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POLYETHYLENE AND POLYPROPYLENE MODIFICATION FOR ENHANCED BITUMEN PROPERTIES

Annotation: This paper presents a review of both the research and practice regarding the latest available information on bitumen modified using polymers, among which special attention is paid to polyethylene (PE) and polypropylene (PP), both widely used to significantly improve the properties of bitumen. In this literature review, the authors concentrate on the chemical composition of modified bitumen, assessing the various approaches utilized in improving its engineering properties in paving, as well as looking at traditional additives and polymers. The latter have been shown to greatly enhance the performance characteristics and properties of bitumen. The viscoelastic behavior of polymer-modified bitumen (PMB) depends on various factors, including initial polymer structure and concentration, mixing temperature and technique, as a well as species of bitumen and its resistance to factors such as solvents and temperature

fluctuations. Though an assertion can be made that both traditional additives and polymers have the potential to improve specific properties of bitumen, PMB appears to provide significant increases to the ability of the composite material to withstand a broader range of climatic conditions.

Key words: Polymer - modified bitumen, polyethylene, polypropylene, modification, coupling agent.

Introduction

Bitumen has been utilized for millennia, and for over a century has been a staple material of the chemical industry, used as an ingredient in both adhesives and waterproofing [1]. At room temperature, in both its natural and refined states, bitumen, often called asphalt, particularly when employed as a road substrate, is a black viscous liquid or apparently solid substance obtained from heavy crude oil or even found in its natural state. The chemical composition of bitumen is extremely complex and varies, according to the crude oil origin and the refining process. It consists of a mixture of hydrocarbons and their derivatives, with a small amount of structurally analogous heterocyclic species and functional groups containing sulphur, nitrogen, oxygen and traces of metals, including vanadium and nickel. The hydrocarbon chains exhibit a saturated polycyclic aromatic, or polyaromatic, structure with a varying number of fused rings. These structures contain saturated hydrocarbon chains of different lengths and substitution structures. The actual bitumen molecule varies greatly, depending upon the aforementioned variables. It is soluble in trichloroethylene and toluene, among other solvents, substantially non-volatile, and, though virtually a solid under normal conditions, it softens gradually when heated [2]. Bitumen, which has been widely used for centuries, has a complex and varied chemical composition depending on the origin of the crude oil and the processing processes.

Bitumen is an inexpensive thermoplastic material that has been widely used in roofing and paving since time immemorial. Approximately 95% of the nearly 100 million tons of bitumen produced worldwide each year is utilized by the paving industry. It serves as an aggregate binder, forming bituminous mixes due to its excellent viscoelastic properties [3]. In paving applications, bitumen must demonstrate resistance to severe conditions, including extreme temperature variations and high traffic loads, thus its rheological properties play an important role. The majority of bitumen pavement around the world must survive such conditions, so it needs to be stiff enough to remain stable under high ambient temperatures to avoid rutting, while remaining soft and elastic enough at low temperatures to resist thermal cracking [4]. Further, bitumen must maintain this balance while under plastic deformation caused by the weight of moving vehicles. As regards functional properties, bitumen must transition to a liquid state at high temperatures, in excess of ~160°C, so as to achieve a homogeneous coating of the aggregate during the mixing process. All the above requirements strain neat bitumen past its natural specifications, so it cannot satisfy all the necessary engineering demands. The main disadvantage of bitumen derived directly from the petroleum refining processes is its limited temperature range, which reduces its use in road pavement. Nowadays, the service life of asphalt pavements has significantly shortened due to increased traffic volume and speeds. Consequently, maintenance costs in the road industry have risen, resulting in elevated prices to governments and thus to road users. Furthermore, the latter group are also put at additional risk should the former forego regular maintenance and replacement of road surfaces. Therefore, there is general agreement that the properties of bitumen must be improved [5]. Production of asphalt pavements with increased performance and quality is necessary for the purpose of reducing the costs of road construction and maintenance. In order to enhance the technical properties of bitumen, a growing number of research efforts have concentrated on chemical modification of the substance, resulting in different types of additives and modifiers being utilized. In recent years, polymers have attracted significant interest as effective modifiers, resulting in their having become preferred additives. Therefore, polymer-modified bitumen (PMB) is emerging as a focal point in much research, with the goal of enhancing the physico-chemical and rheological properties of the binder [6]. The utilization of bitumen directly from oil production imposes temperature limitations that reduce the longevity of the material. Chemical modification, particularly modification with polymers, presents a promising way for enhancing the performance and durability of bitumen, thereby the maintenance costs associated with road surfaces.

For a long time, polymer research and production has been a rapidly developing sphere, primarily due to the opportunity of manufacturing a variety of profitable materials. As they have a great number of applications, polymers are used in multiple fields across the economy, ranging from

very technical ones, such as pharmaceuticals (e.g. polyamino acids – PAAs) and electronics (e.g. polypyrrole - PPy), to more mundane ones, including cleansers (e.g. hydrophobically modified polymers - HMPs) and cookware (e.g. polytetrafluoroethylene – PTFE, or TeflonTM). At present, one of the most promising directions for the use of polymers involves employing them as additives to road bitumen derived from petroleum [7]. Production of PMB is carried out through mechanical mixing of bitumen and one or more polymers. Often, other materials are added in order to enhance the overall properties of road bitumen, or asphalt, including non-polymer chemicals, carbon nanotubes and waste products, such as glass, rubber and even other polymer materials, but this paper only considers the interactions and benefits of the combination of bitumen and specifically chosen polymer additives, though, clearly, greater effects may accrue with broad combinations. Generally, the amount of polymer in relation to the weight of bitumen ranges from 3% to 10%. Some mixtures are said to be simple, because there are no chemical reactions between the bitumen and polymer, thus the polymer is merely considered to be a filler, which enhances the overall properties of the mixture. In the second case, in which the bitumen interacts with the polymer, the mixtures are called complex, because the chemical reactions that occur between the bitumen and polymer additive are necessary in order to achieve any desired enhancements [8].

Commonly used polymer mixtures contain about 75% elastomeric polymer (e.g. styrene-butadiene-styrene – SBS) and 15% plasmomeric polymer (e.g. ethylene vinyl acetate – EVA), while the remaining 10% is shredded rubber and/or other inert materials (e.g. crushed glass). The cross-linked structure formed by elastomers and plastomers gives such polymers excellent technical properties. Therefore, when incorporated into bitumen, they help improve tensile strength, allowing a road to withstand shifting stresses, to stretch and recover its shape, and to have a more resilient and consistent surface. Plastomers are more rigid than elastomers, so provide higher initial strength under load and improve the deformation characteristics of asphalt, permitting resistance to rutting and thermal extremes. However, the use of plastomers may cause some issues, including stiffness and brittleness. The most commonly used plastomers are polyolefins, which have emerged as the leading modifier of bitumen. These include polyethylene (PE), polypropylene (PP), ethylene vinyl acetate (EVA), ethylene butyl acrylate (EBA), ethylene methyl acrylate (EMA), and polyvinyl chloride (PVC) [9]. PP is also now produced in Kazakhstan at the Kazakhstan Petrochemical Industries (KPI) plant, which is expected to output 500 thousand tons of the polymer each year.

The use of polymers enhances the performance of bitumen, but at a financial cost. Therefore, the replacement of raw polymers with recycled plastic waste is considered to be an important development, given both the potential cost savings and environmental benefits. With the increased production of polymer products in a great number of fields, as noted above, the issue of further utilization of this type of waste becomes urgent. Because used polymer materials are practically nonbiodegradable, they are typically buried in landfills, potentially exposing the environment to incalculable and unknown damage. Integrating used plastics into road construction materials is an approach that could mitigate their environmental impact by redirecting plastics that would otherwise be disposed of in landfills [10]. The utilization of recyclable and waste materials in bitumen modification should also lead to a major reduction in the total cost of adding polymers to bitumen. Consequently, plastic waste is currently considered to be the most effective substitute for traditional polymers in road applications, and has been widely studied globally over the last decade and more. However, plastic waste often consists of unknown composition and mixtures. PE and PP represent the most widely produced plastics, as they are employed in consumer products, which are most often single-use applications. Therefore, researchers often use pure PE and PP in their work, hoping to find positive applications for these ubiquitous materials. Generating interest in these polymers has increased their value, as they can potentially achieve a double life cycle [11]. In future, the current research team hopes to obtain modified road bitumen that meets the extreme continental climatic requirements of Kazakhstan, while utilizing locally produced materials, including refined bitumen, PE and PP, as well as their recycled variants. The use of polymers as bitumen modifiers is a promising way to obtain stable and durable road surfaces in different climates and infrastructures. Using recycled plastic waste as a replacement for traditional polymers not only benefits the environment, but also provides significant cost savings.

The application of plastomers such as PP and PE as polymers for the production of PMB arose as a result of the high cost of the currently utilized styrenic polymers, which suffer rapid degradation

due to unsaturation. Polyolefin plastomers, PP and PE, have a low cost and high availability, as well as a demonstrated higher stability, than styrenic ones. For these reasons, PE and PP now play a leading role in PMB. Although PE and PP are the most commonly used plastomers, their non-polar nature creates certain compatibility issues with bitumen. The thermodynamic instability of this system can lead to phase separation, or sedimentation, under certain conditions. Moreover, the crystallization tendency of PE and PP severely limits their interaction with bitumen, so these polymers are not able to increase the elasticity of PMB [12-14]. Researchers have employed other plastomers to tackle compatibility and crystallization issues, utilizing polymers containing ester functional groups, which are capable of forming bonds. The ester groups in these polymers increase their polarity and reduce their tendency to crystallize. These polymers, thus, improve the consistency and storage stability of PMB [15]. Examples of such plastomers include EVA, EMA and EBA, among others, though such polymers are not as widely available as PE and PP.

The analysis has shown that PE and PP modified bitumen exhibits better performance characteristics, such as being stiff enough at high temperatures to resist rutting, than conventional mixtures. Another way to increase the compatibility of PE and PP with bitumen is to add a coupling agent to the mixture. Bitumen is known for being hydrophobic, thus why it has been used since ancient times in order to protect from moisture. PE and PP are also known, and used, for their ability to repel water. In order to achieve a concerted benefit, a coupling agent that acts as a bridge between these two is necessary. Such a coupling agent needs to be both hydrophilic and hydrophobic. Using an amorphous polymer has become a solution to this problem, as such a polymer has hydrophobic and hydrophilic functional groups. Therefore, with an amorphous polymer acting as a coupling agent for a bitumen and plastomer mixture, the resulting PMB is much more suitable for road construction applications under extreme conditions [16]. In addition to a wide range of amorphous polymers, other bitumen modifiers, such as polyphosphoric acid (PPA), sulfur, maleic anhydride, and a variety of clays, have been utilized as binding agents for PMB, acting as stabilizers. Such modifiers are characterized by their low cost and easy availability in sufficient quantities [17].

Modification of neat bitumen with synthetic PE and PP allows the creation of high-performance binders that yield additional technical requirements, such as improved thermomechanical resistance. Compared to the conventional variant, modified bitumen has a broader working temperature range. The properties of PE and PP in modified bitumen depend on the form and amount of polymer added. Previous research shows that the higher the polymer content, the faster the final properties are reached [18]. PE and PP addition to a base asphalt binder results in a stiffening action of the binder itself. This effect, particularly evident at high temperatures, becomes more pronounced at greater modifier concentrations. PE and PP, being plastomers, as stated above, add rigidity to the binder and reduce the deformation under load, though, unfortunately, do not show significant improvement to the elastic behavior [19]. Incorporating synthetic PE and PP into bitumen modification not only increases the thermomechanical resistance of the resulting binder, expands its operating temperature range, but also shows significant potential in solving problems of tearing at high temperatures.

The addition of polyolefin polymers generally increases the stiffness of bitumen and provides good rutting resistance. Given their relatively low melting point and high thermal stability, these polymers are well suited to the requirements of PMB production. Even if phase stability problems arise, these modifiers still result in improvements to the mechanical properties of bitumen. Furthermore, the addition of a coupling agent eases the mixing of PMB. Higher modification generates a better framework for polyolefin. Visual evaluation and FTIR analysis of recovered polymers suggest a different interaction between the bitumen and polyolefin. Additionally, PE recovered after solvent extraction contains a higher amount of bitumen residue compared to the recovered PP, indicating a more intrinsic interaction with the bitumen [20]. The development of new PMB of specific properties is a most difficult task, as it is related to the behavior of multi-phase formation, which controls the rehology of the resulting PMB and its mechanical properties [21].

Despite the considerable number of publications on this topic, many aspects of PMB remain unclear or even, likely for trade reasons, undisclosed. On one side, in fact, the literature shows that PMB is often evaluated through empirical methods, including penetration testing and softening point testing, which effectively categorize unmodified binders, but have been inadequate when evaluating the performance of more complex compounds. On the other side, the manufacturing protocols generally adopted for PMB in a laboratory setting emulate the standardized protocols used for

traditional neat bitumen. In the production of such materials, the different nature of the modifiers and the optimization of the blending process, including mixing time and temperature, must be carefully evaluated, especially if the results are then shared with the industry in expectation of later adoption. In addition to materials utilized, such parameters have a significant impact on bitumen-polymer interactions, and, thus, the characteristics of the final product [22].

Conclusion

This article summarizes the results obtained from a literature review on the modification of different types of bitumen with polymers such as PE and PP. As a result of processing crude oil from different deposits, bitumen with varying chemical composition is produced. Unfortunately, the complexity of the chemical composition of bitumen from a variety of deposits and refineries results in significant differences in mechanical properties. With global economic development has come a significant increase in the number of cars and trucks, and, thus, the demand for bitumen has jumped sharply. Further, bitumen should also be adapted to local climatic conditions, which is a challenge that requires modern material science. As neat bitumen does not meet all desired requirements, many polymers have been tested as modifiers, so as to match the performance of the binder to specific applications, ranging from ambient temperatures near the natural melting point, all the way down to those below freezing, which makes it brittle. The ultimate properties of any resulting PMB depend on the characteristics and amount of polymers added. Among them, PE and PP are the most common, due to their availability and low cost. PE and PP modified bitumen binders are suitable for improvement of deformation resistance of bituminous compounds and asphalt concrete mixtures under high stresses. In spite of the proven advantages regarding the utilization of polymers in bitumen, compatibility issues arise when modifying bitumen with PE and PP, such as the occurrence of phase separation. Various solutions for overcoming the disadvantages of these polymer modifiers have been found, which has resulted in their wide adoption over the last few decades. Binding agent compounds overcome some of the issues, such as compatibility, but cannot completely solve them. Therefore, in the future, more research, both in the laboratory and the field, is needed so as to solve such problems and find new ways to maximize the properties of PMB both efficiently and cost effectively.

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ПОЛИЭТИЛЕН ЖӘНЕ ПОЛИПРОПИЛЕНМЕН БИТУМ ҚАСИЕТТЕРІН АРТТЫРУ ҮШІН МОДИФИКАЦИЯЛАУ

Бұл мақалада полимерлерді қолдану арқылы модификацияланған битумдар туралы соңғы қол жетімді ақпаратқа қатысты ғылыми зерттеулер мен тәжірибелерге әдеби шолу берілген, олардың арасында битумның қасиеттерін айтарлықтай жақсарту үшін кеңінен қолданылатын полимер - полиэтиленге (ПЭ) және полипропиленге (ПП) ерекше назар аударылады. Бұл әдебиеттік шолуда авторлар модификацияланған битумның химиялық құрамына ерекше назар аударады, оның жол төсемдерінде қажет пайдалы инженерлік қасиеттерін жақсартуда қолданылатын әртүрлі әдістер мен тәсілдерді бағалайды, сонымен қатар дәстүрлі қоспалар мен полимерлерді де қарастырады. Модификациялауға қолданылатын полимерлер битумның техникалық сипаттамалары мен қасиеттерін айтарлықтай жақсартатыны көрсетілген. Полимер — модификацияланған битумның (ПМБ) тұтқыр серпімді қасиеті әртүрлі факторларға, соның ішінде полимерлердің бастапқы құрылымы мен концентрациясына, араластыру температурасы мен техникасына, сондай-ақ битум түрлеріне және оның еріткіштер мен температура ауытқулары сияқты факторларға төзімділігіне байланысты екені көрсетілген. Дәстүрлі қоспалардың да, полимерлердің де битумның арнайы

ерекше қасиеттерін жақсартуға мүмкіндігі бар деген тұжырым жасауға болады, ПМБ композициялық материалдың климаттық жағдайлардың кең ауытқу ауқымына төтеп беру қабілетін айтарлықтай арттыруды қамтамасыз етеді.

Түйін сөздер: Полимер – модификацияланған битум, полиэтилен, полипропилен, модификация, байланыстырушы зат.

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МОДИФИКАЦИЯ ПОЛИЭТИЛЕНОМ И ПОЛИПРОПИЛЕНОМ ДЛЯ УЛУЧШЕНИЯ СВОЙСТВ БИТУМА

В данной статье представлен обзор как научных исследований, так и практического опыта. касающихся последних доступных данных о битумах, модифицированных с использованием полимеров, среди которых особое внимание уделяется полиэтилену (ПЭ) и полипропилену (ПП), которые широко используются для значительного улучшения свойств битума. В рамках этого литературного обзора авторы сосредотачиваются на химическом составе модифицированного битума, оценивают различные подходы и методы, применяемые для улучшения его технических характеристик при строительстве дорожных покрытий, а также рассматривают традиционные добавки и полимеры. Исследование подтверждает, что полимеры значительно улучшают эксплуатационные характеристики и свойства битума. Вязкоупругие свойства полимерномодифицированного битума (ПМБ) зависят от различных факторов, таких как исходная структура и концентрация полимера, температура и технология смешивания, а также разновидности битума и его устойчивость к таким факторам, как растворители и колебания температуры. Хотя можно утверждать, что как традиционные добавки, так и полимеры обладают потенциалом для улучшения специфических свойств битума, ПМБ, по-видимому, существенно повышает способность композитного материала выдерживать более широкий диапазон климатических условий.

Ключевые слова: Полимер — модифицированный битум, полиэтилен, полипропилен, модификация, связующее вещество.

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БИОМЕДИЦИНАЛЫҚ КӨМІРТЕКТІ АДСОРБЕНТТЕРДІҢ КЕУЕКТІ ҚҰРЫЛЫМЫ МЕН МЕНШІКТІ БЕТІН ЗЕРТТЕУ

Аңдатпа: Мақаланың мақсаты белсендірілген көмірдің беткі қабатын, микропора көлемін және жалпы кеуек көлемін йод пен метилен көк сандарымен бірнеше регрессияны ескеріп, талдау жолын байқату. Бұл әдіс күріштің қауызы прекурсорларынан дайындалған белсендірілген көмір үлгілерін зерттеу арқылы әзірленген. Және де адсорбенттің физикалық және химиялық сипаттамалары бойынша таңдау критерийлерін негіздеу болды. Кеуек құрылымын және беттік химияның әсерін жүйелі түрде бағалау үшін активтендірілген көмірді зерттелді. Йод саны мен метилен көк санын бірнеше регрессия арқылы белсендірілген көміртегі үлгілерінің бетінің ауданын, микропора көлемін және жалпы кеуек көлемін бағалау әдістемесі әзірленді. Күріштің қауызын фосфор қышқылымен түрлі температура жағдайында активациялаумен алған карбонизацияланған күріш қауызы (ККҚ) үлгілері серияларының ішінен жоғары меншікті беттік ауданы мен йод санына 400-500°С температураларда активацияланған үлгілері (ККҚ-Р-400 және ККҚ-Р-500) екені зерттелді. Бастапқы және соңғы өнімде оттегі мөлшері көп болған сайын, соншалықты белсендірілген көміртекті материал (БКМ) йод саны мен меншікті беттік ауданы арасындағы қатынасы жоғары