Review

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Radiation and Radical Grafting Compatibilization of Polymers for Improved Bituminous Binder Performance

Wiktoria Baranowska [1,2,*], Magdalena Rzepna [1], Przemyslaw Ostrowski [2,3] and Hanna Lewandowska [1,4,*]

[1] Centre for Radiation Research and Technology Institute of Nuclear Chemistry and Technology 16 Dorodna St., 03-195 Warsaw
[2] ORLEN Asfalt sp. z o.o., 39 Lukasiewicz St., 09-400 Plock, Poland
[3] Department of Transportation Engineering, Faculty of Civil and Environmental Engineering, Gdansk University of Technology, Gdansk, Poland
[4] School of Health & Medical Sciences, University of Economics and Human Sciences in Warsaw, Okopowa 59, 01-043 Warsaw, Poland
* Correspondence: wiktoria.baranowska2@orlen.pl (W.B.); h.lewandowska-siwkiewicz@vizja.pl (H.L.)

Abstract: The review scrutinizes the currently performed research on the new methods for enhancing bituminous binder performance through radiation and radical grafting of polymer modifers of bitumen. It investigates innovative methods, including using waste polymers as modifiers, and applying radiation for polymer grafting, to overcome challenges like high costs, low aging resistance and storage stability issues, of which separation of phases polymer/bitumen is the most significant obstacle. These advanced modification techniques promise sustainability through the decrease of the carbon footprint of transportation systems by improving the properties and durability of binders. Additionally, the review discusses the parameters and mechanistic aspects from a scientific perspective, shedding light on the underlying processes that contribute to the improved performance of modified bituminous binders.

Keywords: bituminous binders, asphalt mixture, polymer modification, road pavement deterioration, additives and modifiers, colloidal dispersion system, grafting

1. Introduction

Bituminous binders may occur in nature e.g. in the form of sedimentary rock or they can be obtained as a product of the crude oil refining process. This brown or black binding material has a range of consistencies, from a viscous liquid at high temperatures and long loading conditions, to a glassy solid at low temperatures or under rapid loading – this behavior is due to its viscoelastic and thermoplastic properties. Bituminous binders are either completely or partially soluble in toluene [1–5]. In terms of chemistry, the bituminous binder is an extremely complex mixture of high-molecular-weight hydrocarbons that contain heteroatoms such as nitrogen, oxygen, and sulfur, along with trace amounts of metals like vanadium and nickel [4,6]. The complexity of the chemical nature of bitumens makes it extremely difficult to understand [7], and it has yet to be fully discovered and characterized [6]. Several scientific theories have been proposed to describe the structure of crude oil and its refining products, including bitumen [8–12] among them, the most widespread is the theory that describes bitumens as a colloidal dispersion system in which asphaltenes, stabilized by resins, are dispersed in an oil medium consisting of saturates and aromatics [6]. The relative proportions of these components determine the phase stability of bitumen, the loss of which affects the deterioration of bituminous binders' properties.

Bitumens of various types and grades are primarily applied in road construction, railway, hydrotechnical, isolation materials, and chemical industries [2,4]. In road construction, bitumen plays a crucial role as a binder in the asphalt mixtures, which are used to pave road surfaces. Bituminous

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binders typically make up approximately 4-6% (w/w) of the asphalt mixture, while the remaining part consists of a properly composed mineral mixture [5], which is a set of carefully selected stone components - aggregates, sand, and filler in appropriate proportions [3]. Although bitumen constitutes a relatively small mass proportion of the entire mixture, its impact on the durability of the road surface is significant [7,13].

In recent years, the increasing transport and communication needs of the global economy and society are putting pressure to expand, upgrade and maintain the world's road network to a high level of safety and standard of travel. As a consequence of increasing transport and environmental needs, the durability of pavement structures is becoming increasingly important, which translates into road network reliability [14]. As a crucial and integral part of the transportation system, road surfaces play a significant and measurable role in promoting socio-economic sustainability [15]. It is proven [16,17] that improving the performance of bituminous binders allows to reduce the need of frequent road maintenance and repair, and can lead to a decrease of carbon footprint of transport system, aligning with principles of sustainability.

In order to improve the performance properties of asphalt mixtures and extend the service life of asphalt surfaces, various types of additives and modifiers are used for bituminous binders [3,4,18]. Polymer modification is a frequently used approach to improve the performance of bitumen by reducing its sensitivity to temperature changes. Elastomers, plastomers, and recycled tire rubbers are the most frequently introduced polymers. The viscosity modifiers, and reactive polymers being used less commonly [4]. Although polymers improve bitumen properties to some extent, there are still some drawbacks limiting the future development of polymer-modified bitumens (PMB), including high cost, low ageing resistance and difficulty with storage stability [19]. Recently, researchers have investigated the use of waste polymers as modifiers to reduce expenses and enhance environmental protection [20–22]. However, various modifiers pose different challenges associated with their integration into bitumen. Modified bitumens, which contain various additives, exhibit tendency to lose stability when stored at high temperatures for extended time. This phase separation issue significantly limits their practical applications [23,24].

The crucial parameter is chemical compatibility between modifiers and bitumen. Issues arise most commonly due to the two-phase nature of polymer-rich and asphaltene-rich mixtures, leading to thermodynamic instability and potential phase separation [25]. Achieving compatibility involves different approaches, including cross-linking with bituminous binder molecules, surface activation treatment, additives-grafting or the hybrid approaches involving more than one of the aforementioned methods [23,24,26]. Promisingly, range of modifications frequently involving radical and radiation-induced processes offer viable ways for addressing this challenge. Examples of these novel and developing approaches will be reviewed herein.

2. Electromagnetic and Electron Beam Radiation

Gamma rays, X-rays, UV radiation, and non-zero resting mass electrons are forms of ionizing radiation employed in industrial polymer modification. Ionizing radiation refers to radiation that has enough energy to remove electrons from atoms, leading to the formation of ions. In the context of industrial polymer modification, gamma rays and electron beams are particularly utilized. While photons are forms of electromagnetic radiation, manifesting as quantum mechanical excitations of the electromagnetic field, and behaving as particles with zero mass, zero charge and spin one, the electrons are elementary particles with a negative electric charge. Electrons possess rest mass, and their behavior is governed by both classical and quantum mechanics. Electrons engage with matter through scattering and ionization, and they can be redirected by electric and magnetic fields. In contrast, photons interact with matter through the photoelectric effect, Compton scattering, and pair production [27]. Unlike electrons, they lack an electric charge and remain unaffected by electric or magnetic fields. This results in different characteristics of dose deposition [28]. Electrons, even in the highest utilized in industry energies below 10 MeV (to minimize the unwanted here Bremmsstrahlung) exhibit limited penetration depth (nm-cm depending on energy) as they rapidly lose energy through interactions with matter, unlike photons, which therefore penetrate in a wider

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range depending on energy (from between 20 and 150 μm for UV up to several metres for gamma) [29].

Nevertheless, despite these differences, all types of ionizing radiation induce a similar chemical effect by dislodging electrons with energies significantly higher than the energy associated with an electron in a molecular or atomic orbital (the ionization energy of an electron in an atom typically ranges between 4 and 20 eV depending on the atom, while ionizing radiation can deliver energies in the keV or MeV range [30]). The dislodging of electrons by ionizing radiation leads to the generation of secondary electrons, which can generate ion pairs and free radicals, leading further to chemical bond breakage and formation. Beside the production of single-atom or low-molecular-mass products, ionizing radiation generates macroradicals located on the polymer chain, recombination of which can result in chain branching, cross-linking, or scission. The prevalence of each reaction is influenced by multiple factors, including reactive species concentration and reaction kinetics [31]. These derive from the kinetics of individual reactions, the content and permeability of gases (oxygen) in polymer mixtures, temperature of treatment, dose rate, as well as the energy and type of radiation used [32].

3. Radiation Treatment and Grafting for Tailored Bitumen Modifiers

The utilization of high-power electron accelerators in industrial irradiation processes is appealing due to their significantly high throughput rates, and the treatment costs per unit of product frequently rival those of conventional chemical processes [28,31]. Radiation treatment is applied mostly to the bitumen modifiers, enhancing surface properties through processes like oxidation, degradation, and grafting.

3.1. Radiation-Induced Grafting (RIG)

One approach to enhancing the performance of modified bitumen that is currently gaining attention is through the use of radiation and radical grafting of polymers, which can significantly improve their properties over a very wide range. In the following subsections the findings have been described, to highlight the potential of radiation and radical grafting of polymers as a means of enhancing the performance of modified bituminous binders.

Grafting is a versatile technique in polymer science, which involves attaching one polymer (the "graft") onto another polymer matrix (the "backbone") [33]. This process allows for the modification and enhancement of the base polymer's properties, introducing new characteristics and functionalities. Applications range from altering solubility, nano-dimensional morphology, and compatibility to improving charge transport properties. Various chemical approaches, such as free radical reactions, click reactions, amide formation, and alkylation, are employed for polymer grafting. Typically, these chemical methods are both expensive and complex, often requiring the use of various solvents and specific reactants. In contrast, radiation-induced grafting (RIG) presents a more practical and cost-effective approach, particularly when applied as a method for bitumen modification [32]. RIG is a technique known for its reduced reliance on additional chemical additives and solvents [33]. RIG can be accomplished using various ionizing radiations with different energies, including gamma, X-rays, electron beam (keV to MeV), ultraviolet radiation (a few eV to about 100 eV) [32]. These forms of radiation are capable of penetrating various materials of petroleum origin to varying depths or interacting only with their surfaces, which can be effectively utilized for modifying these materials, offering precision and versatility in grafting [25,34,35]. Additionally, microwave radiation, known for its efficient and controlled heating properties, serves as another valuable tool in the arsenal of radiation-induced grafting methods [36–38]. Currently, microwave-induced devulcanization and pyrolysis are viewed as promising methods, particularly for the modification of waste tire rubber recyclate for bitumen additives [39]. Described exploration will center on how these methods can enhance polymer structures and introduce new functionalities, particularly within the realm of bituminous binder performance. Radiation-induced grafting, in particular, can modify surface properties without altering the bulk properties of the base polymer, making it advantageous for a wide range of industries. It is important to mention that various radiation-based initiation methods, including γ-irradiation and UV radiation, can be employed, offering versatility and expanded possibilities in polymer synthesis. These methods are cost-effective also because they operate at low temperatures and do not require catalysts or initiators. The combination of these techniques opens up new avenues for the controlled synthesis of graft copolymers in an industrially-achievable manner, with a specific focus on improving bituminous binder performance.

4. Poly(Styrene-Butadiene-Styrene) (SBS) and Its Modification

Modified bitumens, which contain various additives, are developed to improve their performance. Poly(styrene-butadiene-styrene) (SBS) block copolymer-modified bitumen is the binder of choice in asphalt mixtures for paving roads subjected to heavy traffic. This preference is attributed to its exceptional performance in road durability, providing superior resistance to the stresses of high-volume vehicular loads [40–44]. SBS, a triblock copolymer, exhibits a biphasic morphology where rigid polystyrene (PS) forms a dispersed phase within the flexible polybutadiene (PB) continuous phase [4]. At typical pavement operating temperatures, the PS blocks are in a glassy state, lending strength to SBS, while the PB blocks remain in a rubbery state, adding elasticity [45,46],. When SBS is compatible with bitumen, the PB blocks absorb maltenes, leading to swelling, whereas the PS blocks undergo minimal swelling and serve as physical cross-linking points [47]. This interaction results in a two-phase morphology between the swollen SBS and bitumen. With lower concentrations of SBS, it is dispersed within the continuous bitumen phase. However, as the concentration of SBS increases, a phase inversion (PI) occurs. This transition leads to the formation of two interlocked continuous phases, which is considered the ideal phase morphology for SBS-modified bitumen (Figure 1) [45]. Within the range of the glass transition temperatures (Tg) of PS blocks (approximately 100°C) and PB blocks (around -90°C), PS exhibits a glassy behavior while PB remains rubbery [48], facilitating the formation of physical crosslinks primarily involving entanglements and interactions between the polystyrene (PS) end-blocks [49]. This capacity to form physical crosslinks positions SBS as a prime contender for bitumen modification. SBS in the bitumen matrix improves its viscoelastic properties, making the bitumen more durable and resistant to temperature variations, rutting, and cracking. This network also contributes to better handling and application properties of the bitumen during road construction by improving adhesion, and allowing longer workable time [40,42].

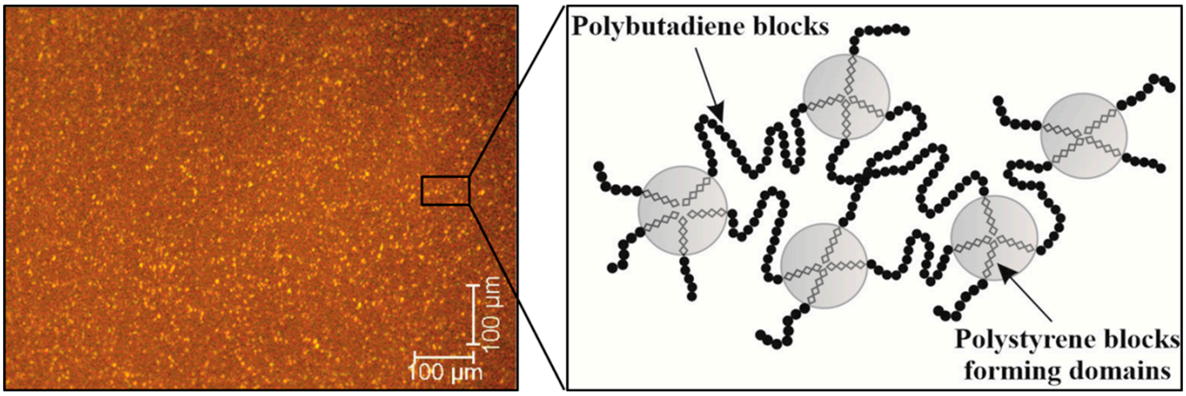

Figure 1. The microscopic image of morphology of SBS-modified bitumen (left) and a schematic representation of how the molecular structure of the SBS copolymer translates to the observed morphology (right) [50].

However, one major challenge with bitumen/SBS blends is their tendency to lose stability when stored at high temperatures for extended time. This tendency may depend on the chemical nature of the base bitumen and the properties of the polymers used. This phase separation issue significantly limits their practical applications [23,24]. Nonetheless, researchers have been increasingly focused on improving the thermal stability during the storage of SBS-modified binders [17,24,51–55].

4.1. Radiation-Induced Grafting of SBS

Fu et al. [24] investigated the use of methacrylic acid as a polar monomer to modify SBS using ^{60}Co γ-rays radiation (SBS-g-M). The grafting degree achieved of approximately 6% for SBS-g-M. The impact of SBS-g-M on the mechanical properties of the binder was evaluated using a dynamic shear rheometer (DSR), both before and after grafting. The results showed that the addition of SBS-g-M had a significant effect on the rheological properties of the binder, leading to improved high-temperature performance and reduced temperature susceptibility compared to SBS-modified bitumen. Specifically, the G/sinδ parameter was used as a criterion for assessing the properties of the binder at high temperature. The temperature at which G/sinδ was equal to 1000 Pa was 67.5°C for base bitumen, 78.2°C for polymer modified bitumen (PMB) with the addition of 5.0% SBS, and 82.4°C for PMB with the addition of 5.0% SBS-g-M, respectively (Figure 2).

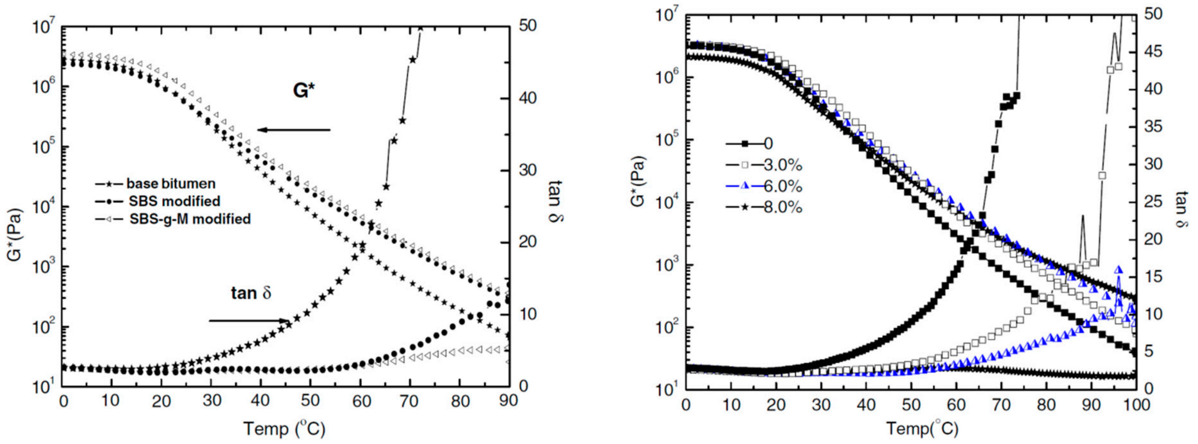

Figure 2. Left panel: Complex modulus (G*) and tan versus temperature for base and modified bitumen at 10 rad/s. Right panel: Effect of SBS-g-M content on dynamic mechanical properties of PMB. Adapted from [24] with the permission of Elsevier, copyright 2006.

It is important to note that the rheology of modified bitumen is dependent on the polymer content. When the polymer content is sufficient (>6%), the phase angle (δ) decreases, and the complex modulus (G*) increases considerably. Higher SBS-g-M content results in a stable tan δ, but increasing complex modulus due to polymer network formation. Direct observation of the morphology using a fluorescence microscope revealed that the compatibility between SBS-g-M and bitumen was effective, and the storage stability of the binder was significantly improved compared to standard SBS-modified bitumen. Furthermore, the use of SBS-g-M led to smaller particle sizes and more homogeneous dispersion in the bitumen matrix than non-grafted SBS, under the same high temperatures and high shear stress. The addition of SBS-g-M to bituminous binder significantly improves its properties, as the blended system can form a more robust network in the modified bitumen. This network structure gives the binder superior high-temperature performance and reduced temperature susceptibility.

In order to improve the mechanical properties and high-temperatures resistance of PMB, various additives, including fibers, are also used. In recent study [56], the researchers used UV radiation to induce a „thiol-ene click reaction" through the creation of the covalent bonds of vinyl-terminated dendritic polyester (VTDP) and polyester (PET) fibers to create a hyperbranch-structured PET fiber called VTDP-PET. The PET or VTDP-PET fiber was then blended with SBS-modified bitumen to make fiber/SBS-modified binders. The preparation of VTDP-PET fiber involved the two-step method. First, OH and SH functional groups were introduced to the surface of PET fiber through chemical modification. Secondly, a dendritic VTDP was grafted onto the modified PET fiber using a "thiol-ene click reaction" (Figure 3). Chemical analyses, including FTIR, XPS, and SEM, showed that the polymer activating groups were successfully grafted onto the PET fibers, resulting in increased surface roughness and shape gradient.

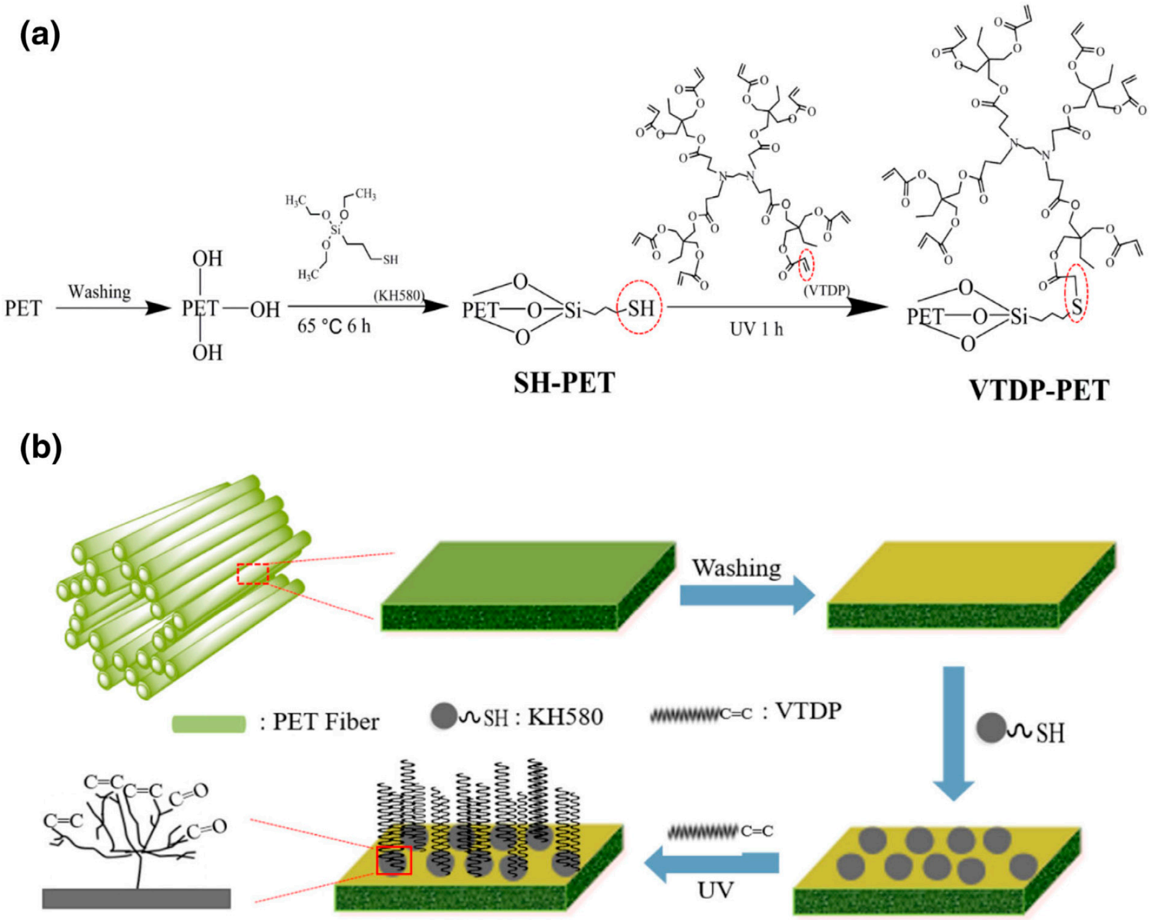

Figure 3. Reaction scheme (a) and flowchart (b) of venyl-terminated dendritic polyester-polyester (VTDP-PET) fiber preparation. Reprinted from [56] with the permission of Wiley, copyright 2021.

The addition of VTDP-PET or PET fibers significantly improved flow resistance, viscoelasticity, and rutting resistance of PMB modified by SBS. Notably, VTDP-PET/SBS-modified binders exhibited more significant enhancement than PET/SBS binders. Additionally, VTDP-PET/SBS-modified bitumen showed higher thermal stability, as demonstrated by TGA, compared to PET/SBS-modified binder. The shear stress, storage modulus (G′), and loss modulus (G′′) at 46°C of 2.5% VTDP-PET/SBSMA were 64%, 54.9%, and 76.9% higher than those of 2.5% PET/SBSMA, respectively. Overall, VTDP-PET fiber offers a promising alternative for creating modified bitumen for heavy traffic roads.

4.2. Chemical Grafting of SBS

SBS grafting typically involves the use of chemical initiators, with radiation initiators being used less frequently. Overall, chemical modification of elastomers involves the use of various grafting monomers, most commonly including maleic anhydride (MAH), maleic acid (MA), dibutyl maleate (DBM), and acrylic acid (AA) and its esters [57,58]. Recent research has focused on carbon-based nanomaterials, such as carbon nanotubes (CNTs). CNTs have been shown to reduce fatigue and permanent deformation in hot mixt asphalt (HMA) compared to conventional HMA [59]. CNTs can also improve thermal cracking resistance, and reduce bitumen aging [60,61]. However, the high cost of CNTs makes them unsuitable for a large-scale use in asphalt pavements. This motivates the search for more cost-effective carbon-based nanomaterials for asphalt roads. One potential candidate is graphite nanoplatelets (GNPs) [61–64]. GNPs are nano-discs with a sub-micrometre diameter and a nanometre thickness. GNPs can be produced from either graphene or natural graphite. GNPs produced from graphene typically consist of several layers of graphene sheets, each of which is a single layer of carbon atoms. Depending on the type and carbon purity of GNPs, their cost is comparable to some existing bitumen modifiers such as SBS and significantly lower than the cost of multi-wall CNTs [62]. Han et al. [65] proposed a composite material consisting of polystyrene-grafted graphene nanoplatelets (PS-GNPs) that were prepared and used as a modifier for SBS in bitumen preparation. Polystyrene-grafted graphene nanoplatelets (PS-GNPs) were prepared from graphene oxide by ultrasonic shock-induced grafting of styrene, followed by reduction of the oxygen functional groups with hydrazine. For the research, the bitumen was modified using 5% SBS, which had been pre-modified with GNPs or PS-GNPs within the range of 0% to 0.04% admixture. The modification of SBS influenced its ability to increase bitumen ductility (by up to 50% for 0.05% GNP and 20% for PS-GNP-modified SBS) and softening point temperature (by ca. 8% for both modifications) relating to SBS alone. It also reduced penetration (by 15% and 9% for GNP- and PS-GNP-modifed SBS, respectively). In summary, the polymer stabilization of graphite nanoplatelets appears to enhance hardness and thermal stability of the resulting modified bitumen. A closer examination of the micro-properties of the PS-grafted GNPs (Figure 4) provides valuable insight into their macroscopic behavior, offering understanding of how these microscopic changes translate to altered macro properties. Young's modulus and reduced modulus of GNPs were 2180 MPa and 2395 MPa, respectively, and for PS-GNPs, were correspondingly reduced to 586 MPa and 644 MPa (372% decrease compared to GNPs). This suggests that the modified GNPs became more deformable, indicating an increase in toughness and a decrease in rigidity. The authors proposed that the change in properties is mainly attributed to the expanded layer spacing and the PS coating on the GNPs, forming a spring-like structure. Additionally, the PS grafted onto the GNPs has similar styrene groups to those in SBS (Styrene-Butadiene-Styrene), facilitating easy physical entanglement with the PS phase in SBS macromolecules and thereby significantly enhancing dispersion in SBS-modified bitumen. The addition of PS-GNPs into bitumen has improved the bitumen binder capacity to resist both pressure and permanent deformation.

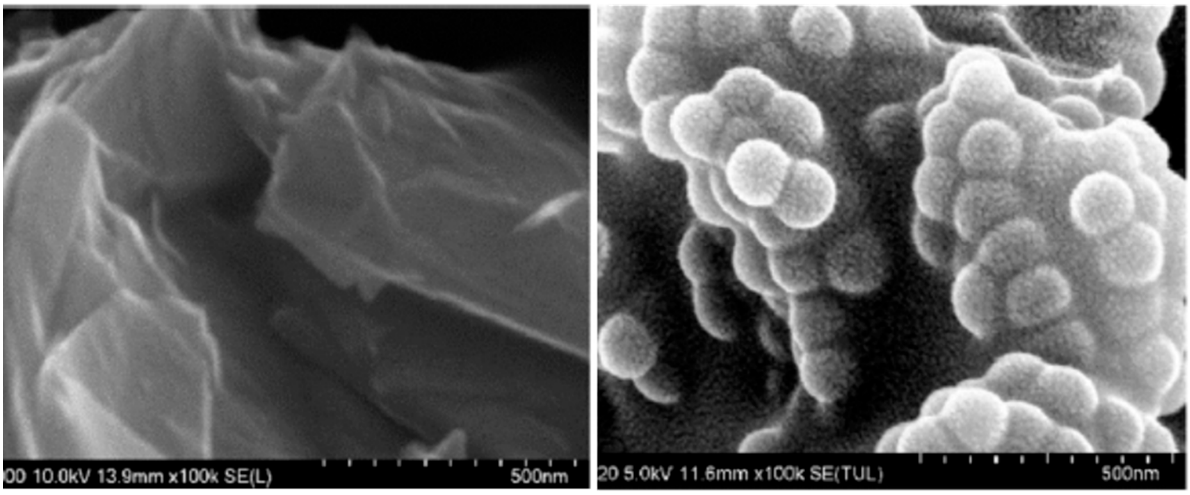

Figure 4. SEM of GNPs (left) and PS-GNPs (right). Adapted from [65] with the permission of Elsevier, copyright 2018.

Another study by Han et al. [66] proposed a modifier of SBS waste rubber powder (WRP) with octadecyl-amine (ODA) through a covalent grafting reaction. The ODA-WRP was then combined with SBS to prepare ODA-WRP/SBS-modified bitumen. In the process, the amine group (–NH_2) present in ODA reacted with the carboxyl group (–COOH) on the surface of WRP, leading to the formation of an amide (–NHCO–), which facilitated the attachment of ODA to the surface of WRP. The mechanical properties of the designed PMB showed significant improvement as compared to the pristine SBS-modified bitumen, as confirmed by various tests, including DSR, MSCR, and separation tests. The enhancement in properties was attributed to the better compatibility of various components in bitumen and the establishment of a network structure between ODA-WRP and SBS (Figure 5).

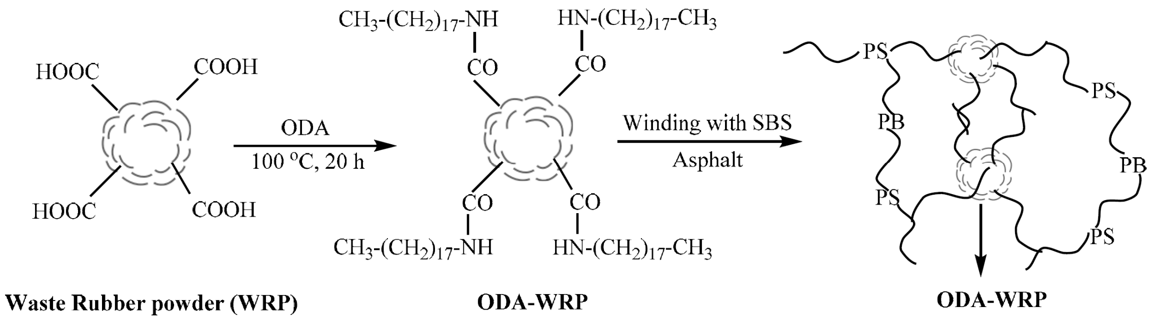

Figure 5. Formation mechanism of the ODA-WRP/SBS network structure. Reprinted from [66], with the permission of MDPI (creative commons license).

The successful synthesis of ODA-WRP was confirmed through FT-IR and SEM analyses. The study has proven potential applications of ODA-WRP binders in constructing highways and other infrastructure.

In another case [58], the SBS was modified with glycidyl methacrylate (GMA) using dicumyl peroxide (DCP) as an initiator at a temperature 170°C. The study aimed to investigate the impact of different factors such as % GMA, % DCP, and reaction time on grafting degree, conversion of GMA, and cross-linking using a factorial design approach. This provides a good opportunity to illustrate the influence of both concentrations and grafting factors on the grafting outcome and its impact on the material properties. Grafting increased with increasing GMA content. Yet, the concentration of GMA did not significantly affect the conversion and torque. The latter where highly influenced by the concentration of the initiatior, DCP, within the studied range. DCP content had a strong positive effect on the final torque due to the crosslinking reactions of the matrix SBS. It was not possible to increase the grafting degree without increasing the torque level due to crosslinking reactions. This is an important consideration when designing the synthesis, as the initiator can significantly alter the properties of SBS in addition to grafting GMA. An optimum % DCP point of 0.1% w/w was identified, which allowed for the highest incorporation and conversion values at a low cross-linking level (Figure 6).

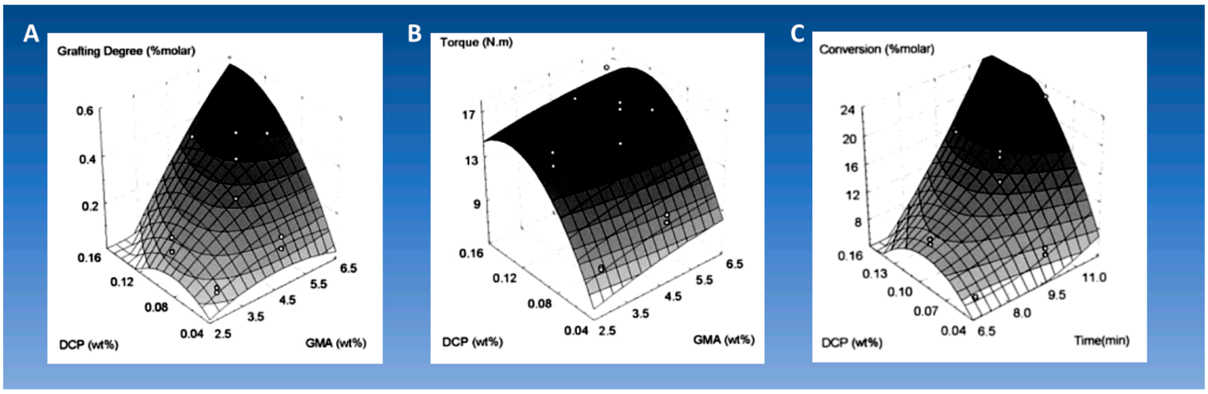

Figure 6. A, effect of % dicumyl peroxide (DCP) and % glycidyl methacrylate (GMA) on grafting degree; B, effect of % DCP and % GMA on final torque; C, Effect of % DCP and reaction time on conversion during the synthesis of GMA-grafted SBS. Adapted from [58], with the permission of Springer-Verlag, copyright 2001.

Li et al. [52] developed a novel bitumen modifier by reacting thiolated graphene oxide nanoplatelets (gOs-SH) and SBS using a thiol-ene click reaction, which is initiated by Ammonium persulfate (APS). They tested the temperature resistance and mechanical properties of the PMB using a dynamic shear rheometer (DSR) and multiple stress creep recovery (MSCR) tests. Characterization of gOs-SH was conducted using various techniques such as FTIR, EDX, AFM, XRD, and SEM. The thiol-ene click reaction was elucidated using XPS. The study found that an optimal amount of gOs-

SH was 0.02%, which improved the anti-rutting performance of the bitumen. Results confirmed that SBS-g-gOs exhibited excellent stability and dispersion in the base bitumen and that the addition of gOs-SH promoted the formation of an SBS network structure. Overall, the use of click chemistry for the preparation of gOs-modified-SBS bitumen was deemed a promising approach for industrial applications (Figure 7).

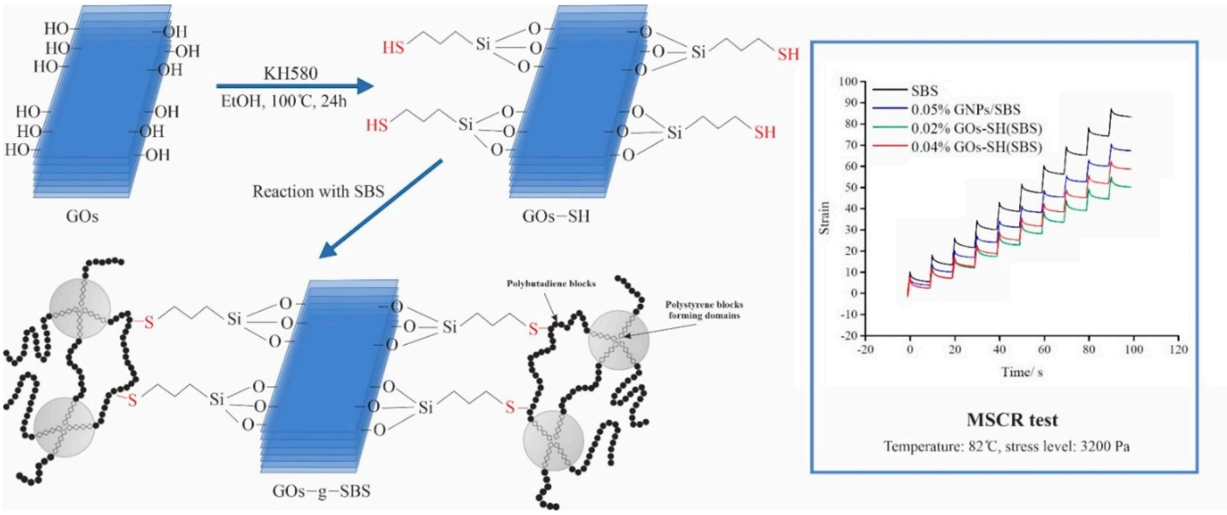

Figure 7. Preparation and properties of SBS-g-gOs-modified bitumen based on a thiol-ene click reaction in a bituminous environment Adapted from [52] with the permission of MDPI (creative commons license).

Wang et al. [67] synthesized SBS copolymers with different functional groups, including end amino, carboxylic acid, and hydroxyl, using 1,5-diazabicyclo [3.1.0]hexane, carbon dioxide, and epoxy ethane as capping agents, respectively. The study aimed to investigate the impact of these end-polar groups on the morphology and dynamic mechanical properties of the copolymers. The results of morphology showed that the PS domains changed from uniform spheres in SBS to disordered, incompact strips in end-functionalized SBS (Figure 8). Furthermore, the study concluded that end amino and carboxylic acid were effective in improving the storage stability and compatibility of SBS-modified binders, as evidenced by comparing the softening points and DSC curves of end-functionalized and non-functionalized SBS-modified bitumens.

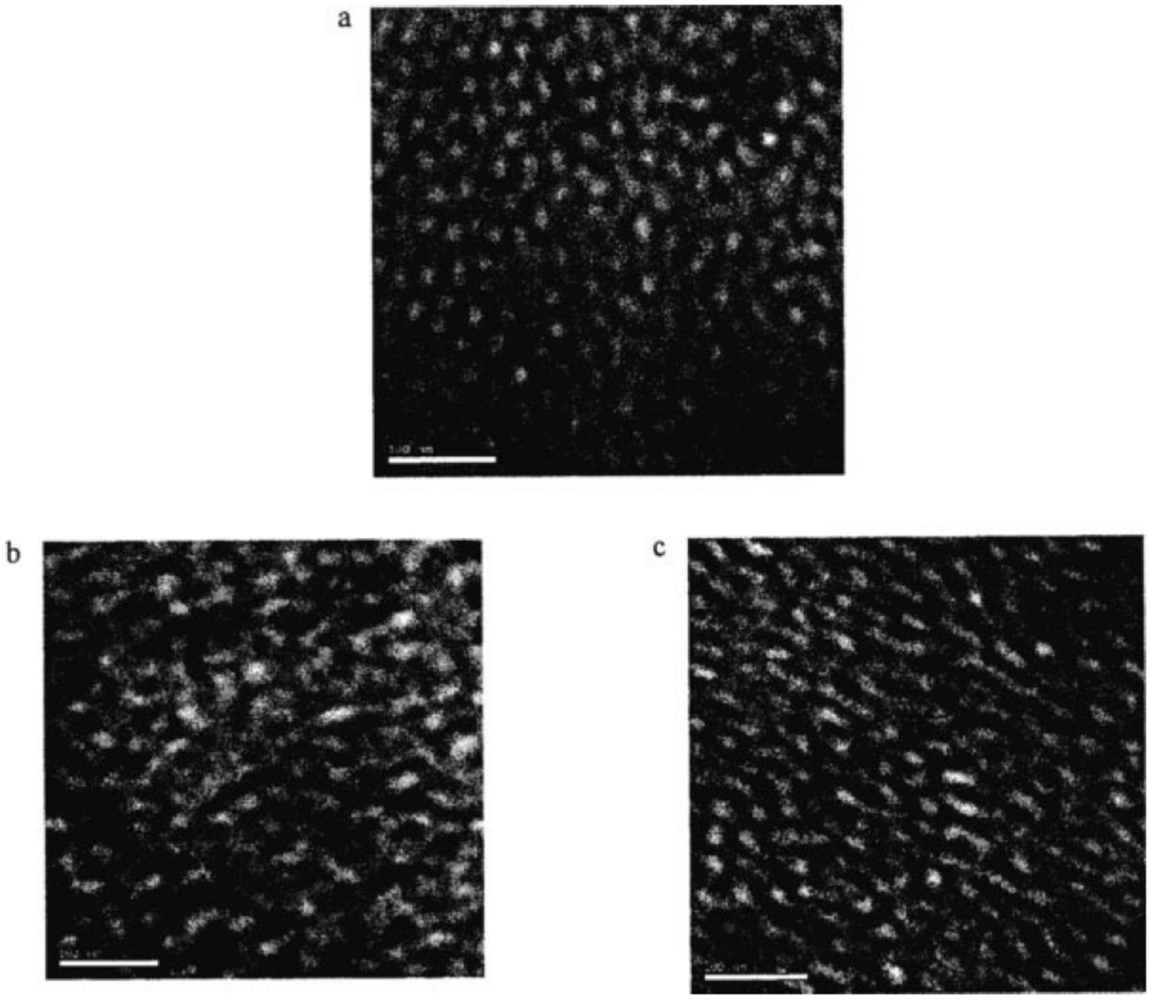

Figure 8. TEM images of SBS and end-functionalized SBS: (a) SBS, (b) SBS–COOH, and (c) SBS–N. Adapted from [67] with the permission of Wiley, copyright 2007.

Trials of grafting SBS with most commonly used monomers, such as GMA [58], or maleic anhydride (MAH) [68] in the melt using peroxides as initiators, had low grafting efficiencies and could lead to undesired cross-linking.

5. Radiation Treatment and Grafting Strategies for Reclaimed Polymers

The use of polymer-modified binders (PMB) in asphalt mixtures offers numerous benefits, such as their lower thermal susceptibility and greater resistance to rutting and fatigue. Nonetheless, their higher cost presents a limiting factor to their widespread use [20,41]. On the other hand, while polymers are known for their endurance and accessibility, a downside to their usage is the accumulation of substantial quantities of complex and challenging-to-handle waste with high molecular weights [21,69]. In recent times, researchers have investigated the possibility of utilizing of waste polymers as modifiers in order to reduce expenses and promote environmental sustainability [21,22,69,70]. Consequently, the topic of using waste polymers for bituminous binders is currently the subject of many review papers [20–22,70].

The use of recycled polymers presents a cost-effective alternative to raw materials in PMB, which can extend the life of road asphalt pavements. It can be used in all categories of roads and layers. Unfortunately, a significant amount of plastic waste ends up in landfills without any recycling process [20]. However, due to the EU's Green Deal climate policy, it can be seen that the amount of recycled polymers is increasing, e.g., in 2021, 5.5 million tonnes of post-consumer recycled plastics were re-introduced into the EU27+3 economy, an increase of 20% compared to 2020 (European production of plastics reached 57.2 Mt in 2021) [71]. Polymer waste processing methods vary depending on the origin, composition, and properties of the waste polymers [72]. There are different types of polymer waste processing. Although chemical conversion for reusing waste polymers is preferable, their high chemical resistance makes this approach challenging. The already-mentioned insufficient chemical bonding between the reclaimed polymer and bitumen, which may lead to separation of phases [25] is the most significant obstacle. As a result, radiation technologies are gaining popularity as they offer innovative ways to modify the properties of polymers, resulting in unique plastics and composites while adhering to green chemistry principles [21,69].

The most commonly studied waste polymers as bitumen modifiers are: high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), Ethyl Vinyl Acetate (EVA), polyvinyl chloride (PVC) and ground tire rubber (GTR). Waste plastics can be effectively reused in high-value applications in highway construction, particularly in hot mix asphalt (HMA) [20,22]. The percentage of different polymers by weight of bitumen vary between 0.5 to 25%, the most commonly reach 2-7% for PE, PP and EVA, and 5-15% for GTR [20]. Polyolefins, such as PE and PP, are widely utilized thermoplastics and constitute a substantial part of recyclable plastic waste. They possess properties similar to rubber and fiber that can improve the characteristics of polymer-modified bitumen (PMB) used in asphalt pavement. However, due to their high crystallinity, they can cause issues with the bitumen matrix, resulting in phase separation, decreased cohesion, and the requirement for longer mixing times. Chemical modification of the polymer can enhance compatibility with bitumen [73]. The following subsections describe selected applications of radiation grafting of waste polymers to bituminous binders used to improve the properties of modified bituminous binders.

5.1. Waste Polypropylene (PP)

Günay et al. in [35] to improve the compatibility of waste polypropylene with bitumen used gamma irradiation. The process involved modifying polypropylene by grafting maleic anhydride (MA) onto the polymer surface. Dicumyl peroxide was used as an initiator, and MA was dissolved in acetone and mixed into PP granules. The pre-treated PP granules were then exposed to gamma rays for 28 minutes with a dose of 10 kGy and monitored with a chemical dosimeter (Figure 9). Unreacted MA was removed by washing with water and drying. This process aimed to provide a chemical interaction between the modifier polymer and bitumen. Irradiated waste polypropylene (PPR-γ-MA) was then used as a bitumen modifier.

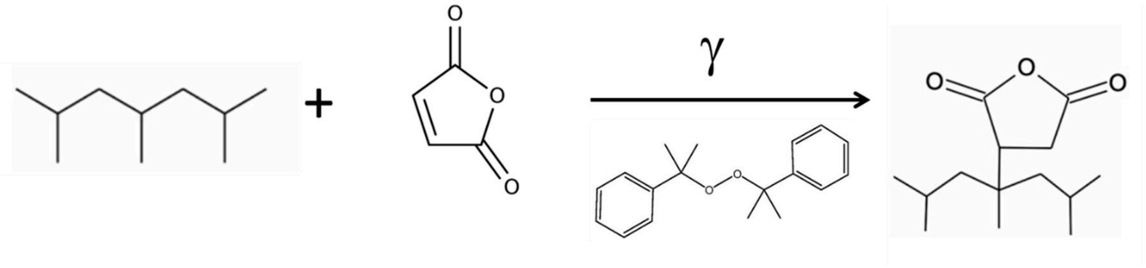

Figure 9. Grafting of waste polypropylene (PPR) with maleic anhydride (MA) with the use of dicumyl peroxide as an initiator and irradiation with gamma rays. [35].

The physical properties of PPR-γ-MA-modified binders were tested with conventional methods. Various rheological methods were also used to determine low and high-temperature performance, as well as fatigue resistance, using LAS test. The MA grafting of waste PP improves its interaction with bitumen, as confirmed by FTIR spectroscopy findings. This process creates carbonyl groups on the grafted MA (or carboxyl groups in acid form) and an activated surface that contains radicals and oxygen-containing groups due to γ-irradiation in an air atmosphere. The authors suggest that the carbonyl groups of PPR-γ-MA will react with the asphaltenes in bitumen during the hot mixing process, which will facilitate the effective distribution of the polymer modification within the bitumen. Addition of PP-γ-MA to the bituminous binder results in a stiffer material with decreased penetration and ductility, increased softening point and improved temperature susceptibility. However, the mixing and compaction temperatures calculated on the basis of the rotational viscosity of bitumen increase with higher levels of modification, suggesting a limitation on excessive use of PP-γ-MA. Gamma-irradiation reduces phase separation between the waste PP and bitumen, leading to better compatibility and physical performance of bitumen. However, using an excessive amount of waste polymer (7-9%) in bitumen can increase phase separation, regardless of gamma irradiation. Thus, it is recommended to use a maximum of 5% of PP$_R$-γ-MA as a modifier in bitumen to achieve optimal results. The high-temperature performance of bituminous binder is improved by waste PP, with better elastic response compared to base bitumen and increased fatigue damage resistance. The MSCR test findings showed that the use of PP$_R$-γ-MA results in decreased non-recoverable compliance J_{nr} and increased elastic recovery R of the material. The low-temperature performance grade (PG) of bitumen decreases after modification, but overall performance is improved. The findings suggest that waste PP can be used in bitumen with improved performance after MA grafting via gamma-irradiation. The results of the study indicated that using PP$_R$-γ-MA as a modified material in binders is feasible and has the potential to improve fatigue life and resistance to damage.

As for an instance of chemical grafting modification, an interesting amphiphilic system was recently reported by Malus et al. [74]. Hydroxyl-functionalized isotactic polypropylene (FPP) was created using solution polymerization. This was then attached to an alternating styrene-co-maleic anhydride copolymer via a transesterification reaction, to yield FPP-g-SMA, amphiphilic graft-copolymers with varying contents of comonomers. Adding FPP and FPP-g-SMA30/35S modifiers significantly raised the softening point (the highest increase in softening point was achieved with the incorporation of 2.5 wt% FPP-g-SMA30S into bitumen, 62.0 °C to 76.9 °C) and improved the morphology of the end products. After the addition of FPP or FPP-g-SMA into bitumen, the heterogeneous "bee" microstructures, which are characteristic of unmodified bitumen, disappeared completely. The greatest compatibilizing impact was observed with FPP and FPP-g-SMA30S modifiers, which resulted in a fine, interlocked polymer distribution in the bitumen matrix, leading to improved rheological properties [74].

5.2. Waste Polyethylene (PE)

Ahmedaze et al. have carried out a number of research works on the application of radiation to enhance the properties of various types of polyethylene [25,34,75].

In one of their studies [25], an electron beam irradiation (EBI) was applied to improve the properties of recycled high-density polyethylene (HDPE$_R$) obtained from the waste bottle, which was used as a modifier for bitumen. The HDPE$_R$ was irradiated with a dose of 20 kGy to improve chemical interaction and adhesion in the polymer/bitumen interface. Linear accelerator of electrons was used as a source of electrons with an energy of 4 MeV[1]. The results showed that the irradiated HDPE$_R$ modification improved the compatibility of the components in the bitumen. The HDPE$_{Re}$ polymer phases ranged in diameter from 3 to 20 μm and were well dispersed within the continuous bituminous phase. The polymer phase contained some dispersed bitumen inclusions, indicating a typical microphase separated structure. Notably, each particle in the bitumen-swollen polymer phase was surrounded by a dark brown narrow ring, signifying an interface formed by the chemical grafting of both components. This result aligned with FTIR spectroscopy, confirming the chemical interaction between HDPE$_{Re}$ and bitumen components. Furthermore, DSC analysis revealed partial mixing and improved compatibility of the blend components. The DSR tests indicated that HDPE$_{Re}$ modification significantly raises the complex modulus (G*) and reduces the phase angle (δ) values of the bitumen. As a result, the HDPE$_{Re}$-modified bitumen displays improved resistance to temperature-related changes and greater elasticity in response to shear stress compared to the base bitumen. HDPE$_{Re}$ modification effectively reduces the temperature susceptibility of bitumen at high temperatures due to the stiffening effect of the HDPE$_{Re}$ modifier, albeit with a slight adverse impact

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[1] Information provided by the authors on request, for the purpose of this review

on creep stiffness and m-value, resulting in a slight decrease in the low-temperature performance grade of the binders. Therefore, the use of irradiated HDPER modifiers in cold regions should be limited to avoid thermal cracking.

In another study [34], the aforementioned authors applied electron beam irradiation (EG-2.5 Van-de-Graf accelerator 2.5 MeV) with a dose of 20 kGy to modify recycled low-density polyethylene (e-LDPER), which resulted in the formation of free radicals and certain functional groups that could potentially assist in the development of strong chemical bonds between the polymer modifier and bitumen (Figure 10). Particularly, in the FTIR spectrum of recycled LDPE (LDPER), the authors observed the presence of a peak at 1147 cm^{-1}. This feature, indicative of the tertiary carbon group $(CH_3)_2C$ [76], is not typically found in the spectrum of pristine LDPE. The emergence of the CH_3 group in LDPER is attributed to the degradation of polymer chains, prompted by UV irradiation from sunlight, which generates free radicals leading to alterations in the macromolecular structure, including some branching. Under the exposure of LDPER to electron beam irradiation, the occurrence of band at 1157 cm^{-1} in e-LDPER, along with the reduction of band at 1147 cm^{-1}, was attributed to the increase of unsaturation in the regions of tertiary carbon atoms (formation of $(CH_3)_2$-C=CH- group) [76]; Hydrogen abstraction is more favorable at carbon sites with higher degrees of substitution [77]. Additionally, a novel band at 1086 cm^{-1} in the e-LDPER spectrum denotes the formation of secondary alcohol groups, likely resulting from the radiation-induced oxidation [76].

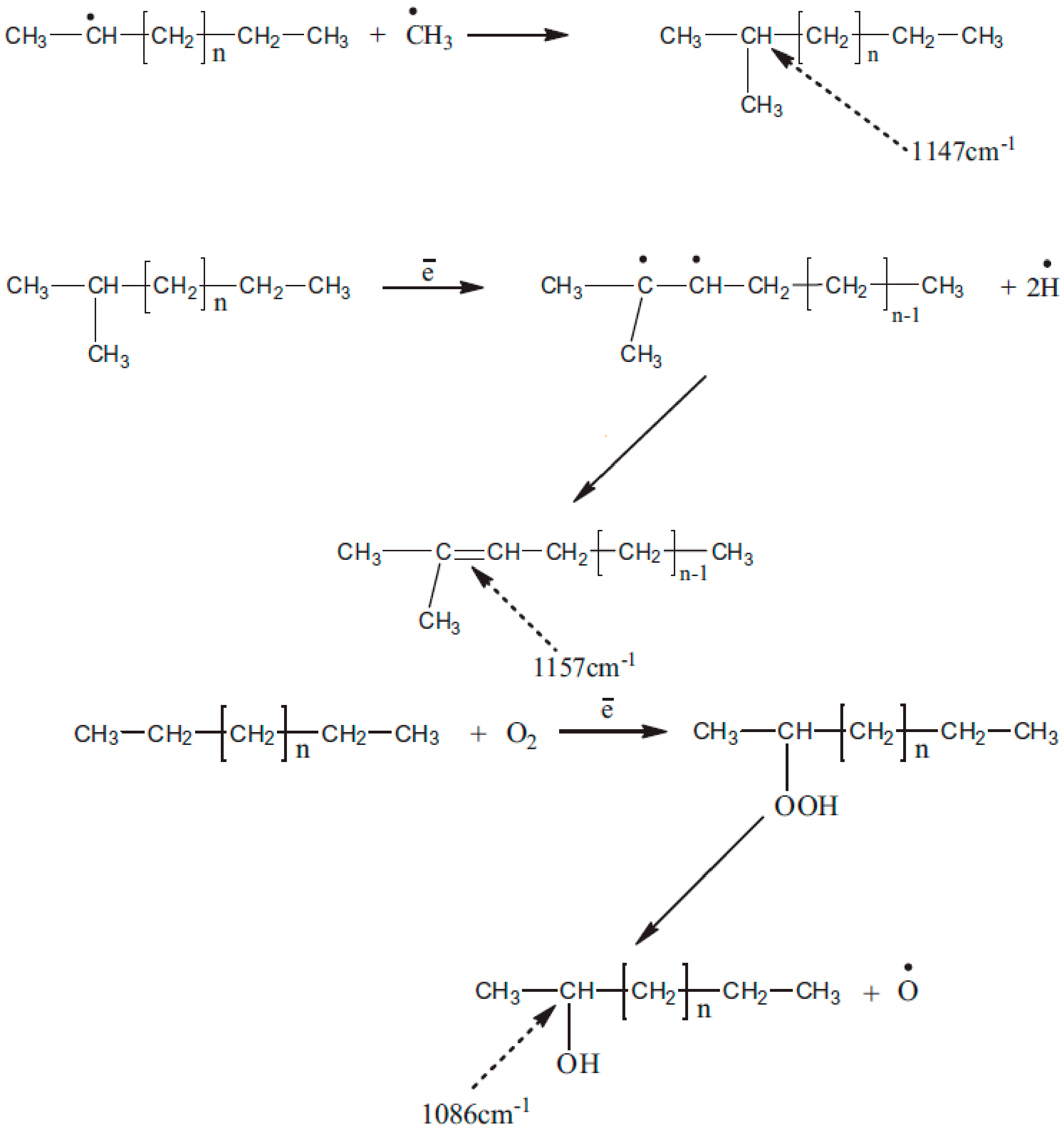

Figure 10. Scheme of chemical transformation in the recycled LDPE polymer chain under the influence of electron beam irradiation. First process illustrates the formation of tertiary carbon atoms during LDPE$_R$ aging, before irradiation. Adapted from [34] with the permission of Elsevier, copyright 2014.

Authors suggested that the formed during irradiation reactive chemical bonds and secondary hydroxyl groups can bond with bitumen components during mixing. The DSC results indicated improved blend compatibility between bitumen and e-LDPE$_R$ due to the formation of a mixed amorphous phase. Fluorescent microscopy confirmed the chemical interaction between bitumen and the polymer phase. Conventional tests showed improved stiffness and reduced aging effects on bitumen after modification with e-LDPE$_R$. Based on fundamental rheological parameters, and high mixing and compacting temperatures, it is suggested that e-LDPE$_R$ can be used as a modifier at a level of 5% polymer in bitumen for optimized performance in flexible pavements.

In another work [75], the researchers investigated the use of ion-irradiated recycled high-density polyethylene (i-HDPE$_R$) as a modifier in bitumen, showing an increase in the rutting parameter with a gradual increment in i-HDPE$_R$ modification. These studies of Ahmedaze et al. [75] highlight the potential of using waste polymers in bitumen through the ion irradiation process.

Chemically-Grafted LDPE Compatibilization

Another approach attempting the reduction in phase separation of LDPE was achieved with combination of classic additive, sulfur, and emerging new radically-grafted polymer blend compatibilizer PE-g-MA [78,79]. The enhancement in the softening point of LDPE-modified bitumen with the addition of compatibilizers was significant, for 3% LDPE-modified bitumen, the softening point increased from 57.2 °C to 65.1 °C when 1% PE-g-MA and 0.15% sulfur were added. For 6% LDPE, the softening point rose from 72.3 °C to 80.9 °C with the addition of the compatibilizers, and the most dramatic increase was observed for 12% LDPE, where the softening point went from 86.3 °C to a notable 120.5 °C with the addition of compatibilizers. Also the difference in softening point values between the top and bottom portions of the test tube after a standard storage stability test were significantly decreased, from 15.9 C for 12% LDPE without compatibilizers to 7.25 C with 1% PE-g-MA and 0.15% sulfur. The LDPE-based blends and those with PE-g-MA and sulfur showed major weight loss at higher temperature ranges (380–520 °C for LDPE-only blends and 400–540 °C for blends with compatibilizers), reflecting improved thermal stability [79]

5.3. Waste Rubber

Rubber constitutes a significant component of municipal solid waste and must be recovered after disposal [80]. The use of crumb rubber (CR) or ground tire rubber (GTR) from scrap tires as a modifier for paving bitumen has become popular due to its sustainability benefits, resulting in a product called rubberized bitumens. However, the compatibility issues between GTR and bitumen have limited its applications [81]. Cross-linking during vulcanization prevents the chemical degradation of GTR particles in bituminous binders, leading to poor cross-linking between GTR and bitumen [82]. This is due to the incompatible cross-linked network of GTR. To achieve the desired compatibility, GTR needs to be uniformly dispersed and bonded with the molecules of the bituminous binder, creating a homogeneous system [26]. To solve this problem, surface activation methods have been proposed to modify the chemical and physical characteristics of the GTR surface [81], including mechanical, microwave, low-temperature plasma (LTP), plasticizer, and other methods [26,39]. On the other hand, using high-energy electrons, X-rays, UV, or visible light could also serve to initiate the reaction. There are several ways to create initial points on GTR, such as exposing it to radiation, using radical initiators (either photochemical or thermal), acid etching, hydroxylation, and living radical initiation techniques like atom transfer radical polymerization initiators [26,83]. These processes have been successful in grafting monomers such as styrene, allylamine, acrylamide, and methacrylate onto the GTR surface [84]. Although grafting is more effective in achieving compatibility, it typically involves multiple steps of synthesis and purification procedures, making it challenging to apply in industry.

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Therefore, the combination of surface activation treatment of GTR and additives-grafting appears to be a potential approach for improving the compatibility of rubberized binder [26]. Moreover, mixing reclaimed rubber with new polymer materials reduces the overall production costs and helps minimize environmental pollution [80]. Many papers are available on various methods which could try to resolve the problems with the poor compatibility thermoplastic polymer/GTR systems [85–89], also by using radiation techniques – gamma radiation [80,90,91], including water-medium ionizing radiation treatment [92], and electron beam [93–95]. Following review focuses on the application of gamma and electron beam processing of waste tire rubber to produce rubberized binders.

Gamma and Electron Beam Processing of Ground Tire Rubber

Various radiation methods have been used to activate the surface ground tire rubber (GTR) particles, with or without air present, as stated above. The number of radicals produced on the surface of the rubber particles depends on several factors, such as the type of radiation used, the radiation dose, and the duration of the radiation exposure. The irradiation process follows typical for polymers four reaction steps: chain initiation, propagation, chain termination, and chain branching, according to the Bolland-Gee scheme (Figure 11). During the initiation step, hydrogen is abstracted from the GTR particle surface, resulting in the formation of two radicals (GTR· and H·). The GTR radical (the most likely carbon- and sulphur-centered mixture of distinct radicals [96]) can undergo various reactions, including reacting with oxygen to form peroxy radicals, propagation for polymer growth, chain termination, and chain branching (Figure 11) [84].

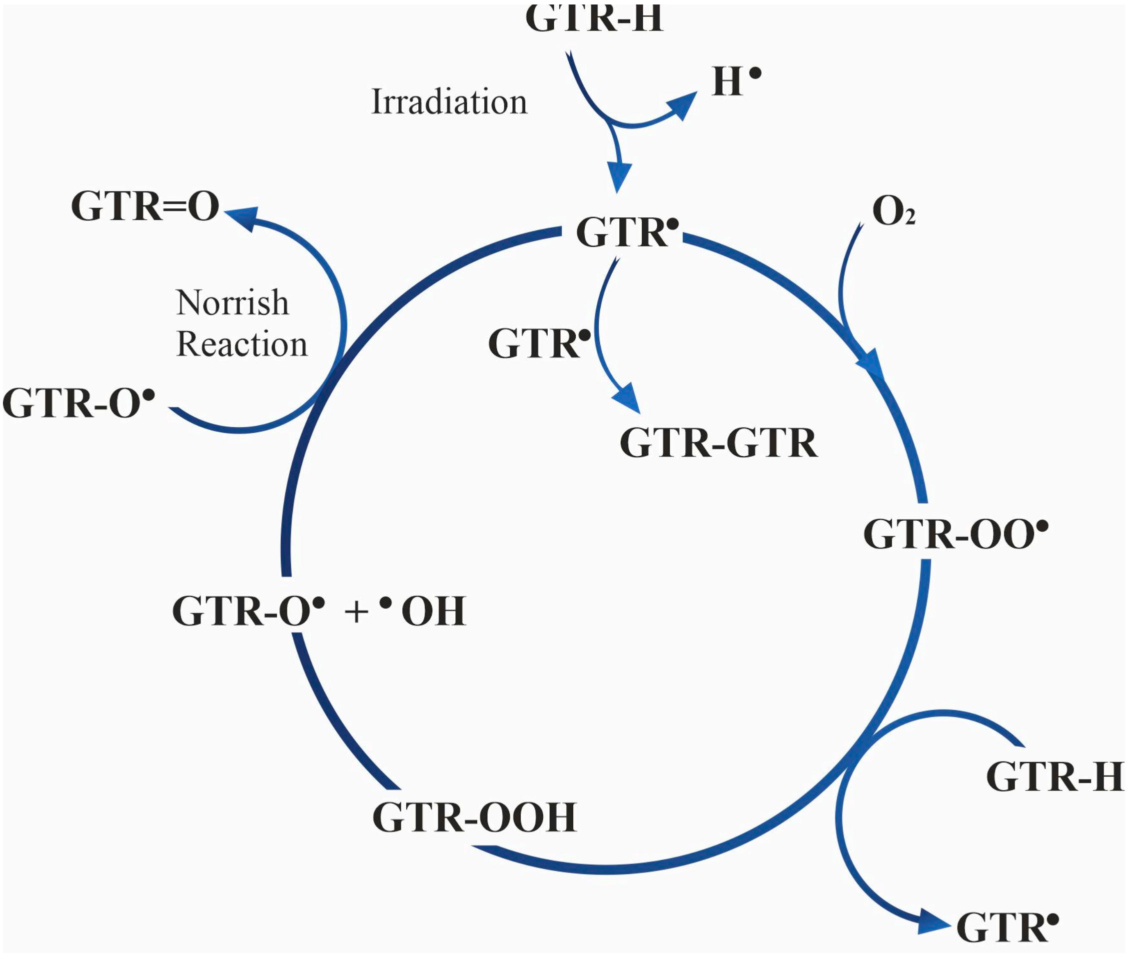

Figure 11. A depiction of the process by which radiation triggers oxidation in GTR particles [84].

Gamma rays and polymers undergo an interaction that generates free radicals, which can result in chain branching, cross-linking, or scission. The prevalence of each reaction is influenced by

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multiple factors, including reactive species concentration and reaction kinetics [83]. In a study conducted by Ibrahim et al. [97], the impact of gamma radiation exposure on waste tire rubber was investigated with regard to its potential as a modified bituminous binder. Samples of crumb rubber were obtained from waste tires and irradiated with gamma rays at doses of 100, 200, and 300 kGy, at a dose rate of approximately 2.8 kGy/h. The irradiated CR samples were then combined with two different weight percentages of 5% and 10%. Results of FT-IR spectroscopy showed that the acrylonitrile butadiene macromolecules in CR samples lost the nitrile group, most likely due to an oxidation process by gamma rays, converting the cyanide group into O-H, C=O, and C-O groups. The study aimed to investigate the anti-aging performance and rheological properties of the modified crumb rubber binder. The anti-aging performance was evaluated using the Rolling Thin Film Oven Test (RTFOT), and it was discovered that increasing gamma radiation to 300 kGy decreased viscosity, making it easier for bitumen molecules to be absorbed. Additionally, CR irradiated with 300 kGy modified binder displayed significant improvements in stability and low-temperature ductility. The residue of CR irradiated at 300 kGy modified bitumen showed lesser loss of penetration, softening point, ductility, and weight loss, indicating stronger resistance to aging.

The study conducted by Hassan et al. [98] focused on materials composed of various compositions of maleic anhydride (MA)-treated reclaimed rubber powder (RRP) and natural rubber (NR), with the aim of exploring the potential of electron beam radiation-cross-linking to enhance the properties of fiber-matrix composites. The study exposed the samples to irradiation doses of 30 and 50 kGy using an electron accelerator with an energy level of 1.5 MeV. The results showed that the tensile strength of non-irradiated composites increased gradually with the addition of glass fiber (GF), and the same trend was observed for irradiated composites at higher irradiation doses. The hardness of the composites also increased with increasing GF content, except at 50 kGy, where it decreased due to high degradation levels. Furthermore, the swelling percentage decreased with increasing RRP content, and the introduction of GF increased the hydrophobicity of the blends in motor and fluid oils. The swelling index increased with increasing GF content and decreasing irradiation dose, except for 50 kGy. The study suggested that the incorporation of GF into composites can significantly improve their thermal stability, and SEM images revealed good adhesion between the GF and polymeric matrix after exposure to electron beam irradiation.

Hassan et al. [99] conducted a study on the radiative compatibilization of mechanochemically devulcanized waste rubber (DWR) from various tire types and its impact on the physical, mechanical, thermal, and morphological properties of virgin SBR using gamma irradiation. The devulcanization process involved introducing waste rubber particles between mill rolls with different devulcanizing chemical materials, including benzoic acid, zinc oxide, stearic acid, hydroquinone, and rosin. These materials were added to break the sulfur bonds in vulcanized rubber and render the sulfur passive. The blends of DWR was added to the SBR rubber and the blends were exposed to gamma radiation using a ^{60}Co gamma rays. The total integral doses used were 25, 50, 100, and 150 kGy, with a dose rate of 3.3 kGy/h. The gel fraction increased with a higher radiation dose. The best tensile value was obtained for DWR ratio of 20% irradiated with 100-150 kGy. Elongation at break increased within the dose range 50-150 kGy for up to 20% DWR, and the elastic modulus of virgin SBR improved with radiation dose. The optimal abrasion resistance was observed for SBR loaded with 30% DWR. The solubility % decreased with increasing DWR content and showed the least value of brake oil resistance at DWR ratio of 30%.

Microwave Radiation

Microwave radiation can destroy the vulcanization network on the surface of rubber particles, thereby enhancing the surface activity of the rubber. This process leads to an improvement in the viscoelasticity and storage stability of modified bitumen [36]. According to Hirayama's research [37] microwave radiation resulted in the disintegration of polysulfidic bonds and the decomposition of chemical groups that had sulfur. However, the monosulfidic bonds with higher energy were not affected and remained intact (Figure 12). The study [38] also found that the intensity of the C-N functional group increased after microwave irradiation, which can prompt interactions and alleviate separation.

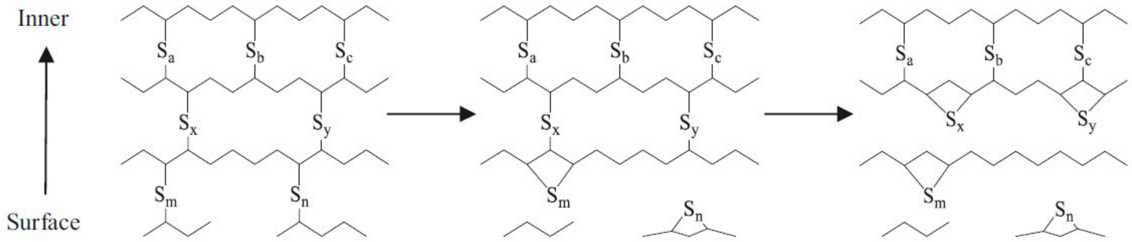

Figure 12. The disintegration of polysulfide bonds in CR following exposure to microwave radiation. Reprinted from [26] with the permission of Elsevier, copyright 2021.

Hosseinnezhad et al. [100] conducted a study to investigate a sustainable hybrid method combining microwave radiation and bio-modification to modify crumb rubber for use in bitumen. The method promotes the grafting of polar bio-molecules (bio-oil from animal-derived waste) onto the rubber surface, creating surface-activated rubber, which aims to reduce segregation and workability issues. To create microwave-activated crumb rubber (M-CR), 60g of crumb rubber was exposed to 400W of microwave radiation for 4 minutes. The resulting surface-activated crumb rubber (SAR) exhibited improved properties, including a reduction in viscosity and segregation index compared to conventional crumb rubber modified (CRM) bitumen. SAR binders also showed improved thermo-mechanical properties. The hybrid process offers a sustainable solution to mitigate segregation and workability issues while enhancing bitumen performance by altering rubber particle surface polarity and promoting secondary network formation. In turn, Lyu et al. [101] studied the potential of combining bio-derived molecules with CR particles to produce bio-modified rubberized bitumen with improved resistance to thermal and ultraviolet aging. Microwave radiation was used to graft waste cooking oil molecules onto rubber particles. The research found that waste cooking oil and rubber work together to enhance the aging resistance of rubberized bituminous binder. Bio-modification of crumb rubber particles improved their interaction with the binder, resulting in reduced aging. The bio-oil also helped maintain a higher healing capacity in the bitumen after aging. Although the bio-modified rubberized binder showed promising results against thermal and ultraviolet aging, further research is needed to study its performance under combined aging and the impact on moisture resistance in asphalt pavements. The combination of waste cooking oil and scrap tire crumb rubber, as additives to bitumen, leads to improved aging resistance, promoting sustainability in construction (Figure 13).

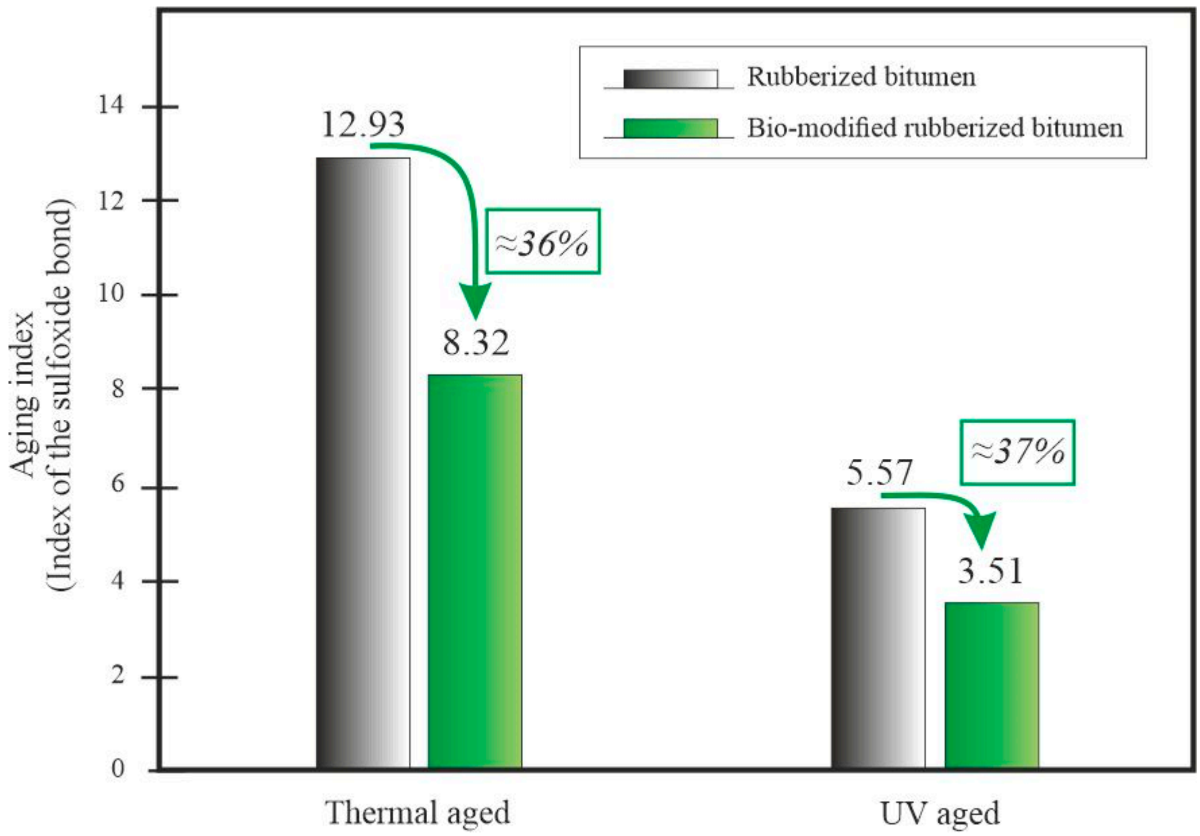

Figure 13. Bio-modification with waste bio-oil significantly enhances aging resistance of rubberized bituminous binder. Adapted from [101] with the permission of Elsevier, copyright 2021.

Chemical Grafting

Xie et al. [102] improved the storage stability and performance of the modified binder by grafting acrylamide onto the surface of crumb rubber (CR) using solution polymerization. The process involved purifying CR with acetone and then activating it through a chemical grafting method using potassium persulfate as the initiator. An orthogonal test was designed to optimize the preparation process, and the study found that rubber content was the most significant processing parameter. The optimized preparation technology included a rubber content of 20%, a shear temperature of 170 – 190°C, and a shear time of 90 min. The grafting activation of rubber improved the storage stability and compatibility of modified bitumen by enhancing the interaction of the mixture system through a chemical reaction between amide groups in rubber and acid groups in bitumen. Other studies [103] investigated the use of two methods to activate CR, coating by polyamide and grafting by acrylamide. The results showed that both activation methods improved the high- and low-temperature performance of the bituminous binder by enhancing the interaction between the rubber and binder, however grafting activation by acrylamide was found to be more effective due to the chemical reaction between groups of acrylamide and binder.

Jiang et al. [104] proposed a modified method of dynamic vulcanization to prepare blends of ground tire rubber (GTR) and high-density polyethylene (HDPE) by combining surface devulcanization of GTR and in-situ grafting technology. The process involved the mechanochemical devulcanization of GTR using intense shear and tetraethylenepentamine (TEPA), followed by grafting amine groups to the surface of devulcanized GTR (d-GTR) and adding grafting monomers of styrene (St) and glycidyl methacrylate (GMA) and initiator of DCP to the d-GTR/HDPE blends during the melt blending process. The study investigated the effects of initiator and grafting monomers on the mechanical, crystallization, and rheological behavior of the blends. Results showed that the modified method improved the compatibility and mechanical properties of the blends, which could be tailored by adjusting the initiator/grafting monomers ratio. The results of ATR-FTIR confirmed the devulcanization of GTR and the occurrence of grafting and cross-linking reactions between d-GTR and HDPE. The blends exhibited enhanced interfacial compatibility, and their crystallization behavior was affected by the grafting and cross-linking reaction. The blends had stable processing and reprocessing ability.

Kocevski et al. [105] developed a method to modify bituminous binder by grafting ground rubber tire particles with acrylic acid (AA), resulting in improved binder properties, increased viscosity, and elevated failure temperature, with potential for broader application pending further research.

5.4. Synthetic Rubbers

Ethylene propylene diene monomer (EPDM) and ethylene vinyl acetate (EVA) are the polymers used in bitumen modification [106]. It is more economically attractive to use recycled materials instead of virgin materials.

EPDM can withstand large deformations due to its stable structure caused by the cross-linking of the diene monomer, which makes the bond difficult to break [107]. Other properties to consider when determining the service life of EPDM are its high level of ultraviolet (UV) resistance, resistance to weather damage, ability to prevent fatigue damage, and water resistance. According to Ito [108] and Zaharescu et al. [109], the chain degradation by gamma radiation starts on propylene and so far the dominant feature that influences oxidation of irradiated EPDM is the constitutive ethylene/propylene ratio. Ghoreishi et al. [110] indicate that the addition of small amounts of the EPDM (3%) and hybrid nanoparticles of CNT masterbatch (0.1%) and bentonite nanoclay (1.5%) can highly enhance the viscoelastic behavior of the bitumen at elevated temperatures.

The semicrystalline EVA copolymer provides the modification of bitumen through the crystallisation of rigid three-dimensional networks within the bitumen. Different crystalline structures are formed at different temperatures and have influence on conventional penetration, softening point, Fraass, ductility and high temperature viscosity [111]. Waste EVA has good compatibility with bitumen, so it has been widely studied and applied. The results have shown that the large volume of the vinyl acetate group becomes a non-crystalline area or amorphous area, which plays a role similar to rubber when EVA is mixed with bitumen. The crystalline area of EVA has high stiffness, which acts as a reinforcing bar, and greatly improves the high-temperature stability, low-temperature cracking resistance, and viscosity of modified binder [112]. It also exhibits certain improvements in low-temperature performance when small amounts of waste EVA are added (2–4%) [113].

Gad et al. [114] explored how gamma radiation affects the characteristics of a composite made from waste low-density polyethylene (LDPE), ethylene vinyl acetate (EVA), and bitumen. In the study, blends of waste low-density polyethylene (LDPE), ethylene vinyl acetate (EVA), and bitumen were shaped into 2 cm-thick molds. For the irradiation process, samples were exposed to gamma radiation in air from a ^{60}Co source, at a dose rate of 5 kGy/h. The total radiation dose applied ranged from 25 to 125 kGy. The best mechanical properties were reported at an integral irradiation dose of 75 kGy at a weight composition ratio of bitumen:EVA:waste LDPE blend, 1:1:1. The cited research demonstrated the feasibility of employing radiation compatibilization techniques on the polymer-bitumen blends. This approach has shown promise with certain polymer blends, the option of pre-compatibilization by radiation followed by further high-temperature processing presents a viable pathway [115]. Ultimately, this strategy allows the way for the application of gamma radiation or electron-beam technologies for enhancing pavements also post-construction. Such techniques are already utilized on a smaller scale in the industry, notably in the curing of automotive component lacquers [116]. This indicates the possibility of using high-energy radiation sources to reinforce pavements, contingent upon the success of these technologies in experimental settings.

Grigoryeva et al. [117] investigated the effects of gamma and electron beam irradiation on the properties of thermoplastic elastomers (TPEs) produced by dynamically vulcanizing blends of recycled high-density polyethylene (HDPE), ethylene/propylene/diene monomer (EPDM) rubber, and ground tire rubber (GTR) pre-treated with bitumen. Radiation treatment aimed to enhance the mechanical performance and radiation stability of these TPEs. Two specific formulations containing

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bitumen were tested: a mixture of HDPE/EPDM/GTR/bitumen with a weight ratio of 40/35/12.5/12.5 wt.%, and 40/35/17/8 wt.%, respectively. The mixtures were compared to the respective ones not-containing bitumen. The TPEs were irradiated using a ^{60}Co source with an energy of 1.25 MeV. The dose rate varied between 2.27 and 28 kGy/h, with a full absorbed dose range of 100 to 500 kGy. For electron beam treatment, an accelerator radiation was used with an energy of 3 MeV and a full absorbed dose of 100 kGy. The study found that irradiation significantly improves the gel fraction content and tensile properties of the TPEs, suggesting potential for improving the recycling and utilization of polymer waste in practical applications. Bitumen serves a dual role in this context: it acts as a curing agent for the rubber components of TPEs (EPDM and pre-devulcanized GTR) and as an effective compatibilizer for blending the components together. This dual functionality is crucial for improving the mechanical properties of TPEs, as it facilitates better adhesion between the blend components, thereby enhancing the overall performance of the material. The use of bitumen pre-treated with GTR not only improves the tensile properties compared to bitumen-free TPE but also demonstrates stability to gamma irradiation, which is beneficial for applications requiring durability and longevity.

The research conducted by Kumar et al. examined how aging affects bituminous binders that are either singularly composed or combined, incorporating recycled ethylene-propylene-diene-monomer (EPDM) rubber from non-tire automotive rubber goods manufacturing and tire pyrolysis oil (TPO) obtained from decomposing waste tires. To create these composite-modified binders, three distinct methods were employed: one without any pretreatment, and the others involving pretreatment using either heat or microwave irradiation. The composite-modified binder through the pretreatment yielded significantly improved performance against aging.

6. Discussion

From an asphalt pavements contractor's perspective, maintaining the homogeneity of modified bitumen during storage is crucial, especially in response to abrupt meteorological shifts. Adverse weather conditions can often delay paving activities, necessitating the storage of modified bitumenin mixing plant tanks for extended periods, ranging from a few days to several. Ensuring homogeneity during these periods is vital to maintain the quality and workability of the asphalt mixtures. Conversely, from the viewpoint of road managers and users, enhancing the aging resistance of bituminous binders is a key factor. Improved aging resistance contributes to prolonging the service life of road pavement structures and minimizing the frequency and intensity of required maintenance and repairs. Moreover, the integration of recycled modifiers in bitumen production presents a significant opportunity for reducing the environmental impact of asphalt pavements.

As the popularity of additives for enhancing bitumen performance and recycling grows, radiation and radical grafting of polymers present promising techniques for enhancing the performance of bituminous binders. Along with the additives proposed, there is growing demad for compatibilizers. For effective compatibilization, especially in complex systems like bitumen, it's crucial to use modifiers that can interact with both aliphatic and aromatic phases, or other specific phases present in the blend. Amphiphilic modifiers, to bridge between aliphatic and aromatic phases, are particularly valuable in this regard. In the context of bitumen modification, the goal is often to blend in polymers or additives that can integrate with the bitumen's complex mixture of hydrocarbons. The challenge lies in achieving a stable dispersion of these additives, as demonstrated by the effective elimination of the naturally occurring heterogenic "bee-like" structures through chemical modification [74].

Many compatibilizers, like PE-g-MA are produced via radical polymerization. This process allows for the introduction of absolutely non-compatible functional groups onto the polymer backbone, by covalent bonding, thereby combining uncombinable. Radiation, such as gamma or electron beam irradiation, is an innovative approach used to induce grafting and cross-linking in polymers. This method can be applied directly to the polymer blend, potentially simplifying the manufacturing process by reducing the need for additional chemical additives. However, these methods are still in the developmental stage and may have limitations in terms of scalability and control over the grafting process. Modifying the surface properties of polymers is another strategy to improve blend stability. This can be achieved through various chemical or physical treatments. The utilization of high-energy ionizing radiation in polymer processing offers an economical advantage, as the energy is directly channeled into radical reactions rather than being dissipated as heat. This efficient energy use not only facilitates the desired chemical modifications but also contributes to cost-effectiveness in the manufacturing process.

Emerging methods like radiation-induced grafting and the use of amphiphilic modifiers offer promising avenues for future research and development in the area of bitumen modification.

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