono-olefin is used as mesomer, while isoprene or butadiene unit is di-olefin which is commonly used elastomers such as styrene styrene-ethylene/butylene-styrene (SEBS), styrene butadiene styrene (SBS) and SIS. The structure of the thermoplastic elastomer is typically linear and having poor inter-connection. However, the mostly used bitumen modifier is radial SBS copolymer. The linear and radial form of SBS structures is shown in Fig. 7 [91].

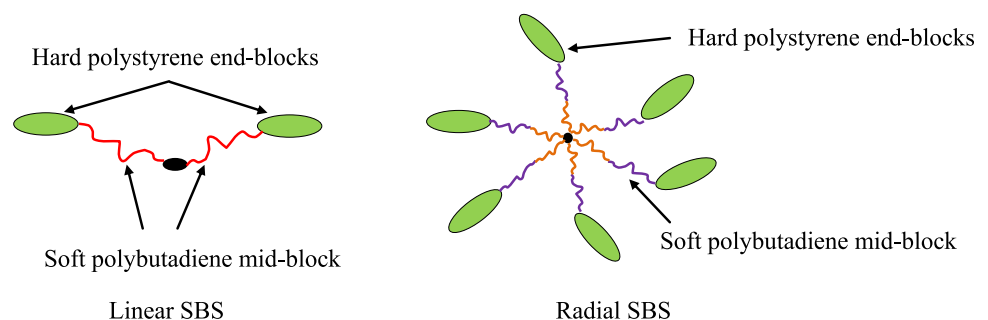
As shown in Fig. 7, the two hard polystyrene blocks are connected by two soft polybutadiene block which are linear SBS, whereas the radial type arrangement by hard polystyrene blocks around the soft polybutadiene block is radial SBS. This configuration characteristic is significant as it indicates the final outcome of the blend. It has been found that the highly stable system and an improved rearrangement of the viscous and elastic constituents of the bitumen are provided by the radial structure. The stability and elastic properties of the styrenic elastomer are because of the three-dimensional matrix arranged by the interlacing of the particles. The 3-D vertexes of the matrix are shaped by polystyrenic blocks that shape split the region in a rubber matrix made by polybutadiene blocks.

The stability in the polymers is due to the presence of polystyrenic blocks and elasticity due to the polybutadiene blocks. The polystyrene starts softens

above its glass transition temperature ($T_g = 100\text{ }^\circ\text{C}$) which results in the instability of the polystyrene domain. This permits a simple processing of the bitumen. The styrenic block restores the strength and elasticity with respect to cool and normal temperature which generally re-accumulates and restores the rigid domains. When SBS polymer is included, certain connections take place among SBS and bitumen. The light constituents of bitumen were absorbed by PS blocks which results in swelling of the PS and cause bitumen hardening [73, 92]. By providing continuously remarkable properties, reasonably good storage stability and cost-effective have gained SBS as most famous bitumen modifier. Several studies proved that the penetration decreases, softening point increases, viscosity increases and lowers the thermal susceptibility on adding of SBS in the bitumen. The amount of SBS to be added in bitumen has an important contribution in the properties of polymer-modified bitumen. Lower concentration of the SBS leads to discrete phase, while higher concentration leads to phase separation and formed two interlinked continuous phase; typically known as bitumen-rich phase and SBS-rich phase. Further, SBS-rich phase is distinguished by two sub-phases: polystyrene domain and swollen polybutadiene matrix [92]. However with the confirmed positive effects by using SBS to modify the bitumen are remains significantly from perfection.

However, with many definite positive effects of using SBS to modify the bitumen, they still remain to be ideal. Such as, the compatibility between SBS and bitumen is not that satisfactory and storage instability of bitumen modified by SBS was recorded even for bitumen having lower SBS content [93–95]. As shown in Fig. 4, the same degree of compatibility may not be achieved with other conventional bitumens. In this regard, an agreement was noticed by Airey among thermoplastic elastomer and asphaltene to absorb

Figure 7 Linear and radial form of SBS structure [91].



the light constituents of bitumen in SBS-modified bitumen [73]. The cause of phase separation in modified bitumen is due to the inadequate amount of light constituents. It was also observed that the presence of high amount of aromatic in the lattice forms a stable and compatible SBS-modified bitumen [83]. From this perspective, it has been found out that the adding of aromatic oil to the lower aromatic content can enhance the compatibility within SBS and bitumen blends [96]. Although, few polystyrene blocks leads to swelling and anti-plasticization due to the excessive aromatic content (70–80%) present in the modified bitumen [90], which signifies the inadequate outcomes of the modified bitumen properties. Linear SBS offers higher stability than radial SBS copolymer, when it blends with bitumen including 50–60% aromatic content which was achieved by Lu et al. [97]. Furthermore to concentration and structure of polymer, it has been found that polymer's molecular weight is an extremely significant to compatibility between polymer and bitumen. It has also indicated that with increase in molecular weight, blend stability and entropy decrease. In this context, Lu et al. studied the blend stability of both linear and radial SBS with same S/B ratios which results in greater stability achieved by linear SBS rather than radial SBS blend. Although, it is questioned about the major differences noticed whether the linear and branched copolymers have same molecular weights because of the different molecular structure mentioned by Polacco et al. [68].

Thermoplastic polymers

Polyolefinic plastomers referred as a thermoplastic which includes PP, ethylene butyl acrylate (EBA), PE, PVC and EVA. There are three different forms of PP; HDPE, LDPE and linear low-density polyethylene (LLDPE) are most widely used plastomers. The application of plastomers polymers is to modify the bitumen that develops as a result of the expensive styrene polymers and the deterioration experiences because of unsaturation. In comparison, the polyolefinic plastomers which is widely available possess high stability and are less expensive than styrene. Increase in the rut resistance and stiffness of the bitumen are effects of the existence of polyolefin polymers [47, 98]. Therefore, plastomers play an essential part in polymer-modified bitumen where they show approximately 15% of the benchmark

trade. Punith and Veeraragavan [99] studied on 80/100 grade bitumen. Polyethylene was used in various proportions. The blends of modified bitumen were examined by performing various tests such as indirect tensile strength, Hamburg wheel track, resilient modulus and an unconfined dynamic creep. These experiments outcomes indicated that the performance characteristics of polyethylene-modified bitumen were better than the conventional mixtures. However, polypropylene and polyethylene are mostly used plastomers, the compatibility issues due to their non-polar nature with bitumen further pointed by their leaning to crystallize which strongly controls the reactions with bitumen [84, 100]. The compatibility issues of thermoplastics such polymer types are unsuccessful to improve elastic properties of bitumen [47]. To overcome the issues of crystallization and compatibility other groups of thermoplastics have been adopted. Basically, the incorporation of acetate groups in polymer will develop the modified polymer, obtaining EVA with vinyl acetate group, EBA and ethylene methyl acrylate (EMA). The polymer having group of esters provides dual benefit of increasing polarity and minimizing the crystallization preference, interrupting the densely packed microstructures [41]. Both of these factors improve the storage stability and compatibility of the bitumen blends. Usually, compare to the plastomer compatibility with bitumen matrix, it is expected that high ester proportion obtains low crystallinity. However, the degree of crystallinity should be well-balanced. Due to the low degree of crystallinity, the matrix part is likely to be broken initially after the crystals get connected with the elements of bitumen. By utilizing the vinyl-acetate in EVA, the optimum degree of crystallinity is obtained from 14 to 28%. Although, in spite of the improved properties achieved by utilizing the EVA and different polymers, like storage stability, the difficulty of elastic recovery of polymer-modified bitumen continues to exist [41, 42, 47]. Additionally, its glass transition temperature relies on the content of acetate is not sufficiently low to enhance the properties of bitumen at low temperature [101]. From this perspective, Ameri et al. showed that addition of EVA ranges from 2 to 4% in bitumen will increase the resistance of bitumen against low temperature cracking, while it get reduced on adding EVA about 6% [102].

Thermosetting polymers

Thermosetting plastics are two liquid blends, namely resins and hardener, are initially mixed together and then mixed with bitumen just before utilization as surface coating or before combine with aggregates for the production of bitumen. These plastics are polymers that change to solid state during heating or enforce rigidity. Prior to hardening, these polymer molecules have similar linear structure as thermoplastic molecules but have considerably smaller size of molecules. The molecules of thermosetting polymer are chemically active. Moreover, they also include various chemically active class or double bonds. As a result, under definite circumstances such as during hardening, heating or irradiating, thermosetting molecules react together and frame a stable structure. Polyurethane, silicone, acrylic, phenolic, epoxy, polyester and other resins are different types of thermosetting polymers [103]. Study shows that when epoxy thermosetting polymer added in bitumen to modify the bitumen exhibits the outcome of the properties of epoxy rather than the properties of bitumen [90]. As epoxy modified bitumen exhibits the outcome of the properties of epoxy, the possible duration to utilize the modified bitumen is restricted and depended on a significant mixing temperature. As the temperature increases, the usage time will be less. After developing this modified bitumen, it starts to heal and enhance the strength after its application. The healing time is as per the room temperature. At high room temperature, the healing time will be longer. Once healing is completed, increase in future temperature, which makes conventional bitumen softens and does not influence the strength of the thermosetting bitumen in any way. The fully healed bitumen is named as an elastic substance with non-viscous nature. However, polymer-modified bitumen with thermosetting polymers has comparatively good bonding with mineral particles and high resistance shall not usual for the use of paving. This is because firstly, during introducing of these polymers, causes to enforce strength, the technical characteristics of polymer-modified bitumen are approximately gets instantly worsened; secondly, at low temperature, the rigidity of the PMB increases which lead to increase in temperature sensitivity; thirdly, the utilization of the thermosetting polymer makes system more difficult and causes increase in its cost; and ultimately, the efficiency of these polymers usually appears in

huge quantities (above 10 wt%) in bitumen. Bitumen mixtures prepared by adding thermosetting polymer show great bonding ability, exceptional resistant against deformation, high modulus of stiffness and better fatigue behavior.

Concluding remarks

Polymer-modified bitumen is continuously getting attention toward road construction practice and in current days approximately all highways are projected by utilizing such binders with a lots of benefits. Such benefits like reducing overall maintenance cost tend to compensate its initial expenditure which is almost one and half of unmodified bitumen. This paper reviewed recent research on virgin and waste polymer used to modify the bitumen for improving bitumen pavement performance. The application of virgin polymers in road construction has proved to be beneficial in the matter of enhancing definite pavement properties as explained through investigation and analysis in the last few years. Researchers have a general agreement that some of virgin polymers are extremely improved the lifespan and performance of the pavement when they appropriately mixed with bitumen at optimum dosages and other conditions. Researchers showed that application of waste polymers in bitumen also proved superior bitumen properties similarly as virgin polymers. Therefore, using waste polymer for the road constructions will be advantageous and economical from various aspects. Furthermore, utilizing of waste polymer in road construction will improve the pavement performance and also reduce the landfill and protect the human health and environment from pollution.

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