MSc Thesis

Development in Waste-Derived Semi-Alternative and Full-Alternative Binder

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SAMENVATTING

Traditioneel bitumen, een essentieel bindmiddel dat toegepast wordt in verschillende infrastructuur zoals wegen, maar ook in daken en afdichtingen, wordt gewonnen uit niet-hernieuwbare aardoliebronnen. Het veelvuldige gebruik ervan in de bouw leidt tot toenemende bezorgdheid over de impact op het milieu, de beschikbaarheid op lange termijn en de kosten. Gezien deze problematiek is de ontwikkeling van duurzame alternatieve bindmiddelen noodzakelijk geworden.

Alternatieve bindmiddelen worden voornamelijk in de wegenbouw gebruikt ter vervanging van aardolie-bitumen. Bij een alternatief bindmiddel kan het bitumen gedeeltelijk worden vervangen door een hernieuwbaar materiaal zoals een natuurlijk (bio-based) of gerecycled afvalproduct. Deze eigenschap van het alternatieve bindmiddel heeft een belangrijke impact op het verbruik en de kosten van het niet-hernieuwbaar materiaal. Hoewel er uitgebreid onderzoek is gedaan naar mogelijke alternatieven uit bio-based en gerecyclede afvalproducten, is het vaak een uitdaging te komen tot goede prestaties op het gebied van compatibiliteit, duurzaamheid en gedrag.

Dit rapport is gericht op het afbakenen van een onderzoekstraject dat zich richt op het onderzoeken van twee categorieën alternatieve bindmiddelen: semi-alternatieve bindmiddelen (SAB) en volledig alternatieve bindmiddelen (FAB). Deze zijn afkomstig uit afvalstromen zoals rubber, afgewerkte bakolie en plastic afval. Het systematisch optimaliseren van een homogene moleculaire gewichtsverdeling, stelt ons in staat uitvoerig deze nieuwe bindmiddelen te evalueren. Er worden geavanceerde analytische technieken gebruikt voor een diepgaande karakterisering van het materiaal. De bevindingen geven aan dat zowel SAB als FAB de prestatie van conventioneel aardolie-bitumen kunnen evenaren of zelfs overtreffen, wat veelbelovend is voor het verminderen van de afhankelijkheid van aardolie.

SUMMARY

Traditional bitumen, a critical binder in various infrastructure applications such as roads, roofs, and sealing, is derived from non-renewable crude oil resources. Its prevalent use in the construction industry raises escalating concerns about environmental impact, long-term availability, and cost. Given these issues, the development of sustainable alternative binders has become imperative.

Alternative binder is a material used in the pavement industry mainly for replacing petroleum bitumen. For alternative binder the bitumen can be partially replaced by renewable materials such as bio-based or recycled waste materials. This property of alternative binder has important impact on the non-renewable material consumption and the cost from raw material. Although extensive research has been devoted to creating alternatives from bio-based and recycled waste materials, these efforts often encounter challenges in achieving compatibility, durability, and effective performance.

This thesis is aimed at delineating a research trajectory focused on investigating two categories of alternative binders: semi-alternative binders (SAB) and full-alternative binders (FAB). These are formulated from waste materials such as crumb rubber, waste cooking oil, and waste plastics. Utilizing a systematic optimization approach based on the principles of homogeneous molecular weight distribution, we conduct a comprehensive evaluation of these new binders. Advanced analytical techniques are employed for in-depth material characterization. The findings indicate that both SAB and FAB can meet or even exceed the performance metrics of conventional petroleum-based bitumen, offering a promising avenue for reducing the construction industry's reliance on oil resources.

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CHAPTER 1. INTRODUCTION

In this Chapter, some research background of alternative binders and literature review are given. In the end, the research approach together with the methodology of this study are presented.

1.1. WHY DO WE NEED ALTERNATIVE BINDER

1.1.1. Background

Given the size of the highway system and our current dependence on it for transportation, the pavement construction industry is a bulk consumer of extracted raw materials[1]. Annually, the pavement stock is augmented by millions of tons of materials to expand, preserve, or rebuild the network[2]. Additionally, geological and social constraints have led to diminishing availability and increasing prices for supplements of these materials. Hence, research for alternative sources or bio-renewable sources is given high priority so that the contradiction between the development of the road transport industry and the shortage of environmental resources can be alleviated.

The road network is one of the world's largest sector in terms of asset management, and among the most crucial components are flexible and rigid pavements[3]—the fundamental distinction between the two lies in the type of binder employed. Flexible pavements use bitumen as the traditional binder, whereas rigid pavements utilize Portland cement as the binder. Bitumen, a residue material generated from the process of crude oil refining, is undoubtedly a non-renewable resource, and the recoverable amount is predicted to become depleted[4]. The growing demand for petroleum bitumen in the road construction industry has attracted long-term attention.

The balance between the consumption of irreplaceable natural resources to fulfill the demand of the current generation and the development of future well-being is sustainability[5]. Climate change and global energy shortage have become the challenge of sustainable development of the international community. The international community has put forward a net-zero pathway to address the challenge of saving energy and reducing emissions[6]. As shown in Fig. 1.1 and Fig. 1.2, there are no new oil and gas fields approved for development in this pathway and future oil supplies will shrink to 1/3 of current levels. In addition, technological advances in crude oil refining will further affect the quantity and quality of bitumen. The reason for this is that crude oil refining aims to improve overall economic efficiency. The focus is on obtaining more beneficial products through the intermediate part of the crude oil fractionation process. This, in turn, enables the oil industry to break down high-chain hydrocarbons into so-called "high-value hydrocarbons" rather than the less economically beneficial product "bitumen"[7].

In addition, sales of non-plug-in internal combustion-powered vehicles reached the peak and have been in permanent decline due to the popularity of electric vehicles and technological advances[8]. Meanwhile, the promotion of renewable diesel is also accelerating the transition to replace traditional fossil energy sources[9]. As the bitumen binder is derived from petroleum, the price of bitumen relies heavily on the price of petroleum[10]. Due to the implementation of environmental regulations and decreased oil extraction, the availability of bitumen and its price stability will inevitably be threatened. Based on the issues presented above, it is imperative to develop alternative binders derived from renewable resources.

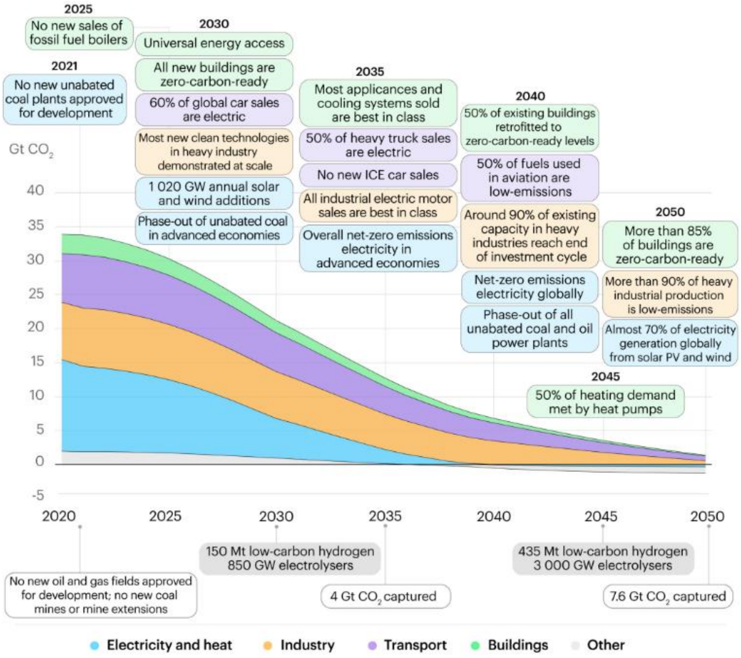


Fig. 1.1Key milestones in the pathway to net zero[6]

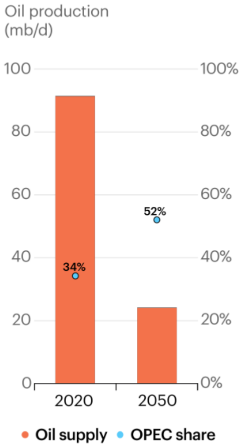


Fig. 1.2 Oil Production Reduction[6]

1.1.2. Alternative binder

Enhancing pavement sustainability can be achieved by reducing energy usage and utilizing recycled and renewable materials in the building process[11]. As conventional pavement bitumen primarily originates from fossil fuels, particularly crude oil, discovering a fresh source of raw materials for bitumen could substantially improve the eco-friendliness of road construction. Alternative binders for flexible pavement are those derived from waste-based or bio-based sources other than crude petroleum[11].

Due to the availability of large quantities of waste-based and bio-based materials, there are good technical and economic prospects in utilizing them to produce multiple types of alternative binders[12] [13]. The effect of material from sustainable sources on bitumen can be categorized into three groups based on the percentage of replacement of the original bitumen (shown in percentage), which are[13]:

i. Bitumen Modifier (<10% bitumen replacement)

ii. Semi-alternative binder (10–75% bitumen replacement)

iii. Full-alternative binder (100% bitumen replacement)

In practice, the properties of bitumen deteriorate during its service lifetime due to vehicle loads and environmental factors[14]. On the other hand, with the development of the economy, the number of vehicles and axle loads are also increasing year by year, which makes higher demands on the road surface. Meanwhile, the sustainability of road engineering also requires a certain service life of bitumen[15]. Use of modifiers in conventional bitumen binder have been utilized to reduce the frequency of maintenance and sustain the pavement's durability. According to practical needs and requirements on site, different modifiers are available to improve the properties of the bitumen. Polymer additives are commonly used to modify bitumen and their technically applicability has been proven many times[16–18]. From an economic standpoint and environmental viability, due to the high cost of polymer additives, modification with other more environmentally friendly materials is being considered.

The use of waste-based additives as bitumen modifiers would allow additive materials to be provided at very low costs, while also facilitating the utilization of waste resources[19]. Researchers have reported that a polymer blend composed of EVA and LDPE could contribute to showing favorable mechanical properties at temperatures for which neat bitumen undergoes permanent deformation and, overall, financially beneficial[20]. Waste plastic films, a common agricultural plastic waste, have been used for bitumen modification to enhance performance in resisting cracking and permanent deformation of bituminous layers. The results showed promising effects on its durability improvement[21]. Also, the optimum ratio of the waste plastic films was found to be 5 wt% for thermal stability on the basis of similar rheological parameters. Sinan, and Emine[22] studied the properties of asphalt mixture after adding high density polyethylene(HDPE) and found that asphalts modified with 4% HDPE showed improved stability and high Marshall Quotient. The use of oil as a kind of modifier in bitumen has been reported. In the research conducted by Xiaoyang[23], the properties of asphalt binder containing waste engine oil residues were evaluated by laboratory study and indicated that the addition of waste engine oil, within a range of up to 5%, brought about a substantial modification in both the infrared spectra and rheological properties of the asphalt binder. This observed alteration holds the potential to contribute to the enhancement of the asphalt binder's performance under low-temperature conditions.

Biomaterials are considered the most common, important, and renewable source of raw materials and are accessible [24]. Because of their short-term renewable nature and hydrocarbon chemical structure, these kinds of materials are appealing as flexible pavement materials[25]. Organic fiber, like various stalk fibers, motivates scholars to investigate the effect and application because of its sustainable, biodegradable, and superior specific properties. Zhexia Li’s group used cotton stalk powder to improve the tenacity, temperature sensitivity, and rheological properties of asphalt[26]. Chen mixed corn stalk fiber with asphalt binder to verify the effect on the performance of asphalt. The results showed that the corn stover had better mixing uniformity and the addition of corn fiber increased the rutting resistance of asphalt[27]. Further, Chen also analyzed the possibility of the application of corn stalk fibers in SMA mixtures, which embodies the value and potential of such materials in pavement[28]. In addition, some studies have used biobased material to modify bitumen because it has some specific chemical components. Seidel et al.[25] investigated the effect of soy oil on rheological properties and found that soy oil have potential application as a fluxing agent for recycled bitumen. Zeng et al.[29] evaluated the regeneration effect of castor oil as a bio-oil and showed that castor oil can rehabilitate aged bitumen and also improve the fatigue resistance of bitumen. Bio-based polyurethanes have demonstrated enhanced affinity with bituminous materials, meanwhile, the presence of a polymer network of polyurethanes improves the overall thermo-mechanical properties of the bitumen and also mitigates the negative effects of aging on the healing ability of the bitumen[30].

However, although the above-proposed bitumen modification has a positive effect in terms of cost, availability, and impacts on pavement performance, the replacement ratio of about 10% will have a relatively minor effect on the environmental protection level in the future when the environmental friendliness of road projects is increasingly emphasized. Hence, upgrading the replacement percentage for petroleum bitumen also has great research potential and value. Based on the above considerations, semi-alternative binder and full-alternative binder have been further developed.

1.2. SEMI-ALTERNATIVE RUBBERIZED BITUMEN

1.2.1. Various semi-alternative bitumen

Modification of bitumen has become very common as the base bitumen is unable to meet the requirements of modern transportation. The amount of this modification added is relatively low. The more modifiers are used, the lower the percentage of petroleum-based bitumen will be and the less pollution it will cause. Therefore, research on how to increase the amount of modifiers added can help protect the environment, reduce the price, and improve road performance[31]. When other materials are used to replace petroleum bitumen by more than 10 percent, it can be called semi-alternative binder.

Waste Cooking Oil(WCO)

The amount of waste cooking oil generated annually in any country is enormous. The waste cooking oil produced through elevated-temperature frying procedures in the culinary sector, encompassing food industry establishments, restaurants, hotels, and residential settings, frequently undergoes inadequate treatment and is illicitly released into water bodies. Broadly speaking, the unregulated disposal of untreated waste cooking oil into landfills or watercourses exerts adverse ramifications on the environment. A prominent ecological concern arises in the form of eutrophication, wherein incident solar radiation is impeded by a superficial oil film upon the water's surface. Consequently, this process disrupts the oxygen provisioning for aquatic organisms dwelling within the river ecosystem. Simultaneously, the ecological disequilibrium engendered by the demise of these aquatic organisms can exacerbate the degradation of water quality [32,33]. Currently, the prospects for recycling this waste are not clear. Since 2022, the European Union (EU) has instituted a prohibition on the utilization of used cooking oils in animal feed production. This is attributed to the creation of numerous deleterious compounds during the culinary frying process. If utilized as additives in livestock feed formulations, the integration of used cooking oils could facilitate the reintroduction of these harmful compounds into the food chain via the animals' meat[34]. Consequently, the proper disposal of waste cooking oils necessitates a secure approach that averts any adverse repercussions on human health. Thus, the management of waste cooking oil disposal mandates a safe and conscientious implementation that safeguards human well-being.

It has been suggested that the application of WCO in the pavement industry may reduce the need for WCO dumping. The effect of WCO on bitumen can be studied in terms of fatigue resistance, stiffness, and rutting resistance. According to Ma et al.[35], the major composition of WCO is oleic acid at 43.67%, which will help the viscosity decrease in asphalt mixture when a 13% amount of WCO is added[36]. Another research revealed that the increment in WCO in bitumen binder can raise the resistance to fatigue[37]. However, although WCO demonstrates potential in alternative binders, the issue of performance degradation caused by the addition of WCO also prevents further increase in its percentage of addition. Ma et al[35] also pointed out that the reduction of bitumen viscosity also makes the asphalt mixture too soft, which leads to a reduction in the rutting resistance of the pavement. Wen et al. investigated the waste cooking oil-based bio-asphalts with 10%, 30%, and 60% WCO respectively, the results revealed that the binder with high-content oils had low resistance to fatigue and rutting[38]. Additionally, the inclusion of Waste Cooking Oil (WCO) serves to rejuvenate both the rheological and physical properties of aging asphalt pavements. However, previous research has indicated that WCO tends to age more rapidly than petroleum bitumen at elevated temperatures. This accelerated aging compromises the long-term durability of pavements that incorporate WCO[39].

Nonetheless, it has also been proposed that by combining WCO with other additives, the amount of WCO added to bitumen can be increased while maintaining similar properties. Sun, Daquan, et al. [40] found that up to 33% of WCO could be added when used with resins, LDPE, and SBS polymers while maintaining similar bitumen properties. Furthermore, rheological tests showed that the optimized bitumen had similar high-temperature performance as SBS-modified bitumen and much better low-temperature performance than SBS-modified bitumen. Based on the results of mixture performance evaluations, the optimized asphalt mixture demonstrated comparable rutting resistance and moisture sensitivity to SBS-modified asphalt mixtures. This finding opens a new pathway for future research focused on increasing the utilization of waste cooking oil in bitumen.

Food Waste

Food waste is mainly composed of fruits, vegetables, meat, bones, and other residues. As outlined by the Food and Agriculture Organization of the United Nations, a substantial quantity of approximately 1.3 × 10^9 tons of food items experience loss or wastage across the food supply chain. These losses are primarily attributed to factors including spoilage, expiration, and inadequate inventory control practices. Over the course of a quarter-century, the escalation of food waste, particularly within Asian nations, is projected to transpire concomitant with population expansion and economic advancement. The anticipated trajectory indicates that the annual accumulation of urban food waste within Asian countries may surge from 278Mt recorded in 2005 to a projected 416Mt by the year 2025[41]. This waste is considered a zero-value resource since it is discarded without any use. As an illustrative case, within the confines of Hong Kong during the year 2012, a daily average of approximately 9278 tons of municipal solid waste was directed to landfill facilities. Out of this total municipal waste, an estimated proportion ranging from 36% to 40% constituted food waste or biobased waste materials[42]. Proper management of food waste materials is crucial to mitigate environmental impacts, minimize landfill usage, and potentially harness their value through composting or other sustainable recycling practices.

From a chemical standpoint, food waste encompasses a spectrum of constituents, including lipids, carbohydrates, amino acids, phosphates, vitamins, and diverse carbonaceous compounds[42]. This intricate chemical composition underscores the intrinsic capacity of food waste for the recovery of elevated-value commodities such as proteins, gelatins, amino acids, and lipids. Additionally, food waste lends itself to processes involving the generation of fats and oils, along with the sustainable production of energy resources. Hydrothermal liquefaction(HTL) is a promising technique for converting biomass into liquefied products using hot, pressurized water to break the chemical structure into major liquid components[43]. HTL of food waste has been studied. The artificial food waste mixed with cabbage, boiled rice, boiled and dried sardine, butter, and the shell of a short-necked clam was prepared to simulate the typical municipal food waste. The report indicated under specific HTL conditions a yield of 27.6% oil on an organic basis, which could be co-fed to a refinery or used as a source of valuable chemicals[44]. In contrast to the recovery process for light bio-oil, the production process for the high-viscosity product from HTL is less complex, and the high-viscosity product can be used to modify conventional asphalt binders and achieve a high rate of substitution. Bio-products recovered from the hydrothermal liquefaction of food waste as a potential non-petroleum-based binder in asphalt pavement have been evaluated. It has been confirmed that the HTL product from food waste could achieve 30% replacement of bitumen while the physical and storage stability has no substantial change compared with the conventional petroleum bitumen[45].

Nevertheless, the propagation of food waste as a viable resource encounters constraints due to its inherent variability. The constitution of food waste is substantially influenced by factors including geographic location, dietary preferences, and meal timings. Consequently, before its utilization as a feedstock for biofuel production, a comprehensive assessment of its chemical composition and moisture content is imperative. Unlike conventional feedstocks like plant oils, corn, and lignocellulosic materials, food waste exhibits intricate heterogeneity. Therefore, a proper characterization method should be in place for the complete chemical characterization of different types of food waste so that the food waste can be fully reused in the future.

Bio-Oil

Bio-oils are derived from renewable energy sources encompassing bio-waste materials, encompassing but not limited to wood and woody biomass waste, herbaceous and agricultural residues, among others[45]. Given the global shift towards sustainable energy alternatives, diverse bio-waste resources are being harnessed for energy generation, thereby fostering the development of waste-derived commodities, exemplified by the production of bio-oils.

Bio-oil is an agglomeration of C-, H-, and O-based complex compounds, in which “alcohols, esters, ketones, aldehydes, acids, phenols, and furan” are the main constituents[46]. There exist two distinct pathways for the formulation of bio-oils suitable for replacing bitumen. The first entails the extraction of fresh plant oils from herbaceous and agricultural biomass, while the second hinges on the utilization of biomass from various sources that have undergone advanced processing methods such as pyrolysis and hydrothermal liquefaction[46]. However, for bio-oils derived from sources other than herbaceous and agricultural biomass, a subsequent refinement process is necessitated. A spectrum of upgrading methodologies encompassing "Heat pre-treatment, oxidation process, hydro treatment, supercritical water system, distillation, esterification, transesterification, harmonic mixing, and polymer modification", constitutes established approaches for enhancing the quality of bio-oils intended for blendable bitumen production.

The retail valuation of bio-oil currently stands at approximately $300 per metric ton, in contrast to the valuation of base bitumen which averages around $700 per metric ton. This price discrepancy renders bio-oil-derived alternatives to bitumen economically compelling. Given the reasonably favorable compatibility and stability between bio-oil and bitumen, it is possible to blend in certain circumstances[47]. The addition of bio-oil reduces the energy requirement, thus enabling bio-binders to curtail the production temperature of hot asphalt mixtures. Consequently, this reduction in paving temperature yields cost savings of up to 20% in addition to mitigating greenhouse gas emissions by up to 30%. Thus, the exploration of bio-oil-based alternative bitumen demonstrates considerable promise from a multifaceted perspective encompassing economic, environmental, and technological dimensions.

Many previous studies focused on the basic physical properties of bio-oil alternative bitumen. A comprehensive evaluation of the performance of bitumen and asphalt mixtures modified with a low percentage of wood waste bio-oils has been made[48–50]. The incorporation of bio-oils yielded a noteworthy enhancement in the fatigue resistance of the asphalt mixture, without inducing substantial alterations in rutting performance and dynamic modulus. However, a marginal influence on tensile strength was observed. Moreover, their investigation indicated that elevating the bio-oil fraction to 10% correspondingly led to a reduction in compatibility with petroleum bitumen. The deterioration characteristics of bio-oil alternative bitumen were scrutinized through the incorporation of bio-oils at concentrations as high as 70% into conventional petroleum-based bitumen. Subsequent chemical analyses unveiled that the aging process of bio-oil was influenced by three primary factors: the loss of volatiles, the dehydrogenation which formulates higher molecular weight compounds such as asphaltene, and the oxidation which resulted in chemicals such as acids, alcohol, and ester[50]. Evaluating the rheological performance of bio-oil alternative bitumen, many bio-oil alternative bitumen tend to exhibit enhanced performance at lower temperatures, while concurrently displaying diminished performance at elevated temperatures. Individuals employed bio-oil in conjunction with additional additives to modify the foundational binder, thereby enhancing a spectrum of performance attributes. A renewable bio-oil alternative bitumen is produced by thermo-chemically converting swine manure into a bio-binder for mixing with petroleum bitumen[51]. The study showed that the addition of bio-binder reduces the cracking temperature as the amount of bio-binder increases, while polyphosphoric acid (PPA) is needed to maintain acceptable performance at intermediate to high-service temperatures. Furthermore, the incorporation of Styrene-Butadiene-Styrene (SBS) can complement the shortage in high-temperature performance associated with bio-oil alternative bitumen, consequently extending their potential range of applications[52].

In the context of long-term prospects, the application and subsequent advancement of bio-oil as a bitumen substitute necessitate sustained research endeavors. Thorough investigation and categorization of the impacts arising from variances in bio-oil properties attributed to diverse biomass sources are essential to comprehensively understand their influence on bitumen modification effects, thereby broadening the applicability scope of bio-oil. Secondly, an appraisal of the existing literature reveals that bio-oil alternative bitumen exhibits enhanced effectiveness at lower and intermediate temperatures, yet demonstrates diminished efficacy at elevated temperatures. Consequently, opportunities persist for the implementation of additive modifications and the refinement of bio-oil processing techniques within the ambit of bio-oil alternative bitumen production. Lastly, the intrinsic attributes of bio-oil alternative bitumen are inevitably shaped by factors such as its internal molecular composition, the degree of bitumen mixing, and the physicochemical reactions inherent to bio-oil alternative bitumen. A comprehensive elucidation of these intricate interactions is imperative to enhance the predictive capabilities of crude yield and compositional outcomes, particularly in scenarios involving biomass mixtures. Further exploration in these domains is requisite to achieve a comprehensive understanding of bio-oil alternative bitumen behavior and its subsequent development.

Plastic

Owing to their extensive array of applications, cost-effectiveness, and simplified manufacturing processes, plastics have gained ubiquitous utilization, resulting in a consistent and gradual expansion of plastic production over the span of the past fifty years. In 2019, the global production of plastics has reached 359 million tonnes[53]. However, the industry's attainment of relatively low material recovery rates coupled with the inherent challenges associated with the biodegradation of plastics have rendered waste plastic a formidable environmental hazard. The considerable global accumulation of plastic waste necessitates the exploration of inventive and feasible recycling and reutilization approaches. Multiple efforts have previously been undertaken to demonstrate that the incorporation of plastic waste into bitumen can serve as a transformative advancement in the realm of plastics recycling. This innovation holds the potential to catalyze a substantial improvement in managing plastic waste while concurrently enabling the introduction of recycled plastic products possessing competitive performance attributes into the market. Recycling plastic waste in asphalt pavement provides various environmental, technical, and economic benefits. From an environmental perspective, the integration of recycled plastic waste into flexible pavements yields a twofold benefit: a reduction in the overall volume of municipal solid waste, achieved by incorporating plastic waste into the composition of asphalt pavement materials, and a decrease in the proportion of petroleum-based bitumen. This latter effect contributes to the enhanced environmental sustainability of asphalt compositions. From an economic standpoint, the utilization of polymer-modified bitumen constitutes a comparatively higher-cost road construction material. Notably, the expenses associated with such materials can be optimally curtailed through the utilization of cost-effective polymers, specifically exemplified by plastic waste [54]. From a technological perspective, the incorporation of plastic waste imparts discernible enhancements to the performance attributes of asphalt mixtures, attributable to its analogous polymer network. This manifests in various advantageous aspects, including but not limited to improved thermal stability and degradation kinetics of bitumen, heightened resistance to permanent deformation, augmented stiffness and elasticity of asphalt pavements, dampened temperature sensitivity, and an elongation of the fatigue life of asphalt pavements [21,55]. In recent years, there has been increasing interest in increasing the percentage of plastics to replace bitumen.

Awwad and Shbeeb conducted an exploratory investigation into the potential efficacy of polyethylene in augmenting the performance of asphalt mixtures[56]. The study encompassed the determination of the optimal polyethylene type for incorporation and the corresponding replacement percentage. Specifically, the two types of polyethylene examined were low-density polyethylene (LDPE) and high-density polyethylene (HDPE), each introduced into the mixtures across seven distinct ratios: 6%, 8%, 10%, 12%, 14%, 16%, and 18%, encompassing both grinded and ungrinded states. The outcomes from bulk density, stability, and flow tests revealed that the alternative asphalt mixtures exhibited a heightened void in mineral aggregate (VMA) percentage, along with greater stability compared to the control mixture. This enhancement signifies an augmented resistance to rutting. To ensure adequate room for binder expansion and to counteract scour or seepage, a void ratio of approximately 4% is recommended. Notably, the presence of scour in the mixture exacerbates rut susceptibility and diminishes pavement skid resistance. The investigation indicated that mixtures with a replacement ratio of 12% consistently met void specifications irrespective of the polyethylene type. However, it was observed that air void content surpasses standards when the additive exceeds 12% in replacement. Conclusively, the study determined that the optimal polyethylene content is 12% of the weight of the bitumen. Utilizing this ratio for mixture modification yields the highest bulk density, stability, and minimal air void percentage, all while adhering to prescribed specifications for flow rate and VMA percentage.

Researchers Justo and Veeraragavan, affiliated with the Center for Transportation Engineering at Bangalore University, India, undertook a study focusing on plastic-modified asphalt, employing processed plastic bags as an additive integrated into the asphalt mixture[57]. It was found that the values of ductility and permeability decreased as the percentage of plastic additive increased compared to pure bitumen up to 12% addition. Moreover, the study inferred that the implementation of plastic alternative bitumen holds the potential to extend the pavement's service life beyond that achieved with regular one.

Notwithstanding the manifold benefits associated with the incorporation of recycled plastics into alternative bitumen formulations, there exist unresolved concerns that impede its broader dissemination. Given that the oldest plastic roads built under controlled conditions are less than 8 years old and that asphalt roads are built to last for 20 years, the long-term performance of plastic roads remains unclear[58]. As a petroleum-derived product, bitumen is known to release hazardous fumes. Though replacing some of the bitumen with recycled plastics can reduce fumes because of lower levels of petroleum bitumen, it is essential to acknowledge that this approach might inadvertently lead to further increased fumes because plastics are known to emit fumes when processed above their melting temperatures[59]. Although existing protocols have been established, advancing the widespread acceptance of novel plastic-alternative bitumen necessitates comprehensive datasets about the environmental impacts of such formulations. These datasets serve as a pivotal resource for policymakers in formulating a certification framework, thereby facilitating bitumen producers to assess and benchmark their products against universally recognized standards.

1.3. THE POTENTIAL OF WASTE TIRE RUBBER

The combination of bitumen with rubber has given rise to a distinctive and promising area of exploration within the realm of road construction materials. Rubberized bitumen, an innovative composite born from the marriage of bitumen and recycled rubber, has garnered substantial attention in recent literature. This fusion capitalizes on the unique properties of rubber to enhance the performance characteristics of bituminous binders, resulting in materials that exhibit improved durability, resistance to cracking, and enhanced elasticity. The following section will look at the sources of waste-tire rubber, the advantages and disadvantages of different preparation processes, the unique potential as an alternative to bitumen, and the challenges in the future application to illustrate why rubber is so special among the many environmentally friendly alternative materials.

1.3.1. Waste Tire Rubber Source

Over the past few decades, the global expansion of the automobile industry and the increasing reliance on passenger cars, motorbikes, busses, trucks, and off-the-road vehicles as the primary mode of transportation have markedly amplified the demand for tire production. Consequently, this surge in demand has resulted in the substantial accumulation of discarded tires, creating extensive reservoirs of used tire stockpiles. The sales of new tires in Europe during the year 2020 accounted for 324 million units. Among these, 89.5% (equivalent to 70% by weight) were attributed to passenger cars and light-duty vehicles. Heavy-duty vehicles, encompassing trucks, and buses, constituted 4.9% (20% by weight) of the sales, while motorbikes and scooters contributed 3.6% (1% by weight). Furthermore, agricultural and off-the-road vehicles represented 1.9% (9% by weight) of the total new tire sales[60]. Despite the current commendable recovery rate of approximately 90% for scrap tires in Europe and the USA, it is projected that a staggering total of around 4 billion end-of-life tires (ELTs) are presently found within landfills and stockpiles across the globe. Alarmingly, this quantity is projected to escalate to approximately 5 billion by the year 2030[61,62].

The casual disposition of these waste tires frequently occurs due to the diminishing availability of appropriate waste disposal sites, leading to significant environmental situations. Rubber constitutes the primary constituent employed in tire production, categorized into various types including natural rubber (NR), styrene-butadiene rubber (SBR), nitrile-butadiene rubber (NBR), and ethylene–propylene–diene-monomer rubber (EPDM). Notably, tire formulations incorporate reinforcing fillers, antioxidants, antiozonants, and curating agents, rendering them resilient against biodegradation, photochemical degradation, and elevated temperatures[63]. These additives possess tires of a non-degradable nature. Upon accumulation within landfills or salvage yards, they have the potential to emit chemical compounds that disrupt the equilibrium of the atmosphere, soil, and aquatic systems, consequently inducing ecological alterations. Mere exposure to solar radiation can lead to the emission of methane gas from discarded tires, a greenhouse gas that accentuates the carbon footprint and holds the capacity to contribute to the phenomenon of climate change[64]. Consequently, the effective management of waste tires emerges as a critical concern in tandem with the expansive expansion of the global tire industry. Also, tires deposited in landfills provide an optimal breeding habitat for vector-borne diseases such as West Nile Virus[64]. The hollow interior of a tire accumulates rainwater when stationary, forming stagnant water reservoirs. These reservoirs serve as ideal breeding sites for mosquitoes to deposit their eggs. Storing tires in such a manner essentially creates a conducive environment for the proliferation of these troublesome insects. At the same time, the concentration of oxygen within the tire interior is sufficiently substantial to instigate combustion under appropriate conditions due to the presence of inflammable constituents, thereby inducing adverse effects on both the atmospheric milieu and human well-being. If the tire catches on fire it can emit voluminous plumes of noxious black smoke into the atmosphere. This smoke carries with it many of the chemicals that are used in tire manufacturing. The application of water to extinguish tire fires leads to the dispersion of these chemicals, enabling their infiltration into subterranean water reservoirs and thereby contaminating lakes and ponds. In the past decade, the State of California has encountered two significant tire stockpile conflagrations, situated in Tracy and Westley. In the latter instance, situated on the western fringes of Stanislaus County, approximately 7 million discarded tires were engulfed in a fire caused by a lightning storm[65]. The occurrences of such calamitous incidents triggered by wasted tires have underscored the imperative to eliminate existing tire stockpiles and cultivate diversified avenues for tire utilization. From another point of view, the substantial accumulation of waste tires in existence, combined with the ongoing inflow of discarded tires in the foreseeable future, serves as an adequate reservoir that can sufficiently meet future application needs.

1.3.2. Types of Rubberized Bitumen

Over the past two decades, the integration of waste tire rubber into asphalt pavements has been introduced as a strategic measure to mitigate the challenge posed by waste tire accumulation. Rubberized bitumen has been proven to have better skid resistance, reduced fatigue crack, improved rutting resistance, and longer pavement life compared with conventional bitumen. There are two ways to introduce rubber into the flexible pavement. The first method is the "dry" method, in which rubber granules are added to replace a small portion of the mineral aggregate in the asphalt mixture before the bitumen is added. Rubberized asphalt mixtures produced by the dry process were first used in Sweden in the late 1960s to improve asphalt pavement skid resistance and durability[65]. Subsequently, it has been established that the incorporation of rubber into rubberized asphalt mixtures imparts heightened elasticity to the composition. This addition also serves to improve the adhesion between the binder and aggregate components, consequently elevating the fatigue life and resistance against rutting. Moreover, it effectively mitigates thermal and reflective cracking in such mixtures. An additional noteworthy aspect is that this method of introducing rubber into bitumen roads is characterized by its simple implementation, necessitating no specialized equipment. However, despite its effectiveness, this approach has garnered relatively less popularity within the field. This unpopularity is because of the increased costs of having to use specially graded aggregate to incorporate the reclaimed tire rubber, in addition to construction difficulties, poor reproducibility, and premature failure of asphalt road surfacing[66]. Furthermore, the optimization of rubber modification in asphalt mixtures is most effective when the rubber content added constitutes 1-3% by weight of the overall mixture. Despite the method's potential to assimilate substantial quantities of rubber from discarded tires, the actual consumption remains relatively small. It's important to note that this approach demands 1.5-2% greater bitumen compared to conventional mixtures. This increment in bitumen requirement, in turn, diminishes the overall environmental sustainability associated with this method.

Another method is the “wet method”, where rubber particles are mixed with bitumen at elevated temperature before mixing with the hot aggregates. In the traditional wet process, finely ground tire rubber is mixed with bitumen before mixing with the aggregate. This modification of the bitumen leads to physical and compositional changes during the interaction process, whereby the rubber particles swell in the bitumen by absorbing a certain percentage of the lighter components of the bitumen, forming a viscous gel while increasing the viscosity of the rubber binder. The implementation of the wet process necessitates an additional specialized mixing unit to achieve homogenization of the bitumen and rubber granules. The typical traditional wet process was introduced by Charles McDonald in the 1960s[67]. Rubberized bitumen is produced in a blending tank by blending crumb rubber and bitumen. Then this modified bitumen undergoes a transfer into a holding tank equipped with augers, which facilitate continuous circulation. This circulation process serves to facilitate an adequate duration for the interaction of the blend. Following this requisite period, the rubberized bitumen attains its optimal state for deployment and is utilized for the subsequent mixture production stages (Fig. 1.3). The rubberized bitumen produced by this method is also more promising as it can consume a larger volume of tires and can replace a portion of petroleum bitumen.

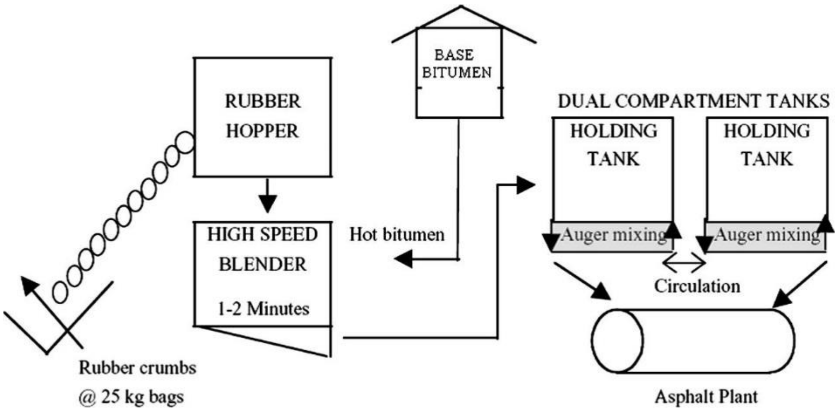


Fig. 1.3 Schematic diagram of McDonald's wet process [67].

Tortum et al. [68]investigated the impact of incorporating a low percentage of tire rubber in bitumen on the performance of mixture under different experimental parameters including tire rubber gradation, mixing temperature, aggregate gradation, tire rubber ratio (0–10% by weight of bitumen), binder ratio, compaction temperature, and mixing time. Through the comprehensive integration of multifarious objectives and judiciously navigating the inherent trade-offs among them, optimum results were obtained for the combination of the above parameters. Drawing upon these findings, the conclusion was made that the incorporation of tire rubber into asphalt overlays proffers the distinct advantage of enhancing the Marshallian stability of said overlays. Moreover, this strategic approach not only addresses waste mitigation but also attains elevated mechanical attributes, rendering it a good choice for application on heavily trafficked thoroughfares.

The maximum rubber addition was increased to 20% in the study of Lee's group to investigate the performance properties of crumb rubber modified bitumen (CRMB) due to processing method and percentage[69]. Meanwhile, the aging resistance of CRMB was also tested under a laboratory artificial aging process by PAV procedure. It was drawn that the rutting properties of CRMB improved as the crumb rubber(CR) percentage increased. Also, the fatigue cracking properties of CRMB seemed to be improved by higher CR percentages. But as expected, the higher CR percentages added to CRMB led to an increase in the viscosity at 135℃.

The growing attraction towards rubberized bitumen stems from its distinctive acoustical characteristics, rendering it a viable solution for noise mitigation in urban areas grappling with sound pollution concerns. Previous studies have demonstrated that surfaces with and without crumb rubber added to the binder show significant noise differences. In a field study conducted by Paje's research team, a 1600-meter-long test segment was paved utilizing bitumen infused with 20 percent by weight of CR, specifically designed to evaluate its efficacy in reducing noise emissions[70]. The results show that there is a significant difference between the acoustic test results of pavements with and without CRMB in continuous sections. The incorporation of CRMB led to a substantial decline in noise levels, registering a reduction of approximately 2.5 dB at a velocity of 80 km/h. This observation underscores the efficacy of employing CRMB as a potent strategy for mitigating noise pollution within urban areas because this noise reduction equates to an approximately fifty percent decrease in terms of equivalent traffic volume. In addition, the degradation of the noise reduction effect of CRMB bitumen pavements over time has also been studied [71]. Following a span of 3 years operating under service conditions, it has been observed that the efficacy of CRMB mixtures in mitigating pavement noise exhibits a diminishing trend of approximately 0.5 decibels. This decline is potentially attributed to alterations in dynamic stiffness and surface texture over time.

In 1991 South Carolina’s legislature passed the Solid Waste Policy and Management Act which requires the South Carolina Department of Transportation (SCDOT) to investigate the use of waste tires in various aspects of highway construction. The SCDOT initiated a study where approximately 11,000 metric tons of rubberized bitumen were placed at a section of highway. The crumb rubber was added at the rate of 18% by the total weight of the bitumen. During the construction of this project, all roadway densities were satisfactory. Furthermore, the introduction of rubber posed no additional impediments during the construction process and proceeded at a rapid pace. Subsequent field measurements and visual assessments corroborated the satisfactory performance of the mixtures[72].

Although there are many proven advantages to using wet-method CRMB, they are not the solution to all pavement problems. Reasons that limit its popularity include:

- The viscosity of CRMB made by the wet process is higher, and it is clear that the higher CR percentages added to CRMB led to an increase in the viscosity. Consequently, the construction process is characterized by increased complexity due to the necessity for meticulous temperature control. Compounding this challenge is the fact that mixtures incorporating CRMB demand compaction at higher temperatures compared to their conventional bitumen counterparts. This difference in temperature requirements stems from the similar behavior of rubber and polymers, as both tend to solidify the binder at high temperatures. This differential in compaction temperatures contributes to escalated energy consumption during the compaction phase.

- The presence of an auger or paddle mechanism within the storage tank is necessary for CRMB to prevent adverse effects when stored at high temperatures. In addition, CRMB may not be usable if there is a delay of more than 48 hours after mixing. Takallou and Sainton [73] underscore that the utilization of CRMB should ideally execute within a few hours post-production. This imperative stems from the potential for over-processing, which could lead to the degradation of the CR. Consequently, the CRMB utilized may fail to exhibit the intended performance characteristics, thereby yielding negative results in the constructed pavement.

Based on the above problems, an improved wet method has been investigated. In fact, the main principle of this technique is to take advantage of the chemical properties of CR and use CR as a replacement agent to produce a storage-stable rubber alternative bitumen (RAB). In this process, bitumen is heated to high temperatures and high shear stresses in a controlled environment in a tank, and then CR is introduced into the tank and digested into the bitumen. In the modified wet method, the conventional swelling process of crumb rubber is substituted by depolymerization/devulcanization mechanisms. The optimization of dispersion is achieved through the employment of elevated processing conditions, encompassing temperatures ranging from 200 to 300 °C, and shear speeds attaining magnitudes in the order of several thousand rpm, resulting in a smooth, homogeneous product (Fig. 1.4). During this process, samples are taken and tested for solubility to ensure that the rubber is fully digested. Most manufacturers use a high-shear process to ensure complete CR digestion. The solubility of the finished product is typically higher than 97.5%. The binder is then trucked to the hot mix plant as a finished product with no additional handling or processing. In the past, the rubber content in rubberized bitumen by the traditional wet method has generally been lower than 20% by weight of bitumen, but by this method, the development of high-content RAB is becoming a reality.

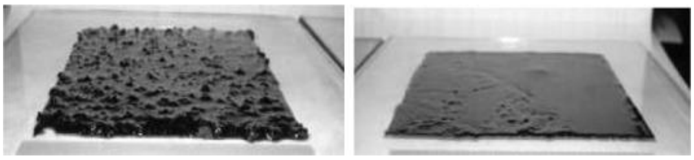


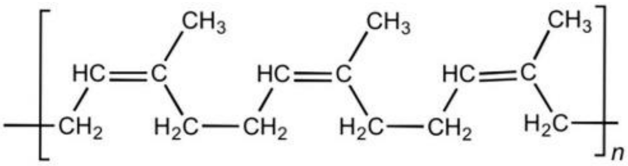
Fig. 1.4 CRMB from traditional wet method(left) and new wet method(right)[67]

In terms of binder properties, the main differences between these products are the viscosity and storage stability. Viscosity for RAB can range between 500 and 1000 centipoises at 135 °C, much lower than the viscosity for High Viscosity CRMB which is in the range of 1500–5000 centipoises at 175 °C. The reduced viscosity characteristic of RAB expands its utility beyond the conventional application scope of CRMB, enabling its incorporation into dense-graded asphalt mixtures. High-viscosity CRMBs are not suitable for use in dense graded bitumen mixtures due to the lack of sufficient mix void volume to accommodate the higher binder content. In parallel, the diminished viscosity attribute of RAB imparts notable advantages. It permits a noteworthy reduction in the required storage temperature (i.e. 15°C), thereby minimizing the likelihood of segregation during storage. This becomes especially pertinent considering the storage of on-site mixtures within mixing tanks, resulting in substantial economization of both energy consumption and financial resources through the utilization of RAB mixtures[67].

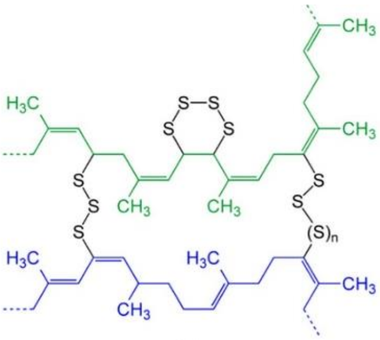
1.3.3. Potential: Adjustable Molecular Weight Distribution

Bitumen is a complex mixture of hydrocarbons with varying molecular sizes, polarities, and degrees of aromaticity, rather than a polymeric substance. Given the highly complex molecular structure of bitumen, it is almost impossible to conduct a detailed chemical analysis. Even though bitumen consists of a continuum of similar molecules, to facilitate classification and the understanding of its properties based on dominant molecular group types, bitumen molecules are generally classified into different molecular groups depending on their size and solubility in polar, aromatic, or non-polar solvents. The widely accepted SARA (saturates, aromatics, resins, and asphaltenes) fractions developed according to the selective adsorption-desorption (chromatography) method can be used to give the relative amounts of these components in bitumen.[74] Bitumen can be described as a colloidal dispersion of high-molecular-weight asphaltene micelles in the low-molecular-weight maltenes (saturates, aromatics, resins). The key aspect of the solubility model is that there is no gap in chemical properties between the fractions of bitumen which are a continuous range of molecules concerning size, polarity, and aromaticity.

As mentioned above, due to the complex molecular composition of bitumen and the distribution of equilibriums, it is inevitable that when trying to replace a large percentage of bitumen, the ratio of single components rises dramatically, which can lead to a disturbance of the equilibriums within the bitumen, resulting in poorer engineering properties and segregation. However, the production of RAB is achieved through the digestion of crumb rubber into bitumen using heat and shear, which means the degradation of CR during the preparation of RAB will cause the transformation of chemical components in bitumen and reduce the molecular size of released components. The crumb rubber used for bitumen replacement is recycled from waste tires. To meet the requirements of vehicle use, in addition to rubber, tires contain carbon black, metal, fibers, zinc oxide, and some other additives. Normally, during the handling and shredding processes, the reinforcing wires and fibers are removed to produce a clean and highly consistent rubber material for bitumen modification. In general, truck and off-the-road (OTR) tires contain higher proportions of natural rubber (NR) than passenger car tires[74]. The main constituent of NR is the polymer cis-1,4-polyisoprene with a molecular weight of 10^5–10^6 Da. As can be seen in Figure 1.2.3., macromolecules of NR are long, regular, flexible, and practically linear. To improve the durability and mechanical properties of rubber, vulcanization is applied to most rubber polymers by forming chemical crosslinks between individual polymer chains to create three-dimensional networks. (Fig. 1.5b)



(a)



(b)

Fig. 1.5 Chemical structure of (a) cis-polyisoprene, (b)crosslinking after vulcanization[74]

Typically, the RAB is produced by mixing bitumen and rubber at high temperatures with high-speed shear for a sufficient period. Under this condition, rubber network degradation occurs. In general, the interaction stages of bitumen–rubber can be divided into three steps. Stage 1: swelling phase (Fig. 1.6a). Rubber particles start swelling by absorbing the light fractions of bitumen and form a gel layer adjacent to the bitumen–rubber interface. When large molecules of rubber are just added to bitumen, the coils still hold together as a solid due to the cohesive and attractive intra- and intermolecular forces. Stage 2: post-swelling and beginning of degradation (Fig. 1.6b). The swelling of rubber particles continues happening.

Meanwhile, chemical degradation takes place through the breakup of the crosslinked network and polymer chains. Swollen rubber particles are split into smaller ones due to the destruction of the network structure. This process involves the scission of disulfide bond (S–S), carbon–sulfur bond (C–S), and carbon–carbon bond (C–C), which eventually results in the breakage of crosslinked bonds and backbone chain bonds reducing thus the average molecular weight of rubber. The S-S or C-S bonds are less stable under thermal disturbances such as chemical and thermal attack, so at certain temperatures and under shear stirring the S-S and S-C bonds break and destroy the network formed by cross-linking. This is why a pungent odor may be detected during the mixing of bitumen-rubber mixtures at high temperatures. Stage 3: degradation and complete dissolution. The degradation of rubber particles continues progressing until they are completely dissolved into the bitumen matrix, which produces a homogenous binder. As shown in Fig. 1.6c, the rubber network degradation removes the constraints for the polymer chains. The free rubber polymer chains will eventually dissolve into bitumen[74].

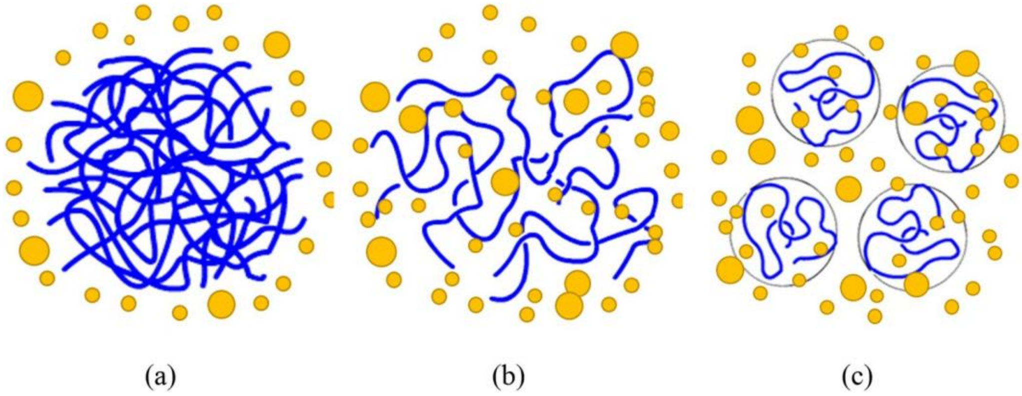


Fig. 1.6 Interaction stages of bitumen and rubber (a) rubber molecules in the solid state just after being added to bitumen; (b) a swollen rubber gel; (c) solvated rubber molecules dispersed into bitumen[74]

The interaction between bitumen and rubber at high temperatures is predominantly characterized by a process of rubber dissolution, encompassing phenomena such as swelling and chain detachment, along with concurrent chemical degradation. Within this intricate breakdown mechanism, due to the effects of time, temperature, shear rate, etc., the significant breaking of the rubber chain gradually happens and leads to an even increase of apparent asphaltenes (molecular weight from 300 to 19,000). The reason for the uniform molecular weight dispersion is that rubber is a complex system rather than a pure substance. Chain breaks in the rubber system vary, resulting in an overall uniform molecular weight distribution from the interaction between rubber and bitumen. This characteristic of uniformity facilitates the compatibility between rubber phase and bitumen phase, effectively preventing the internal molecular weight of the material from segregating due to excessive imbalance[75].

1.3.4. Challenge for RAB

Nonetheless, the exploration and study of this binder must remain ongoing, as it is not free of defects and continues to pose certain challenges during its practical implementation. Notably, there exist three predominant issues, about performance and environmental considerations, that necessitate immediate attention and resolution. Primarily, the complex composition of waste tires inherently results in the introduction of undesirable constituents within the bitumen, thereby engendering potential performance degradation of an unpredictable nature. Secondly, although the storage stability of RAB has been greatly improved compared to CRMB due to the dissolution of rubber, RAB remains susceptible to segregation challenges during real-time production. This phenomenon arises from inherent property disparities among the blend's constituents, notably accentuated at elevated temperatures. Lastly, while the RAB technology serves as a dual solution for substituting petroleum bitumen and managing waste tires, it concurrently introduces a fresh environmental concern due to the high temperature requisite for the production, transportation, and compaction of RAB-containing mixes.

The previous section discussed the behavior of rubber polymer when interacting with bitumen. Nonetheless, in practicality, tire rubber constitutes a composite of diverse constituents. In the course of bitumen-rubber interaction, elements such as oily components, carbon black, and select inorganic fillers that are inherently linked to the rubber structure are also released due to elevated interaction temperatures and the influence of shear mixing forces. Given the substantial presence of these non-polymer constituents post-rubber enhancement, the influences of their introduction into bitumen on binder properties demand serious consideration. It was reported that these non-polymer components significantly affect the aging and rheological properties of RAB, for example, carbon black, which makes up about 20% of tires, has been shown to lead to an increase in bitumen viscosity and cause a deterioration in storage stability[76].

As previously indicated, the devulcanization reaction of rubber at high temperatures involves the breaking of S-S or C-S bonds. This process leads to the release of certain noxious fumes, a critical drawback for RAB, particularly in light of the growing emphasis on environmental protection and occupational health concerns – factors that initially prompted the development of RAB. Research has revealed that RAB exhibits heightened concentrations of emissions, with binders containing CR potentially discharging more hazardous emissions compared to conventional binders[67]. Addressing the challenge of mitigating gaseous emissions from RAB necessitates a comprehensive exploration of effective methodologies.

In order to make a homogeneous RAB, it is imperative for the rubber to undergo substantial degradation and complete dissolution within the bitumen. Achieving these demands elevated heating temperatures and prolonged heating durations. However, this preparation process entails a noteworthy energy consumption, which may result in RAB not being as environmentally friendly as it was intended to be. A potential solution to address this concern could involve the integration of Warm Mix Asphalt (WMA) technology with RAB. The combination of WMA and RAB can be applied at a lower temperature which produces lower emissions at the plant and the construction site. A field evaluation of this trial combination in California demonstrated that there is a wide range of benefits that can be attained, including reduced fuel usage and emissions, improved compaction, longer paving seasons, and flexible paving time (night paving)[77]. Further research is essential to guide the effective implementation of warm mix RAB mixtures.

1.4. FULL-ALTERNATIVE BINDER

In the realm of asphalt binders, a pivotal shift towards environmental consciousness has spurred extensive research into alternatives to petroleum-based bitumen. While modified bitumen and semi-alternative binders have been subject to rigorous examination, their reliance on substantial proportions of petroleum bitumen to maintain performance has left room for a truly transformative solution. The emergence of full-alternative binder has facilitated the attainment of complete environmental sustainability for the asphalt binder. By harnessing the potential of recycled or renewable materials, these binders offer a holistic departure from conventional practices, showcasing a promising avenue for sustainable road construction that addresses both performance demands and environmental imperatives.

As mentioned above by many investigators, several different bio-based alternative binders bio-based alternative binders, encompassing soybean oil, swine waste, and agricultural byproducts, have been subject to examination. Until recently, there has been a lack of extensive research on the feasibility of using bio-oils as a full replacement for traditional bitumen binders in pavement engineering. This is due to the fact that these materials have more or less negative impacts that prevent them from being used in large quantities[48–50,52]. The potential for full alternative binder has been explored by combining these materials with additives to compensate for these deficiencies. The feasibility of utilizing switchgrass bio-oil as a full alternative binder has been substantiated through the efforts of Raouf's research team[78]. They demonstrated the potential by employing pre-treatment on switchgrass bio-oil, effectively eliminating water and volatiles, thus rendering it available for integration into pavement engineering applications. The rheological properties of these bio-based alternative binder were investigated by introducing different types and proportions of polyethylene, subsequently contrasted against conventional bitumen counterparts. Notably, the investigation revealed a remarkable resemblance between the behavior of the bio-oil blends and conventional bitumen binders. Specifically, as temperature escalated, a concurrent decline in viscosity across all blends was observed, mirroring the trend exhibited by bitumen. And the bio-oil blends exhibit the same viscosity temperature susceptibility as bitumen in the presence of polyethylene. Taking into account the consistency index K, and the Newtonian grade, the bio-oil blends can have the same rheological properties as bitumen binders.

Despite the researchers' successful demonstration of the developmental promise associated with bio-based alternatives and there are clear technological, environmental, and societal drivers for the adoption of these innovations, there remain several pivotal factors that necessitate compelling motivations to instigate a substantive transformation within the bitumen industry. These barriers encompass:

■ Cost: Although there are positive environmental benefits to be gained from the adoption of this technology, economic factors remain a major barrier to change in the bitumen industry. From the perspective of algae pricing, a prevalent bio-oil source, Spirulina with a 5% lipid content commands a price of €20/kg, whereas oil-derived bitumen currently resides within the price range of €0.314 to €0.506/kg[79]. Moreover, the conversion of biomass into a bio-based binder suitable for road construction requires subsequent processing, inevitably increasing the overall costs of production.

■ Competing with food production for resources: Bio-based binders are made from plant matter and residues, including vegetable oils, lignin, etc. However, the utilization of edible oils as a feedstock for bio-based binder production, while potentially diverting resources away from addressing global hunger and food scarcity, has come under rigorous scrutiny from numerous international non-governmental organizations[48]. This critique is primarily rooted in concerns over the consequent surge in demand for vegetable or edible oils and the avoidable deforestation practices accompanying plantation expansion.

Employing waste materials presents a potential route to circumvent some of these challenges. Notably, a study have showcased favorable outcomes stemming from the incorporation of waste materials into alternative binder formulations. Porto's research group undertook a creative approach by repurposing waste oils discarded from both vehicle and industrial hydraulic applications that were no longer suitable for their original purpose[80]. They combined these reclaimed oils with rubber powder sourced from end-of-life tires or other discarded polymers, along with cellulose extracted from paper or residual olive pomace waste. This resourceful blend also encompassed other pertinent waste or industrial by-products, complemented by cost-effective chemical additives. This composite was engineered to serve as an alternative binder, effectively replacing conventional neat bitumen. From a rheological perspective, the alternative binder exhibited similar characteristics to polymer-modified bitumen, where a 3% weight incorporation of SBS was implemented. Also, the alternative binder showed good results in terms of stiffness, tensile strength, and water sensitivity when verified at the mix level.

Although research has shown the potential of alternative binder technologies to revolutionize the bitumen industry, there is little motivation within the bitumen industry to realise their potential. Effectively motivating the bitumen industry to explore and adopt environmentally friendly alternatives to traditional crude oil-based binders necessitates a concerted effort from policy makers at national levels and should form part of wider climate and enterprise initiatives. It is clear that lacking such incentives and encouragement, the asphalt industry may be hesitant to embrace the adoption of environmentally friendly alternatives to crude oil-based materials. In addition, more studies on full-alternative binders are still needed. Researchers have concluded that some of the above-proposed alternatives have merits and demerits in terms of cost, availability, and impacts on pavement performance[2,46,81]. Hence, further research investigations must be carried out before their utilization in practice. Furthermore, a multitude of prospective bio-based or waste-derived materials remain available for application. However, to comprehensively verify their viability and sustained efficacy, additional field investigations are imperative to delve into their long-term performance characteristics.

1.5. PROJECT OBJECTIVES AND RESEARCH IDEAS

In recent years, the focus of bitumen research has predominantly centered on partial substitutions or relatively limited percentages of bitumen replacement. Due to the increasing depletion of petroleum resources and the more stringent environmental protection requirements for highway construction in the context of sustainable development, it is imperative to increase the percentage of bitumen replacement and to develop a full alternative to bitumen. This project seeks to address this limitation by embarking on a comprehensive investigation aimed at high-content semi-alternative binders and achieving a full-alternative binder, thereby pushing the boundaries of binder innovation and sustainable road construction practices.

To achieve this goal, this study will start with the development and evaluation of semi-alternative binders by incorporating rubber crumb and assessing their potential to replace conventional bitumen with high rubber content. The feasibility of this semi-alternative binder will serve as a steppingstone toward achieving a full-alternative binder. Subsequently, the research will delve into the optimization of a full-alternative binder formulation using not only rubber but also a range of waste materials. This optimization will be guided by a comprehensive evaluation process and will follow the principles of homogenous molecular weight distribution. This research aims to harness the synergies among waste materials to create a binder that not only fulfills performance criteria but also aligns with sustainable practices.

At the binder level, a thorough analysis will be conducted using Dynamic Shear Rheometry (DSR) and Fourier Transform Infrared Spectroscopy (FTIR) to assess the rheological properties and chemical characteristics of the developed binders. The storage stability of both the semi-alternative and full-alternative binders will be investigated to ascertain their compatibility over time. Moving to the mixture level, a series of tests will be employed to evaluate key performance aspects, including tensile strength, moisture stability, and raveling resistance. These tests will provide critical insights into how the developed binders perform under realistic field conditions.

To structure the presentation of this research, the thesis will be organized as follows: The initial chapter will furnish a detailed overview of various alternative binder formulations explored in the literature. The subsequent chapter will elaborate on the materials employed and the experimental methodologies utilized in this study. The third and fourth chapters will respectively introduce and evaluate the semi-alternative binder derived from Rubber Alternative Binder (RAB) and the full-alternative binder(FAB) formulation. Subsequently, a life-cycle analysis (LCA) will be undertaken in the following chapter to comprehensively assess the environmental impacts of these alternative binders. Finally, the research findings will culminate in a conclusive chapter, summarizing the outcomes and offering insights for future research directions. Fig. 1.7 shows a flow chart of the experimental design used in this study.

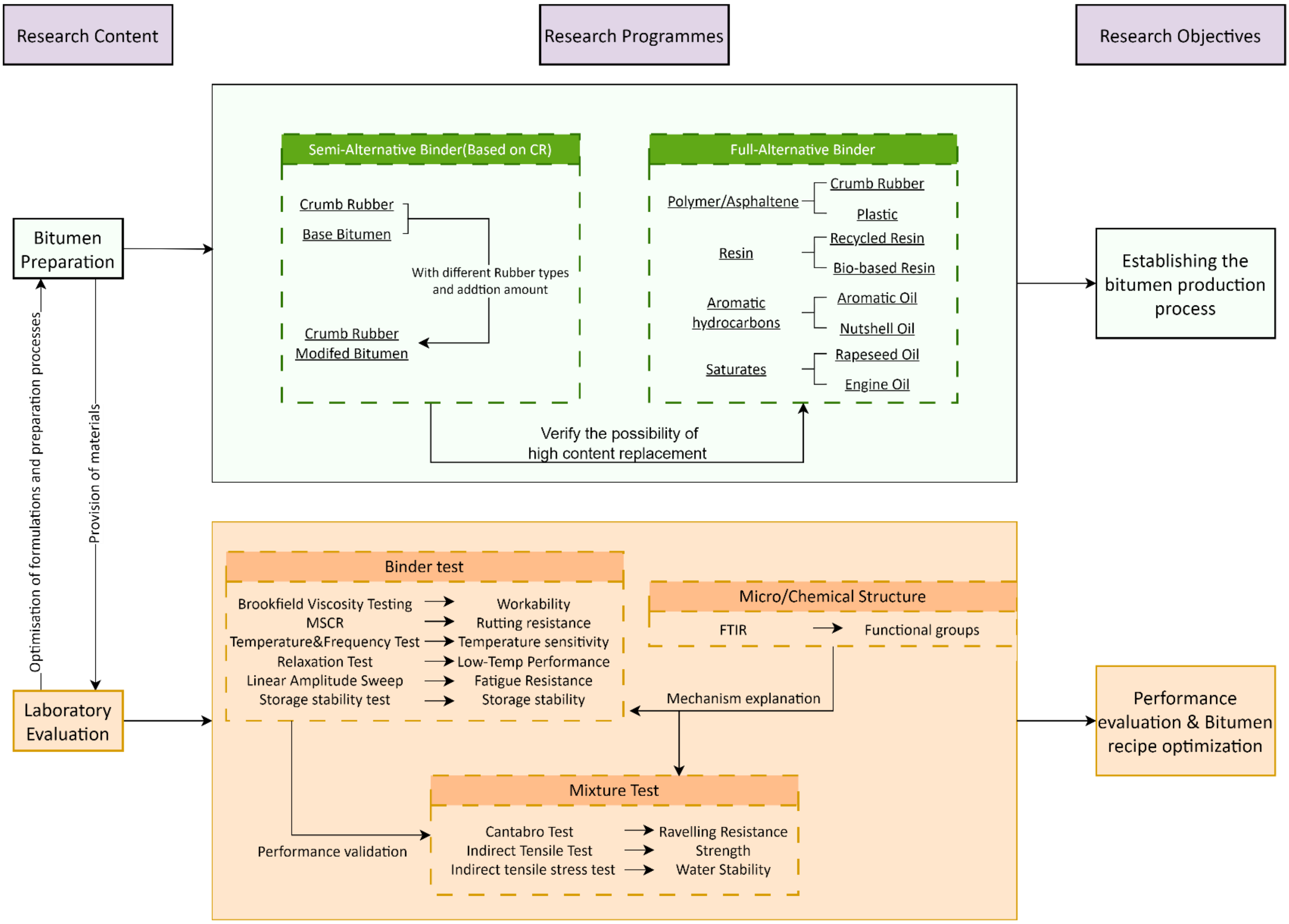


Fig. 1.7 Flow chart of experimental design procedures

CHAPTER 2. MATERIALS AND EXPERIMENTAL DESIGN

This Chapter delves into an exploration of the raw materials, the formulation, and the preparation procedures of semi-alternative and full-alternative binders. Regarding the semi-alternative binder, the focus of this thesis lies in the investigation of the crumb rubber alternative binder. Whereas in the case of the full-alternative binder, crumb rubber, and various recycled plastic materials were used to define alternative binders intended to fully replace petroleum bitumen to produce more sustainable asphalt mixtures. Through an array of laboratory experiments at binder and mixture levels to lay the groundwork for a comprehensive understanding of the synthesized binders' properties and their potential contributions to enhancing asphalt mixture performance.

2.1. RAW MATERIALS AND PREPARATION OF SEMI-ALTERNATIVE BINDER

The bitumen used for blending with crumb rubber is 70/100 bituminous binder from Total Nederland N.V. Table 2.1 shows the physical properties and chemical components of this virgin bitumen.

Table 2.1 Physical properties and chemical components of virgin bitumen

Properties		Value	Test standard
25°C Penetration (1/10mm)		91	ASTM D5
Softening point (°C)		48	ASTM D36
135°C Dynamic viscosity (Pa·s)		0.8	AASHTO T316
25°C Density		1.017	EN 15326
60°C Density		0.996	
Chemical fractions (wt %)	Saturate, S	3.6	ASTM D4124
	Aromatic, A	53.3	
	Resin, R	30.3	
	Asphaltene, AsColloidal Index CI	12.8	
Element compositions	Carbon, C	84.06	ASTM D7343
	Hydrogen, H	10.91	
	Oxygen, O	0.62	
	Sulphur, S	3.52	
	Nitrogen, N	0.9	
Complex shear modulus at 1.6 Hz& 60°C (kPa)		2.4	AASHTO M320
Phase angle at 1.6 Hz (°)		84.5	

Three different crumb rubber were supplied by Atlantis Rubber Powders B.V. (ARP), the Netherlands，as shown in Fig. 2.1. The three types of crumb rubber are: not-functionalized crumb rubber (NCR), devulcanized crumb rubber(DCR), and functionalized with catalyst crumb rubber(FCR). All three rubbers are derived from waste truck tires, and the ingredients of the truck tires are shown in Table 2.2.

Fig. 2.1 Rubber Powder supplied by Atlantis Rubber Powders B.V.

Table 2.2 Ingredients of the truck tires

Truck Tire Ingredient	Percentage
Natural Rubber (NR)	42.6%
Styrene Butadiene Rubber(SBR)	0.0%
Polybutadiene Rubber (BR)	5.4%
Chlorinated Butyl Rubber (CIIR)	1.6%
Brominated Butyl Rubber (BIIR)	6.4%
Furnace Carbon Black	28.6%
Percipitated Amorphous Silica	2.4%
Oil(Naphthenic)	6.3%
Sulfur	1.4%
Zinc Oxide	2.4%
Others*	2.9%
TOTAL	100.0%

*Others include stearic acid, tackifying resins, antioxidants, antiozonants, protective waxes, vulcanization accelerators, bonding agents, peptisers and processing aids

The crumb rubber utilized in this study comes in three distinct forms: Non-Functionalized Crumb Rubber (NCR), Devulcanized Crumb Rubber (DCR), and Functionalized Crumb Rubber (FCR), all supplied by Atlantis Rubber Powders B.V. (ARP).

- **Non-Functionalized Crumb Rubber (NCR)** is obtained by mechanically grinding waste truck tires and removing contaminants, with no additional chemical modifications.

- **Functionalized Crumb Rubber (FCR)** is NCR that has been chemically modified through the incorporation of a specific catalyst, aimed at facilitating the crosslinking of Styrene-Butadiene-Styrene (SBS).

- **Devulcanized Crumb Rubber (DCR)** undergoes a targeted desulfurization process, enhancing its solubility within bitumen.

Each type of crumb rubber possesses a particle size of 80 mesh to enhance solubility in bitumen. For each Rubber Alternative Binder (RAB), the study explores three varying rubber-to-bitumen weight ratios: 40%, 60%, and 80%. The calculation for the rubber replacement ratio relies on these established weight ratios can be calculated according to Equation 2-1.

$$replacement\ ratio\% = \frac{M_{Rubber}}{M_{Bitumen} + M_{Rubber}} \tag{2-1}$$

Then the three replacement ratios are 28%, 37% and 44% respectively. For the subsequent naming of the samples, the ratio of rubber weight to bitumen was followed. The three highest percentage replacements of RAB were mixed with 3.5% SBS（stirene-butadiene-stirene）and sulfur to investigate whether rubber and SBS would exhibit better crosslinking and show better combination performance than individual addition. The properties of SBS are shown in Table 2.3.

Table 2.3 The properties of SBS

Physical Propertires	Metric	Comments
Specific Gravity	0.940g/cc	ISO 2781
Bulk Density	0.400g/cc	ASTM D 1895 method B
Volatiles	<=0.30%	KM 04
Viscosity	3000-5000cP	25% Toluene Solution; KM 06
Melt Flow	<=1.0g/10 min	ISO 1133
Ash	0.15-0.4%	ET;ISO247
Mechanical Properties		
Hardness, Shore A	72	Measure on compression molded slabs; ISO 868
Tensile Strength	33.0 Mpa	Measure on films cast from a solution in toluene; ISO 37
Elongagtion at Break	880%	Measure on films cast from a solution in toluene; ISO 37
300% Modulus	2.90 Mpa	Film cast from poluene; ISO 37

Descriptive Properties		
Content	Antioxidants	0.15-0.4%, KM 08
	Polystyrene	30-32%, KM 03
	Total Extractables	<1.0%, KM05

The mixing procedure for RAB was based on the method outlined by Lee et al.[69]. In order to ensure that the rubber is fully digested in the bitumen, the RAB was prepared by high-speed shear machine and high temperature heater. Under the high temperature and high-speed shear environment, the rubber will be devulcanized and degraded, and then dissolved in the bitumen. For the preparation of SBS-modified bitumen as well as RAB+SBS, the bitumen is sheared for one hour at a speed of 2,000 rpm at 180 °C, and then kept at the same temperature and sheared at a slow speed for 2 h to let the SBS polymer network to fully develop. In summary, all the samples prepared in this RAB-based semi-alternative binder study are presented in Table 2.4.

Table 2.4 Sample list of semi-alternative binder section

No.	Bitumen Sample Name	Description	Group
1	Base	Total base bitumen 70/100	Reference
2	3.5% SBS+Sulfur	3.5%SBS+Additives+0.15% Sulfur	Reference
3	DCR40%	40% Devulcanized rubber	RAB
4	DCR60%	60% Devulcanized rubber	RAB
5	DCR80%	80% Devulcanized rubber	RAB
6	NCR40%	40% not functionalized truck tire rubber+Additives	RAB
7	NCR60%	60% not functionalized truck tire rubber+Additives	RAB
8	NCR80%	80% not functionalized truck tire rubber+Additives	RAB
9	FCR40%	40% functionalized with catalyst truck tire rubber+Additives	RAB
10	FCR60%	60% functionalized with catalyst truck tire rubber+Additives	RAB
11	FCR80%	80% functionalized with catalyst truck tire rubber+Additives	RAB
12	DCR80%+SBS	80% Devulcanized rubber with 3.5%SBS	Modified RAB
13	DCR80%+SBS+Sulfur	80% Devulcanized rubber with 3.5%SBS +0.15% Sulfur	Modified RAB

14	NCR80%+SBS	80% not functionalized truck tire rubber+Additives+3.5%SBS	Modified RAB
15	NCR80%+SBS+Sulfur	80% not functionalized truck tire rubber+Additives+3.5%SBS+0.15%Sulfur	Modified RAB
16	FCR80%+SBS	80% functionalized with catalyst truck tire rubber+Additives +3.5%SBS	Modified RAB
17	FCR80%+SBS+Sulfur	80% functionalized with catalyst truck tire rubber+Additives +3.5%SBS+0.15%Sulfur	Modified RAB

2.2. RAW MATERIALS AND PREPARATION OF FULL-ALTERNATIVE BINDER

2.2.1. Composition

To accomplish the complete substitution of bitumen, an in-depth understanding of its composition is essential. A significant advancement in this area is the group-type separation of petroleum fluid components into Saturates, Aromatics, Resins, and Asphaltenes, commonly known as the SARA analysis[74]. This universally recognized approach employs a chromatographic method based on selective adsorption-desorption processes to determine the relative quantities of these components in bitumen. Both the weight percentages and molecular weights of the SARA fractions are tabulated in Table 2.5. Based on the results of the SARA analysis and considering factors such as cost, material availability, and environmental impact, aromatic oil, waste cooking oil, rubber, C9 resin, and waste plastic were chosen as the principal raw materials for the formulation of full-alternative binders.

Table 2.5 The weight percent and the molecule weight of the SARA fractions

	Weight Percentage(%)	Molecular weight(g/mol)
Saturates	5-15	470-880
Aromatics	30-45	570-980
Resins	30-45	780-1400
Asphatenes	5-20	800-3500

Aromatic oil (AO) and waste-cooking oil (WCO) are used as the replacement for saturates and aromatics in bitumen, and as solvents for solid raw materials in full-alternative binder. WCO, as a waste material, can be recycled to reduce environmental pollution, and as an additive to bitumen it has been shown to increase resistance to thermal cracking and reduce viscosity[38]. However, the weakening of the rutting resistance and fatigue resistance of WCO needs to be emphasized and the amount of WCO added needs to be controlled. The WCO used in this experiment was prepared by mixing various common vegetable oils (canola oil, sunflower oil, etc.) and frying common fried foods such as meatballs and French fries at high temperatures to simulate the waste cooking oil from restaurants. AO mainly acted as an inert component to increase the content of aromatic components. In addition, AO improves fatigue resistance and contributes to the swelling degree of the polymer[82,83]. This will help the diffusion of rubber as well as plastic in the alternative binder. The chemical and physical properties of AO is shown in Table 2.6.

Table 2.6 The chemical and physical properties of AO

	Unit	Aromatic-Oil
Appearance		Dark-brown half-solid
25℃ Density	g/cm^3	0.994
60℃ Density	g/cm^3	0.978
25℃ viscosity	cP	63100
Flash point	℃	>210
Carbon C	(wt%)	88.01
Hydrogen H	(wt%)	10.56
Oxygen O	(wt%)	0.40
Sulfur S	(wt%)	0.48
Nitrogen N	(wt%)	0.55
Average molecular weight Mn	g/mol	409.99

Resin as an original component of petroleum bitumen, has an impact on improving the storage stability and aging resistance of bitumen, and increasing the softening point, viscosity, and complex shear modulus of bitumen, as shown in Fig. 2.2. Due to the limitation of material source and research time, C9 resin is used as the raw material to substitute of the resin in bitumen. In the future research, bio-resin will be applied in full alternative binder to further decrease the environment impact. Furthermore, it has been shown that the addition of resin is beneficial in improving the compatibility of polymer with bitumen and can promote its homogeneous dispersion in bitumen, which will play a key role in the compatibility of the added rubber and waste plastic in the alternative binder[84]. Technical index of resin used in this research is shown in Table 2.7.

Fig. 2.2 Resin used in this research

Table 2.7 Technical index of C9 resin

Technical index	Softening point, ℃	Gardner Color Scale, #	Vcid value, KOH/(mg/g)	Production mode
Measured value	128.4	7	0.1	catalystic polymerization

Based on the results of the semi-alternative binder, and considering the environmental friendliness, performance and price, NCR was used as the rubber type in the full-alternative binder. At interaction temperature of 260 °C, the polymer chain degrades gradually and leads to the increase middle-molecular component (molecular weight from 1,000 to 3,000), which potentially play the similar function of resin. Also, a certain fraction of the rubber molecules is partially degraded in large-molecular (molecular weight from 3,000 to 19,000) may have similar function with asphaltene, which improve the high-temperature performance of the alternative binder.

In addition to crumb rubber, the potential for incorporating waste plastic in the construction of flexible pavements has been a subject of interest for some time. The role of waste plastic in synthetic bitumen parallels that of a bitumen modifier in plastic-modified bitumen; it enhances properties such as rutting resistance and moisture damage resilience[85]. Given the constraints of the research timeline, pre-processed waste plastic pellets were sourced for inclusion in full-alternative bitumen. These comprise recycled low-density polyethylene (LDPE), polyethylene (PE), polypropylene (PP), and recycled ethylene-vinyl acetate (EVA) (see Fig. 2.3 a-d). Furthermore, recycled expanded polystyrene(PS) (see Fig. 2.3e), frequently employed as a filler material in packaging, was also identified as a promising raw material for full-alternative bitumen formulations.

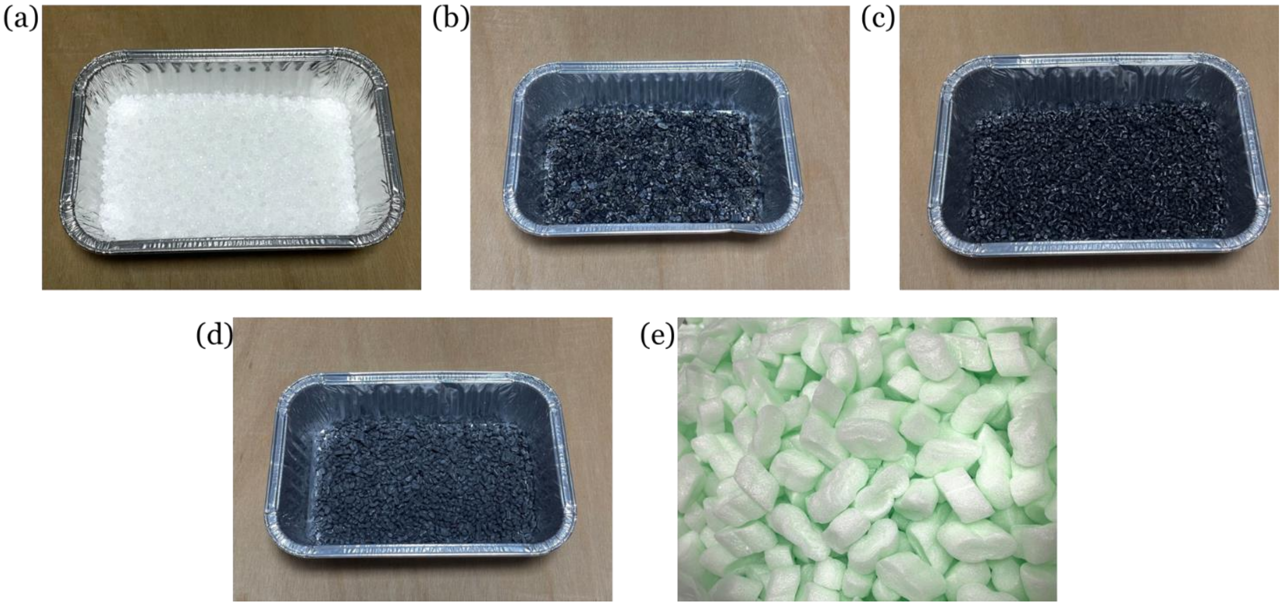


Fig. 2.3 Waste Plastic (a)LDPE, (b) EVA, (c)PP, (d)PE, (e)PS

2.2.2. Key influence factors

Reconstructing bitumen is a complex endeavor, requiring the amalgamation of diverse materials. The process necessitates extensive experimentation and iterative adjustments. The methodology for determining the optimal proportions of each constituent material is outlined as follows:

I. Design Procedures:

A. Start from SARA, CII

With the aim of replacing petroleum bitumen with multiple waste materials, it is crucial to estimate the approximate addition ratio of each component as a starting point for further work. Based on SARA's analysis of the proportions of the bitumen components (Table 5), and considering the characteristics of the components, it is possible to derive approximate proportions of each material to be added. The Saturates component of the bitumen can be provided by AO and WCO, the Aromatics by AO, the Resins by C9 Resin, and the Asphaltenes by rubber degradation.

Furthermore, this proportion is then corrected using the colloidal instable index (CII), which ensures the initial stability of the full-alternative binder. The CII is calculated using the following formula [86]:

$$CII = \frac{w_{saturates} + w_{asphaltenes}}{w_{resins} + w_{aromatics}} \tag{2-2}$$

Where w stands for the mass fraction of saturates, asphaltenes, resins, and aromatics in bitumen, respectively. When the CII value of bitumen is greater than or equal to 0.9, asphaltene deposition is likely to occur.

In addition, waste plastic can be used as a polymer. The polymer content varies between 2% and 10% by weight of bitumen. In the last decade, the most common percentages have been around 5 or 6%, but in the last few years lower polymer contents (2-3%) have been preferred due to the price of polymers[87]. With waste plastic a higher percentage can be considered due to the low cost. The percentage of waste plastic added is therefore 5-10%.

In summary, the approximate addition ratio of each material is shown in Table 2.8.

Table 2.8 Weight percentage range of full-alternative binder components

Components	**Weight percentage（%）**
Rubber	a_1-a_4
Aromatic Oil	b_1-b_4
Waste Cooking Oil	c_1-c_3
Resin	d_1-d_3
waste plastic	e_1-e_3

B. Oil and Rubber : RO1~RO4

The first step in the preparation of an alternative binder is to dissolve and digest the rubber in solvents to produce rubber oil (RO), which will be used to add subsequent materials. Therefore, the proportion of rubber and oil in the alternative binder should be confirmed first. PS was used as the trial polymer, and the RO with better performance was selected based on viscosity, fatigue life, and MSCR results for subsequent experiments.

C. Resin

Resin in alternative binder is beneficial in improving its high temperature properties as well as adhesion and contributes to the homogeneous dispersion of the polymer in the bitumen. However, if it is added in too much amount, it may lead to the problem of reduced fatigue life. The proportion of resin was adjusted while keeping the other proportions the same, and the optimum amount of resin was selected based on the fatigue life and MSCR results.

D. Polymer ratio

Based on the identical RO and the same amount of resin added, the optimal amount of plastic added was tested using PS as the case study. Based on the analysis of fatigue life and MSCR results, the optimal additive amount is obtained, which can be used as a basis for replacing other types of waste plastics.

E. Polymer type

After confirming the proportions of all components, replacement was done only for the polymer type. Based on the results of fatigue life, MSCR and viscosity, the two best performing polymers were selected for final optimization, and then the binder level and mixture level were tested to complete the alternative binder study.

The flowchart of determining FAB formulation is shown in Fig. 2.4.

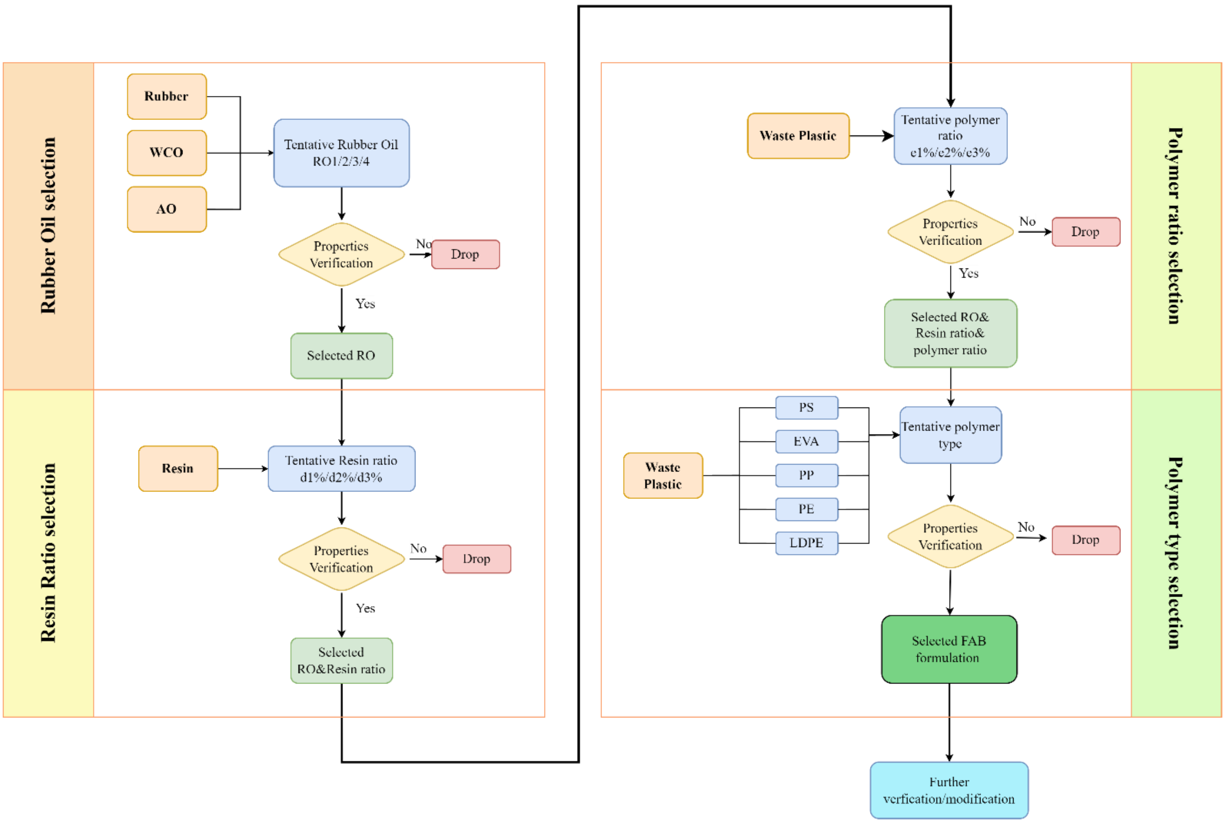


Fig. 2.4 Flowchart of determining FAB formulation

2.3. ALTERNATIVE BINDERS AND PREPARATION PROCESS

Using the materials described above, full-alternative binders were finalized that were similar to the conventional bitumen used for paving. A total of **20** alternative binders were defined, characterized and selected at the binder level, and the optimal bitumen was used to verify mix performance, as shown in Table 2.9. Each row in Table 2.9 represents an alternative binder formulation, The numerical value indicates the weight ratio between the materials.

Table 2.9 Type and weight ratio of constituent materials of the 21 alternative binders

Name	**WCO**	**AO**	**Rubber**	**Resin**	**Waste Plastic(polymer)**					**Additional**
					PS	**PP**	**PE**	**LDPE**	**EVA**	**AO**
RO1+d_2Resin+e_1PS	c_3	b_3	a_1	d_2	e_1	-	-	-	-	-
RO2+d_2Resin+e_1PS	c_1	b_1	a_4	d_2	e_1	-	-	-	-	-
RO3+d_2Resin+e_1PS	c_2	b_2	a_2	d_2	e_1	-	-	-	-	-
RO4+d_2Resin+e_1PS	-	b_4	a_3	d_2	e_1	-	-	-	-	-
RO4+d_1Resin+e_1PS	-	b_4	a_3	d_1	e_1	-	-	-	-	-
RO4+d_3Resin+e_1PS	-	b_4	a_3	d_3	e_1	-	-	-	-	-
RO4+d_1Resin+e_3PS	-	b_4	a_3	d_1	e_3	-	-	-	-	-
RO4+d_1Resin+e_2PS	-	b_4	a_3	d_1	e_2	-	-	-	-	-
RO4+d_1Resin+e_2PE	-	b_4	a_3	d_1	-	-	e_2	-	-	-
RO4+d_1Resin+e_2PP	-	b_4	a_3	d_1	-	e_2	-	-	-	-
RO4+d_1Resin+e_2LDPE	-	b_4	a_3	d_1	-	-	-	e_2	-	-
RO4+d_1Resin+e_2EVA	-	b_4	a_3	d_1	-	-	-	-	e_2	-
RO4+d_1Resin+e_2LDPE+3Aro	-	b_4	a_3	d_1	-	-	-	e_2	-	f_1
RO4+d_1Resin+e_2LDPE +5Aro	-	b_4	a_3	d_1	-	-	-	e_2	-	f_2
RO4+d_1Resin+e_2LDPE +7Aro	-	b_4	a_3	d_1	-	-	-	e_2	-	f_3
RO4+d_1Resin+e_2LDPE +8Aro	-	b_4	a_3	d_1	-	-	-	e_2	-	f_4
RO4+d_1Resin+e_2LDPE +10Aro	-	b_4	a_3	d_1	-	-	-	e_2	-	f_5
RO4+d_1Resin+e_2EVA+4Aro	-	b_4	a_3	d_1	-	-	-	-	e_2	4
RO4+d_1Resin+e_2EVA+5Aro	-	b_4	a_3	d_1	-	-	-	-	e_2	5
RO4+d_1Resin+e_2EVA+6Aro	-	b_4	a_3	d_1	-	-	-	-	e_2	6

The preparation of the full-alternative binder was carried out in stages according to the addition of materials. The preparation procedure of mixing is summarized below:

- Prior to resin and polymer addition, the rubber was add to the solvents that includes WCO and AO and dissolved in a heated bath at high temperature for enough time under the shear action of a high-speed shear to ensure complete dissolution, rubber Oil (RO) is obtained.

- Move RO to overhead stirrer for low-speed blending, add resin when temperature stabilizes at lower temperature, keep temperature constant and blend for half an hour.

- Polymer was added and the specimen preparation was completed by blending for two hours under the same conditions.

- For the final modified full-alternative binder, additives were added after the polymer was finished mixing and mixed for half an hour under the same conditions.

The experimental equipment used and the process of making the experiment are shown in Fig. 2.5 and Fig. 2.6.

Fig. 2.5 High-speed shear machine, overhead stirrer and heating bath used for preparation

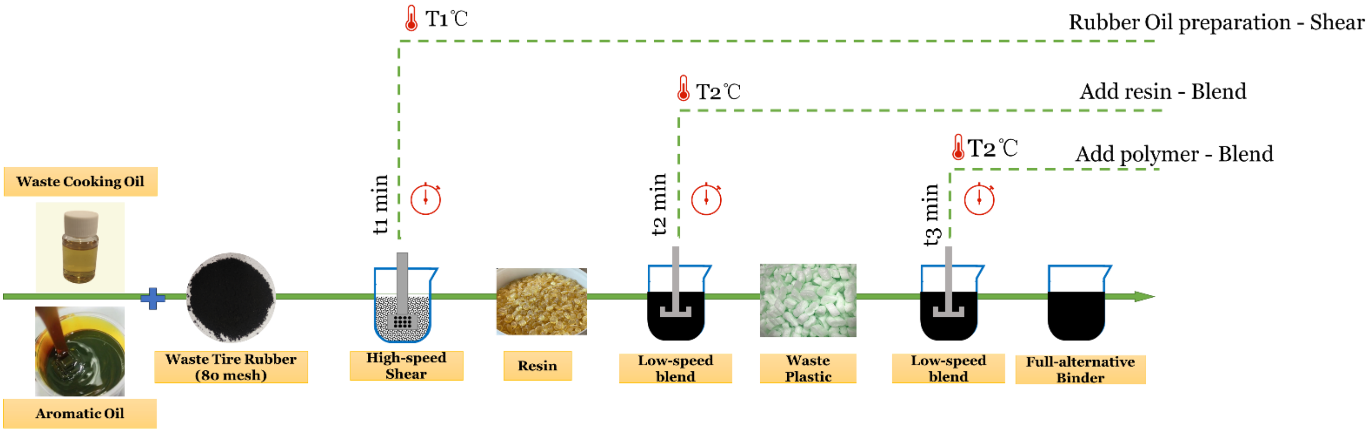


Fig. 2.6 Alternative binder preparation procedure

2.4. EXPERIMENT METHODS

The performance of semi-alternative and full-alternative binders were verfied by laboratory evaluation. Fourier transform infrared spectroscopy was measured to determine functional groups of alternative binders to give mechanism explanation of binder performance by chemical structure of the bitumen. Subsequently, various rheological parameters such as complex shear modulus, phase angle, and viscosity were measured to characterize the rheological properties of the modified bitumen at various temperature ranges[88,89]. At last, for selected semi-alternative binder and full-alternative binder, a mixture level evaluation including Cantabro test, indirect tensile strength test and indirect tensile strength ratio test were performed to verify their realistic field performance.

2.4.1. Chemical Measurements

Fourier transform infrared (FTIR) spectroscopy is used to identify the chemical compounds of semi-alternative and full-alternative binders. FTIR spectroscopy is based on interactions between infrared radiation and the molecules in a sample. The molecules absorb parts of the infrared radiation and, thus, are stimulated to vibrate[90]. Therefore, by analyzing the infrared spectrum, one can readily obtain structure information of a molecule. The FTIR spectra were measured by Nicolet IS50 FT-IR. The spectra were recorded from 4000–400 cm^{-1}.The definition of the peaks of the FTIR spectra is shown in Fig. 2.7.

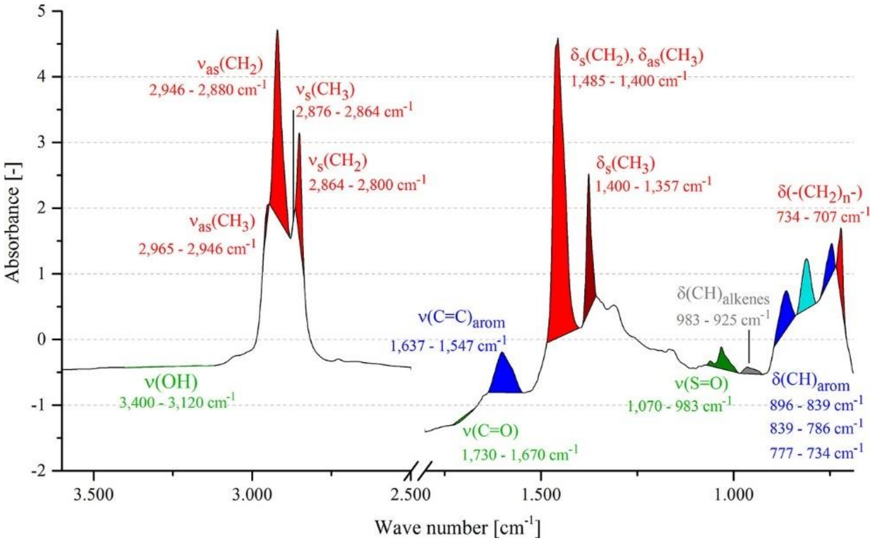


Fig. 2.7 The definition of the peaks of the FTIR spectra

2.4.2. Rheological Measurements

Two devices, a Brookfield Rotational Viscometer and a Dynamic Shear Rheometer (DSR), were used for rheological measurements of the samples. The Brookfield Rotational Viscometer was used to measure the viscosity of the alternative adhesives to verify their workability. The DSR was selected to run the Frequency and temperature sweep test, Multiple stress creeps recovery (MSCR) test, Linear amplitude sweep (LAS) test, and Relaxation test to assess the rheological performance of the alternative binder.

Viscosity

According to the standard rotational viscosity test procedure, the viscosity of the bituminous binder at different temperatures was measured using a Brookfield viscometer and the viscosity-temperature curve was plotted. In this study, ten test temperatures, including 100℃, 110℃, 120℃, 135℃, 140℃, 150℃, 160℃, 170℃, 180℃, and 190℃ were used. The viscosity at each temperature was measured and plotted to evaluate the temperature sensitivity of alternative binders. In addition, the viscosity of the binder significantly affects its workability during the mixing and paving phases, so the viscosity range must be controlled for further applications.

Frequency Sweep Test

The complex modulus and phase angle of the alternative binder will be measured at different temperatures (0°C, 15°C, 30°C, 40 °C, 60°Cand 80°C) and frequencies (0.1–10 Hz). Then the master curves for complex modulus and phase angle had been presented.

Based on the time-temperature superposition principle, the sigmoidal model is utilized to establish the master curve of the alternative binder, which is expressed below.

$$lg|G^*| = \delta + \frac{\alpha}{1 + e^{\beta+\gamma\times\lg(f_r)}} \tag{2-3}$$

Where G^* is complex modulus, δ is value of the lower asymptote of complex shear modulus $|G^*|$, α is value of the upper asymptote of complex shear modulus $|G^*|$, β and γ are shape factors.

Temperature Sweep Test

Except using the master curves of complex shear modulus (G*) and phase angle (δ) generally created by the horizontal shifting of the frequency sweep test results using shift factors to express the viscoelastic properties of binders, temperature sweep based on one frequency but varying the temperature is more accurate and faster in some conditions[91]. Temperature sweep were performed on alternative binders in a range of temperatures between 2 and 150°C and the frequency of 1.59 Hz. By combining the results of the master curves of frequency sweep and temperature sweep, the temperature sensitivity of the alternative binder can be more directly and accurately reflected.

Multiple stress creep recovery (MSCR)

The presence of elastic response in bitumen and the change in elastic response at two different stress levels were identified by the multiple stress creep recovery (MSCR) method following ASTM D 7405-15[92]. The performance of alternative binders on rutting resistance was analyzed by determining the percent recovery and irrecoverable creep elasticity. According to AASHTO, $J_{nr\,0.1}$ and $J_{nr\,3.2}$ indicate the average nonrecoverable creep compliance at 0.1 kPa and 3.2 kPa respectively. This suggests that the higher the J_{nr} value, the lower the rutting resistance of the bitumen. And J_{nrdiff} mean the percent difference in nonrecoverable creep compliance between 0.1 kPa and 3.2 kPa. This value characterizes the stress sensitivity of the material.

Relaxation test

Using an 8 mm diameter plate with a 2-mm gap and testing at 0 °C, bitumen samples were examined by DSR. The relaxation tests began with 1% shear strain (in 0.1 s) and were followed by 100 s of relaxation period. The data collecting frequency was set to 100 Hz. As an example, the stress time curve for the base bitumen is shown in Fig. 2.8. At low temperatures, the relaxation test can be used to assess stress production and relaxation abilities. By normalizing the initial maximum shear stress to 100%, the time for the stress to return to 50% T_{50} and 10% T_{10} are used to evaluate the residual stress relaxation properties.

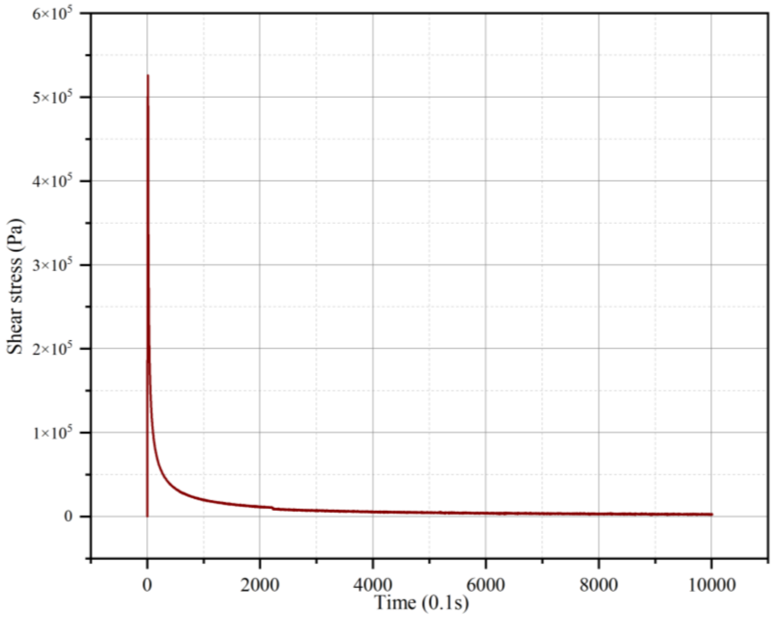


Fig. 2.8 Relaxation test stress-time curve of base bitumen

Linear Amplitude Sweep

The linear amplitude sweep (LAS) test was performed to understand the fatigue criteria. The sample is tested in shear using a frequency sweep to determine rheological properties and then tested using a series of oscillatory load cycles at linearly increasing amplitudes at a constant frequency to cause accelerated fatigue damage. The frequency sweep test employed an applied load of 0.1 percent strain over a range of frequencies from 0.2-30Hz. Test data is used to determine the damage analysis “alpha” parameter. Amplitude sweep is run at 10Hz with linearly increased strain from zero to 30% over the course of 3100 cycles. Peak shear strain and peak shear stress are recorded every 10 load cycles, along with phase angle and dynamic shear modulus. The bitumen fatigue equation can be written

$$N_f = A(\gamma_{max})^B$$

B is calculated by the parameter “alpha” determined by frequency sweep. And parameter A is determined by inputting data from load cycles into the viscoelastic continuum damage mechanism analysis.

2.4.3. Mixture level

Open-grade mixture type were chosen for the mixture. The percentage of aggregate gradation is shown in Table 2.10. A series of tests will be employed to evaluate key performance aspects

Table 2.10 Aggregate gradation of mixture

Op zeef	Cumulative % retained in each sieve	Density[kg/m^3]
22.4	0	2685.852
16	1.7	2685.852
11.2	22.7	2685.852
8	56.2	2678.068
5.6	77.9	2669.758
2	85	2672.862
0.5	85.9	2657.648
0.18	91.4	2657.648
0.125	94.5	2657.648
63 (crushed)	95.9	2657.648
filler (wigras 60K)	100	2638
Bitumen content	5.2	1032

Indirect Tensile Strength Test

This test is an indication of the tensile strength of asphalt mixtures in laboratory. In this test, a continuously increasing vertical load is applied on the specimen, which results in a tensile stress along the horizontal axis and causing splitting failure in the end.

The indirect tensile strength (σ_{its}) in MPa follows from the maximum horizontal stress σ_{xx} during the test. And the horizontal stress σ_{xx} and vertical stress σ_{yy} can be calculated by following equation:

$$\sigma_{xx} = \frac{2F}{\pi \cdot l \cdot D} \tag{2-4}$$

Where
F =maximum force[N]
L =thickness
D =diameter of the specimen

Indirect Tensile Strength Ratio Test

To determine the waste sensitivity of alternative binders, ITSR is performed. The water sensitivity (ITSR) is expressed by dividing the average value, of (at least) 3 samples "retained", by the average ITS of 3 samples "unretained". The ITSR is calculated by:

$$\text{ITSR} = \frac{ITS_{retained}}{ITS_{droog}} \times 100\% \tag{2-5}$$

The samples can be classified as follows:

Table 2.11Classification for the waste sensitivity(ITSR)[93]

Class	A	B	C	D	E	F
ITSR[%]	≥90	≥ 80 and <90	≥ 60 and $<$ 80	≥ 40 and $<$ 60	≥ 20 and $<$ 40	$<$ 20

Cantabro test

This test procedure is used to determine the abrasion loss of asphalt mixture to verify the raveling resistance. The breakdown of compacted specimens utilizing the Los Angeles Abrasion machine(Fig. 2.9) is measured in this test. The percent of weight loss

(Cantabro loss) is an indication of PFC durability and relates to the quantity and quality of the asphalt binder. The Cantabro loss(CL) is calculated by:

$$\mathrm{CL} = \frac{A - B}{A} \times 100\% \qquad (2\text{-}6)$$

Where:
CL=Catabro Loss,%
A=Initial weight of test specimen
B=Final weight of test specimen

Fig. 2.9 Los Angeles Abrasion machine used in Cantabro test

CHAPTER 3.

SEME-ALTERNATIVE BINDER:

RUBBER ALTERNATIVE BINDER

3.1. INTRODUCTION

Over the years, researchers and practitioners alike have explored various alternatives to traditional bitumen driven by a range of motivations, including environmental sustainability, improved performance, and cost-effectiveness. These explorations have led to the development of novel binders such as bio-based alternative binders and waste-derived binders[30,51,54,85]. While these alternatives have showcased remarkable potential, they also come with their unique sets of challenges and limitations. The intricate balance between environmental friendliness and practicality, coupled with performance standards, continues to pose intriguing questions for those seeking the ideal alternative binder for pavement.

Waste tire rubber, often relegated to landfills or by environmentally harmful disposal methods, holds immense promise as an alternative binder material. It has been proven that the addition of crumb rubber derived from waste tires shows better performance of temperature fluctuations resistance and fatigue life[69,72]. Meanwhile, the property of rubber to break up into smaller molecules during the interaction between bitumen also gives rubber more of a replacement ratio for bitumen[74]. However, prior research in this domain has predominantly focused on relatively low replacement percentages of bitumen, often hovering around 20%. While these studies have provided valuable insights, there remains a considerable gap in our understanding of the full potential of high-content waste tire rubber replacement.

In this research, three type of crumb rubber from waste truck tire were utilized for a comprehensive exploration of high-content semi-alternative binder. For each type of rubber, replacement at levels of 40%, 60% and 80% (by the weight of bitumen) will be verified in a series of laboratories. For the best performing group, aging and storage stability tests will be conducted. The flowchart of this section is shown in Fig. 3.1.

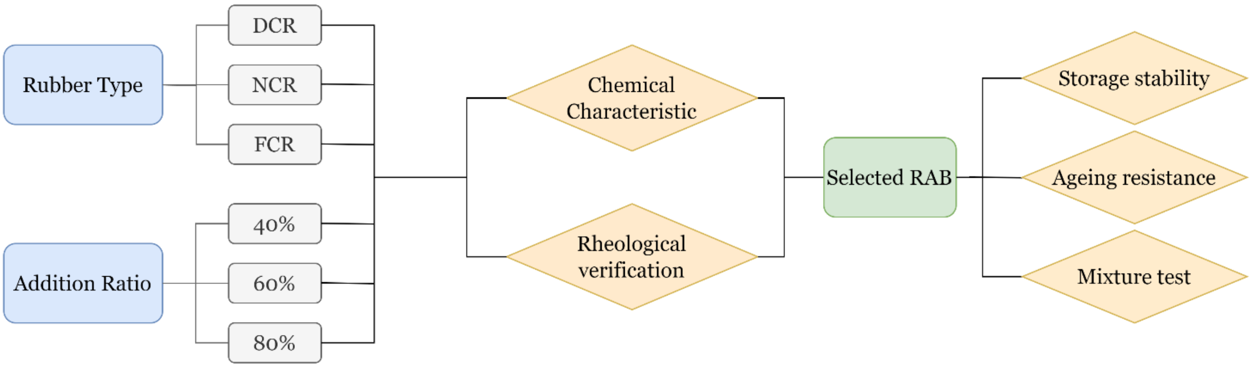


Fig. 3.1 Flowchart of RAB section

3.2. FTIR ANALYSIS OF RAB

The spectra of three types of rubber are shown in Fig. 3.2. It can be observed from this figure that the a peaks at 465cm^{-1}, which can associated to sulfur that is expected to be present in waste tire rubber due to the vulcanization process[94]. The rubber used in this study had a concentration of about 1.4% sulfur from elemental composition analysis (Table 2.2). Also, the spectra of FCR and NCR indicate a strong sharp peak in the region whereas it is not noticeable in the spectra of DCR. Following the devulcanization process within the DCR, the removal of sulfur leads to a significantly reduced peak compared to that observed in both the FCR and NCR. In addition, the peak in the region between 1000 and 1090 cm-1 may caused by the silica and carbon black in the CR[97]. These two peaks may be used as reference in the following FTIR analysis of RAB.

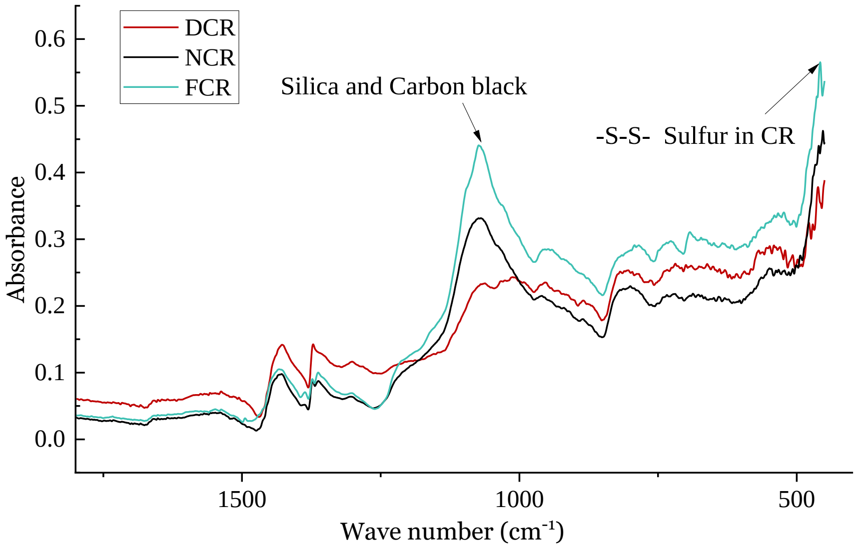


Fig. 3.2 Spectra of DCR, NCR and FCR

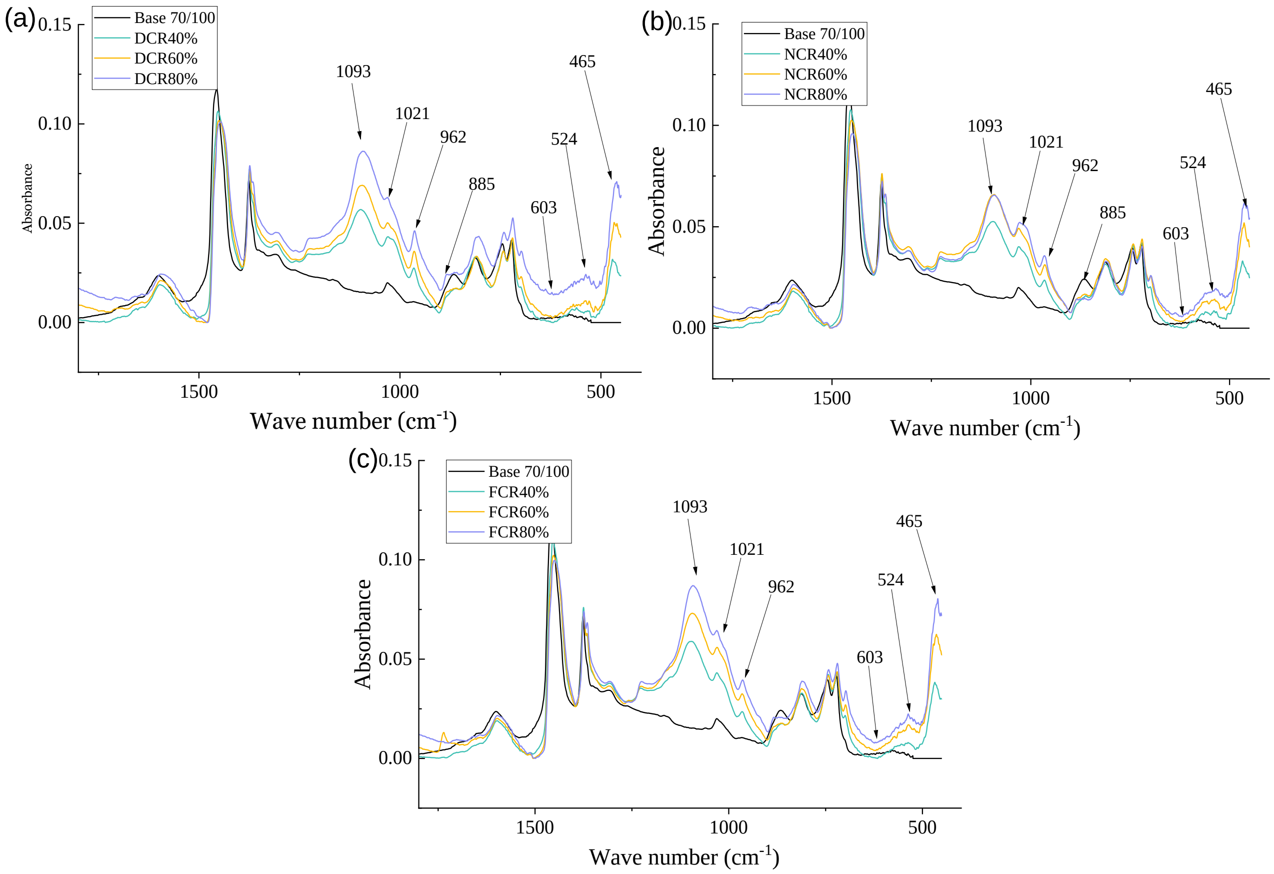


Fig. 3.3 Spectral Analysis of Semi-alternative Binders: (a) DCR, (b) NCR, and (c) FCRr

In accordance with the findings of M Weerasinghe's group, the peak at 1093cm^{-1} for asymmetric stretching of Si-O-Si bonds is characteristics peaks of silica[96]. The spectra depicted in Fig. 3.2, which is corresponding to different types of RABs, all shows notable peak at 1093cm^{-1}. Considering the ingredient of truck tires that used as the rubber source in this study shows around 2 percent of precipitated amorphous silica, this observation suggests the incorporation of silica within the rubber samples into the binder material. Besides, due to its inherent inorganic composition and stability, silica material remains unchanged after the dissolution of rubber. For that reason, the peak assigned to this substance can be used as criterion in order to test the homogeneous diffusion of rubber in alternative binder when promoting RAB in the future. Furthermore, this discovery could serve as a valuable reference point for monitoring spectral alterations in other peaks that may undergo changes. By dividing the peak area of spectral peaks by that of silica, it is possible to quantify the magnitude of the observed change in the selected component based on the amount of silica component in the sample. It can be employed as an indicator for assessing the extent of rubber solubility in bitumen through the analysis of ratios involving various easily decomposable components, such as S-S and C-S. With this method, the dissolution of rubber can be detected under different preparation conditions, which can play a good role in guiding the promotion and industrial production of RAB in the future. Additionally, carbon black, employed as a constituent in truck tire manufacturing, can serve as a reference peak owing to its analogous stability to silica, as represented by the spectra band at 1021cm^{-1} assigned to -C-C- stretching[97].

Truck tires can be made of blends of Nature Rubber (NR), Styrene-butadiene Rubber (SBR) and Butadiene Rubber (BR). The FTIR spectrum of the NR presents characteristics bands such as 2962, 2928 and 2855 cm^{-1}, which are due to C–H asymmetric stretching of –CH3, of –CH2– and to –C–H symmetric stretchin. However, these groups are also present in petroleum bitumen, not being decisive to identify NR. According to HM Nor and JR Ebdon's study, bands around 885cm^{-1} can also identify NR[98]. According to ASTM D3677, bands from 980 cm^{-1} to 965 cm^{-1} are assigned to vibration of C=H link from carbons of butadiene double bond. 962cm^{-1} is one of the characteristic bands of NR. Thus, as shown in Fig. 3.3, FTIR analysis of RAB indicated the presence of NR.

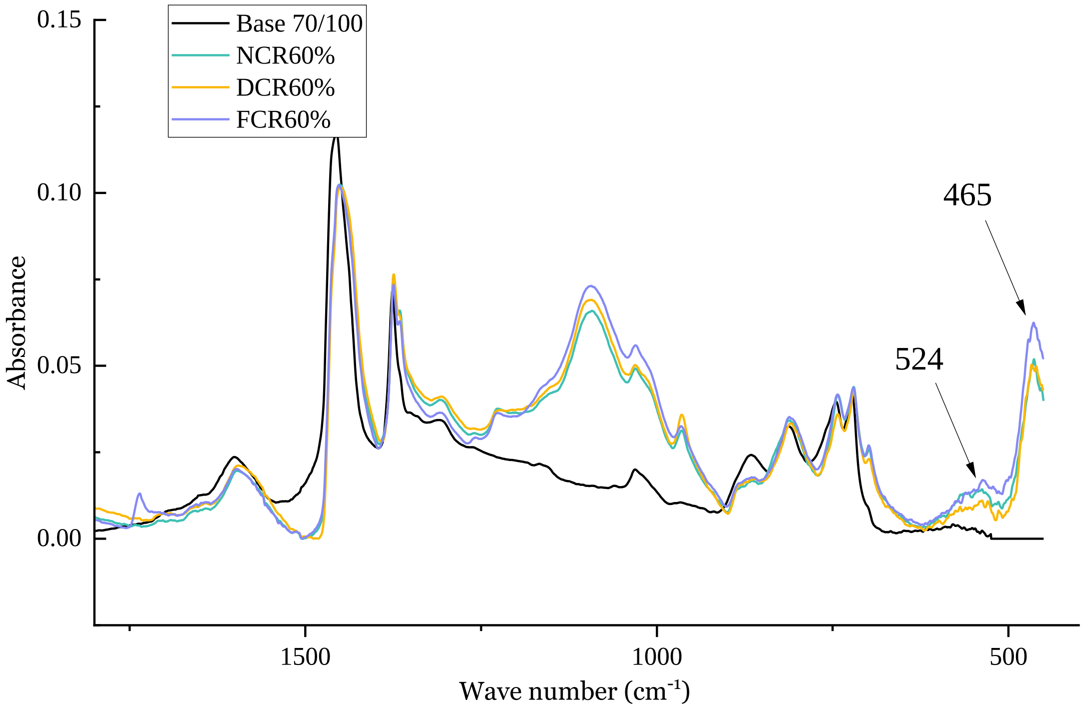


Fig. 3.4 Spectra of three types of RAB at 60% rubber addition

The sulfur in crumb rubber is present either as C-S or S-S. The band at 603cm-1 us assigned to C-S and the bands at 524 and 465cm-1 are assigned to S-S[99]. The S-S or C-S bonds are less stable under thermal disturbances such as chemical and thermal attack, so under the preparation condition of RAB the S-S and S-C bonds break. From the spectra of three types of RAB at same rubber replacement percentage, it can be observed that the DCR alternative binder shows lower peak area than that of NCR and FCR. This suggests that prior devulcanization of the rubber would allow it to dissolve better in the bitumen. Considering the high temperatures required to prepare RAB and the energy consumed for high-speed shearing, the application of DCR gains a competitive edge by offering a more environmentally sustainable approach to rubber desulfurization within the bitumen refining process. This would consequentially lead to a marked reduction in sulfoxide emissions during asphalt production and on-site construction, further contributing to the environmental sustainability of road infrastructure. Furthermore, it is noteworthy that there exists negligible disparity within the spectra of RAB fabricated through NCR and FCR at 524 and 465 cm^-1, signifying that the catalyst employed in the FCR procedure exerts minimal influence on rubber dissolution.

3.3. VISCOSITY

The viscosity of bitumen binders at high temperatures is an important property as it is a good indicator of the binder s ability of pumping in the asphalt mixing plant and the workability in the construction. According to the standard rotational viscosity test procedure, the viscosity of the bituminous binder at different temperatures was measured using a Brookfield viscometer and the viscosity-temperature curve was plotted. In this study, eight test temperatures, including 100°C, 110°C, 120°C, 135°C,140°C, 150°C, 160°C, 170°C, 180°C and 190°C. The viscosity at each temperature was measured and plotted to evaluate the temperature sensitivity of rubberized alternative binders. Fig. 3.5 shows the viscosity results of the RAB tested in this study for various rubber contents and types.

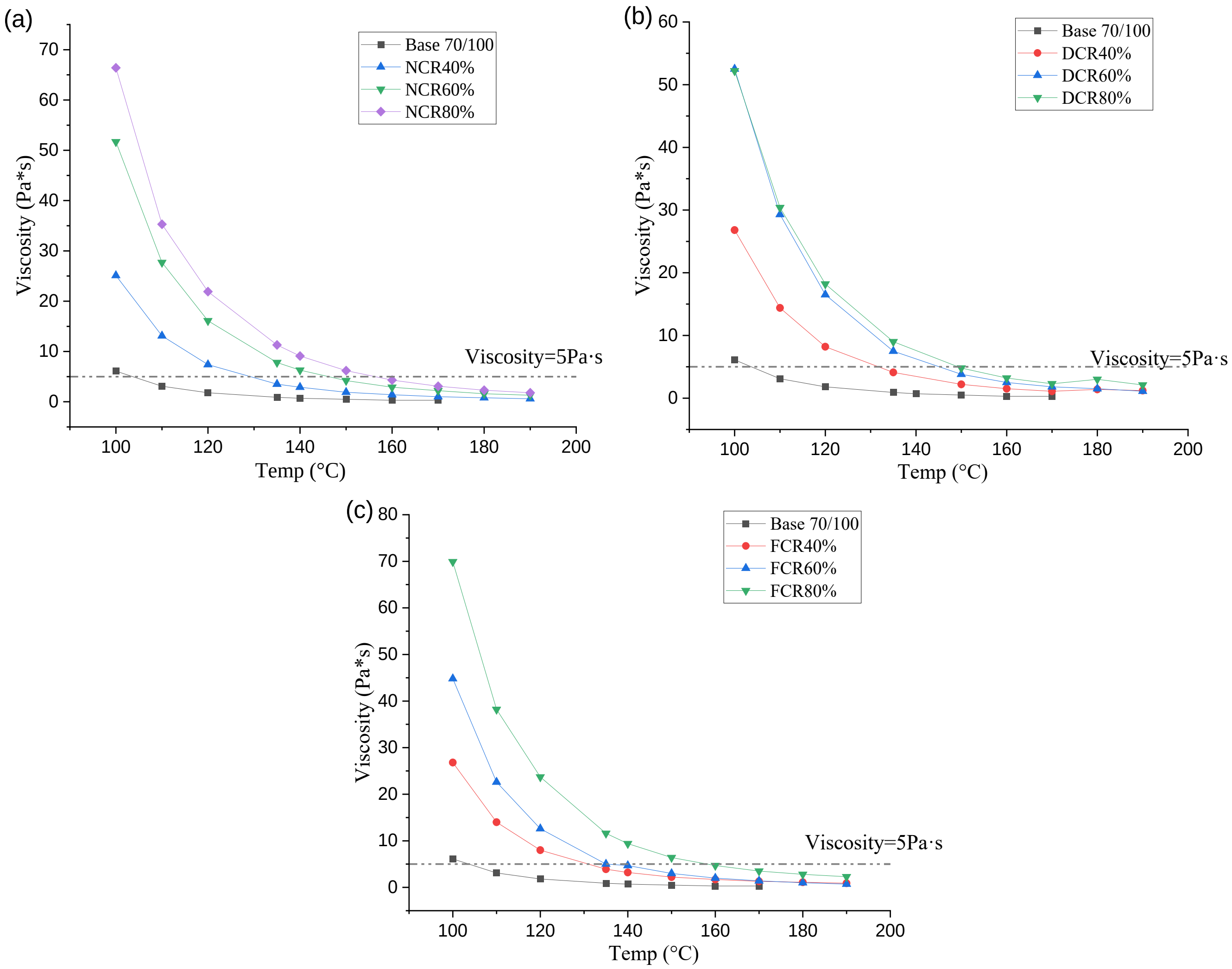


Fig. 3.5 Viscosity as a function of the temperature of RAB

As shown in Fig.3.4, the viscosity of RAB increase with the increasing content of rubber. NCR is similar to FCR in that the viscosity of RAB increases significantly when the amount of rubber is increased. The difference between the viscosity of DCR at 60% and 80% additions did not change much, which may be due to the desulfurization of DCR so that the rubber can still be dissolved in the bitumen more easily when a large percentage is added.

In addition, from the construction temperature perspective, the temperature of RAB needs to be raised appropriately during storage, blending, and pumping. Following the mixing, transportation, and pumping stages, it remains imperative for the mixture to maintain a requisite level of fluidity to facilitate proper compaction. In construction practices, bitumen typically needs to exhibit a viscosity below a specified limitation at 135℃ to ensure the practicality of the construction process[100]. However, in the case of rubber bitumen, its distinctive viscosity characteristics necessitate an elevation in temperature during the construction phase. according to ASTM D6114/D6114M, the viscosity requirement for the asphalt-rubber binder is a maximum of 5.0Pa·s at 175°C.

As depicted in Fig. 3.6, it is apparent that the viscosity of bitumen progressively rises as the ratio of rubber to bitumen substitution increases. Nevertheless, even at the highest level of RAB substitution, the viscosity 175°C remains within acceptable limits, ensuring that RAB maintains its workability to meet the practical demands of construction. Furthermore, upon evaluating the viscosities of the three rubber types at 175 °C, it becomes evident that the varying rubber types exert minimal influence on viscosity. Despite DCR being regarded as the most soluble rubber in these three rubber types, it does not exhibit improved viscosity characteristics even though it has been pre-desulfurization treated. Conversely, NCR, without any treatment, displays the lowest viscosity when incorporated in significant quantities. This indicates that desulfurization may primarily enhance solubility during the initial stages of rubber addition, while it cannot decrease the viscosity of the RAB.

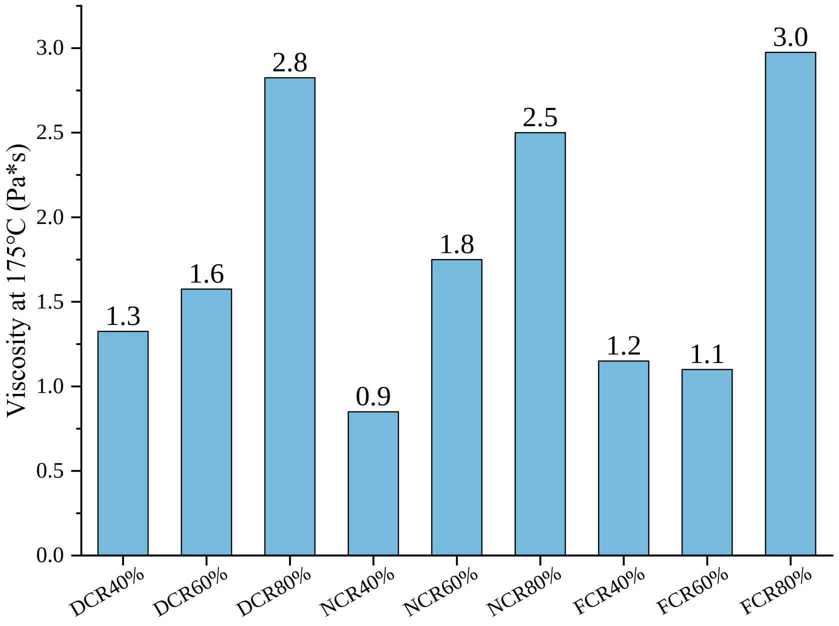


Fig. 3.6 Viscosity at 175°C of RAB

To mitigate the diminution of high-temperature characteristics attributed to the dissolution of rubber, and to investigate the cross-linking interactions between rubber and Styrene-Butadiene-Styrene (SBS), SBS was integrated into RAB as a modifying agent. The incorporation of SBS into RAB introduced a substantial impact on its viscosity, as evident in Fig. 3.7. Following the addition of SBS, a notable increase in viscosity was observed across all RAB types. This effect was particularly pronounced with the NCR-based alternative binder, which exceeded the specification viscosity limit after the addition of SBS. The incorporation of sulfur, intended to facilitate a uniform distribution of the SBS polymer matrix, markedly impacted the properties of the NCR alternative binder. Specifically, the viscosity of the sulfur-modified binder exhibited a twofold increase compared to the RAB without sulfur. In the case of the FCR alternative binder, sulfur addition also resulted in viscosity exceeding the specified limits. However, it is noteworthy that the DCR alternative binder exhibited a comparatively slight response to sulfur addition. This distinction may be attributed to the prior devulcanization process undergone by DCR.

Indeed, it is essential to highlight that bitumen with higher viscosity presents several advantageous characteristics, including increased elasticity, enhanced toughness, superior performance at high temperatures, and strong adhesion to aggregates, when compared to conventional modified bitumen[101]. Nevertheless, it's crucial to recognize that efforts to reduce viscosity in such modified bitumen formulations may inadvertently compromise these desirable qualities. Consequently, when dealing with modified RAB that exceeds specified viscosity limits, the rheological behavior was thoroughly evaluated to determine the degree of improvement in its high temperature performance. These assessments serve as the basis for informed decisions regarding the necessity for additional treatment or modification to strike the right balance between viscosity and the desired properties of the bitumen.

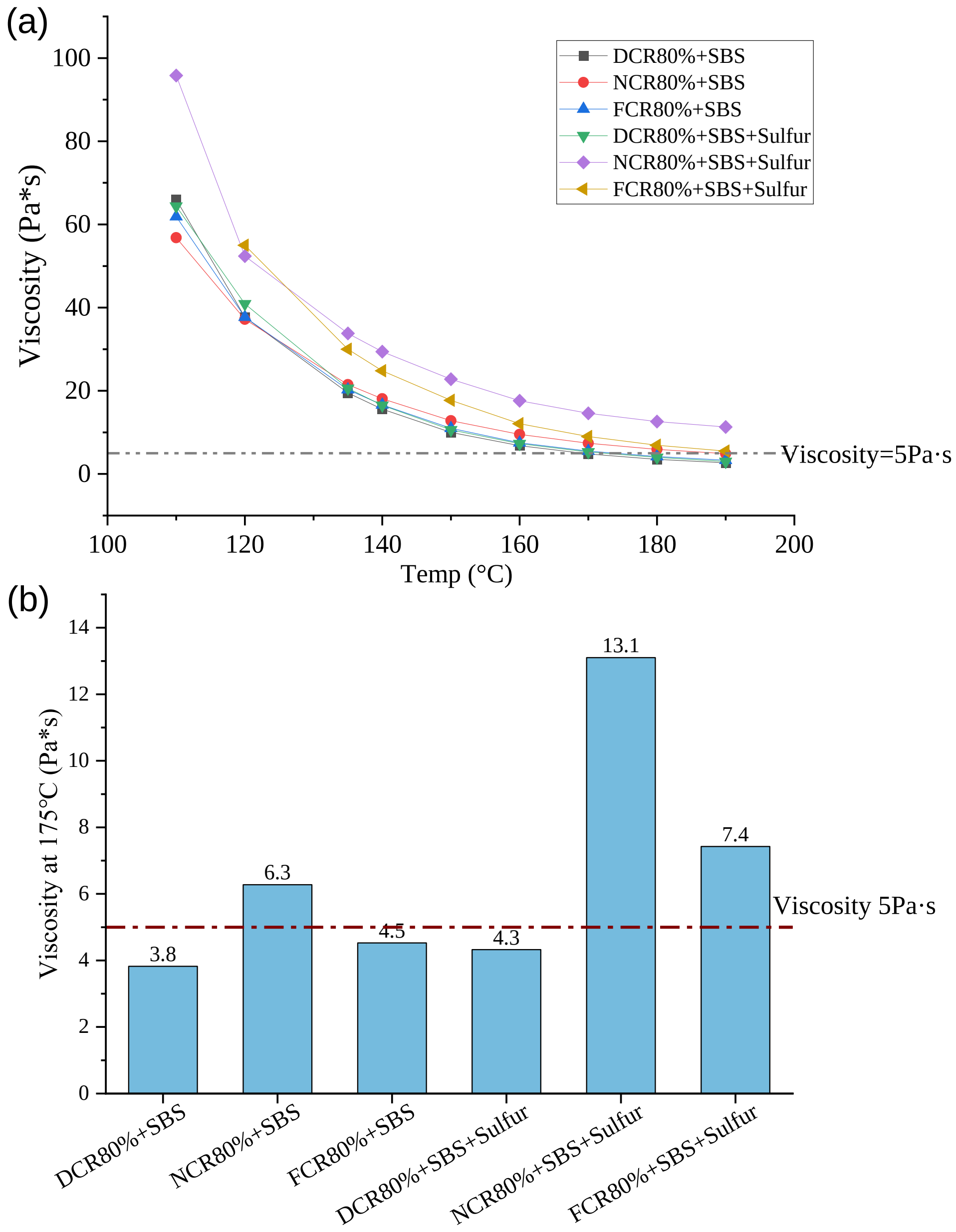


Fig. 3.7 (a)Viscosity as a function of the temperature of modified RAB (b)Viscosity at 175℃ of modified RAB

3.4. RHEOLOGICAL PERFORMANCE

In this section, a comprehensive evaluation of the rheological performance of RAB is conducted, employing a dynamic shear rheometer (DSR). Various tests, including the Temperature Sweep Test, Frequency Sweep Test, Multiple Stress Creeps Recovery (MSCR) Test, Linear Amplitude Sweep (LAS) Test, and Relaxation Test, have been meticulously selected to assess critical attributes such as temperature sensitivity, high-temperature elastic response, fatigue life, and the ability of residual stress relaxation at low temperatures. These assessments collectively provide a detailed understanding of the complex rheological behavior and performance characteristics of RAB, offering valuable insights into its suitability for specific applications in pavement engineering.

3.4.1. Temperature sweep

Effect of temperature on DSR parameters including G^*, phase angle δ, $G^*/\sin\delta$ and $G^*\cdot\sin\delta$ have been shown in Fig. 3.8,Fig. 3.9,Fig. 3.10,Fig. 3.11, and Fig. 3.12.

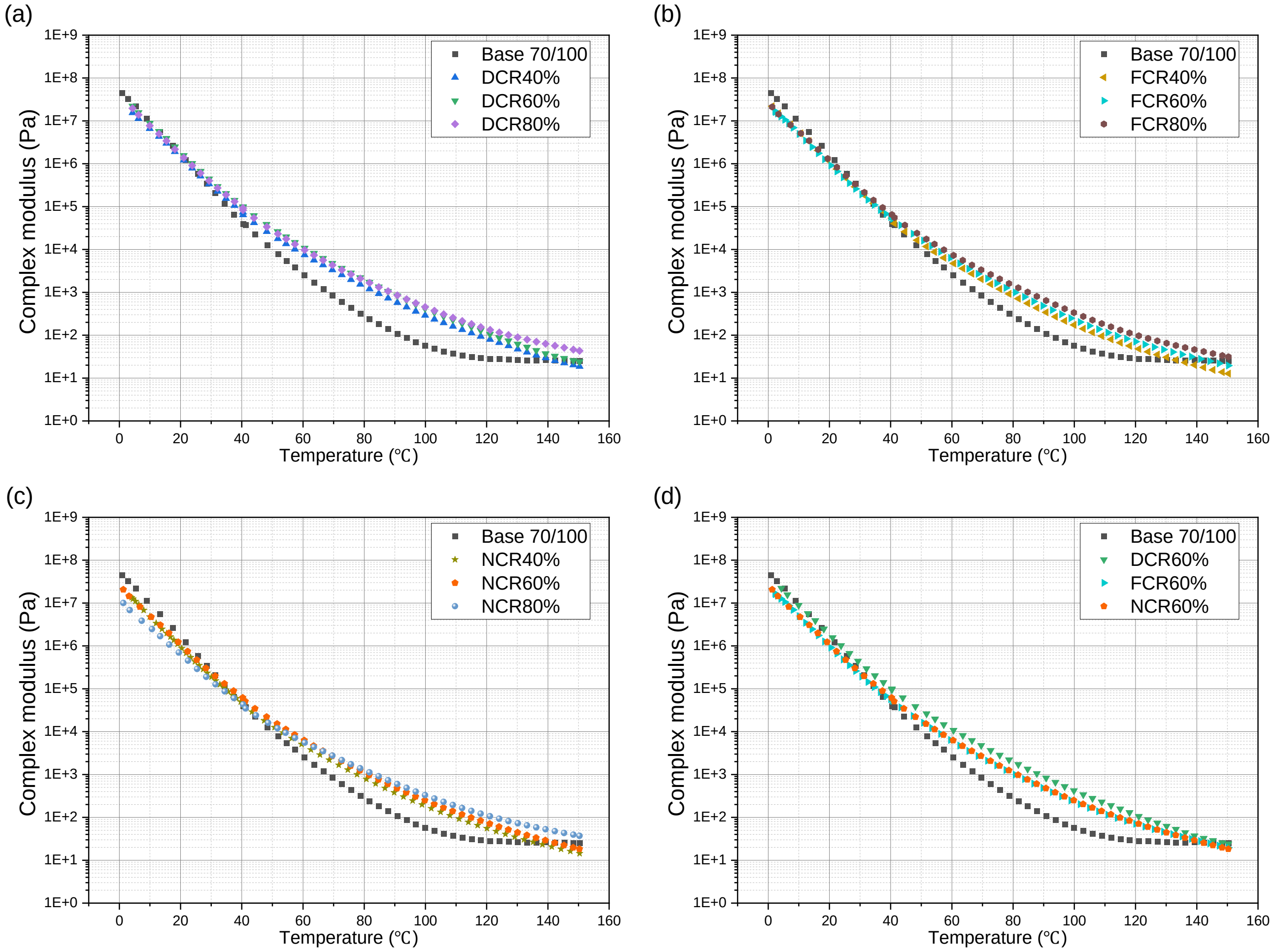


Fig. 3.8 Effect of temperature on G^* parameter

As seen in Fig. 3.8, for all specimens, G^* reduced by increasing the temperature. The complex shear modulus is a measure of total resistance of a material to deform when exposed to repeated pulses of shear stress[102]. Observations indicate a progressive increase in the complex shear modulus with rising rubber replacement ratios. At high temperatures (ranging from 40 to 140 °C), RAB exhibits a higher complex shear modulus than the base bitumen, suggesting that RAB retains rutting resistance under high-temperature conditions.

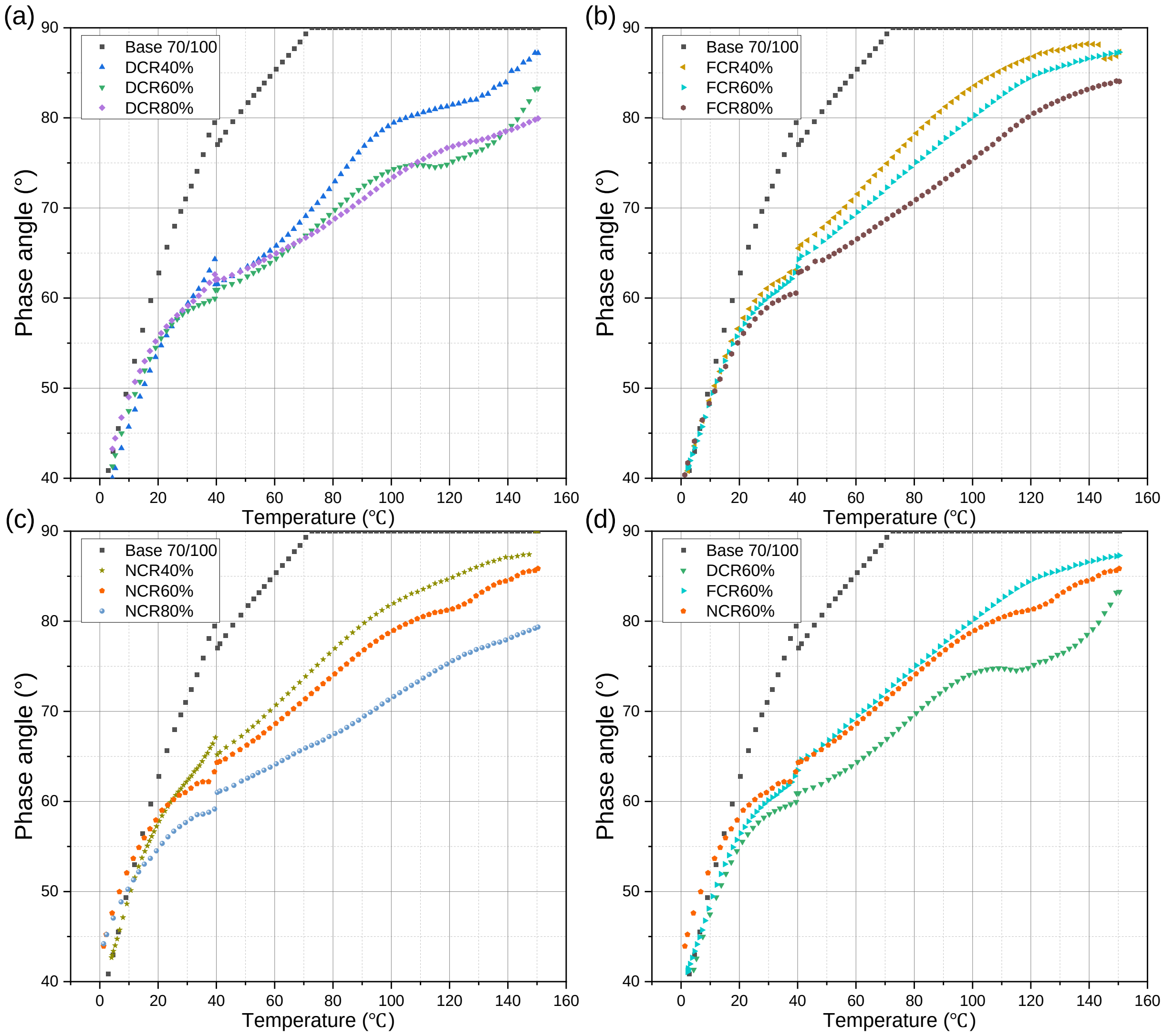


Fig. 3.9 Effect of temperature on δ parameterEffect of temperature on δ parameter

Fig. 3.9 further demonstrates that the phase angle decrease as the rubber replacement ratio increases, reflecting changes in the viscoelastic properties of RAB. The phase angle is an indicator of the relative amounts of the recoverable and non-recoverable deformations[102]. The phase angle serves as a critical indicator of material behavior, with lower values approaching zero signifying a more elastic response, while larger phase angle values nearing 90 degrees indicate a more viscous behavior. Notably, the base bitumen reaches a phase angle of 90 degrees around 70 °C, indicating the complete loss of elasticity at this temperature. In contrast, RAB demonstrates phase angles below 90 degrees even at very high temperatures, signifying the role of rubber in maintaining elasticity within the high-temperature range. Consequently, the rubber component effectively ensures that the alternative binder retains partial elasticity at high temperatures, contributing to its unique viscoelastic behavior.

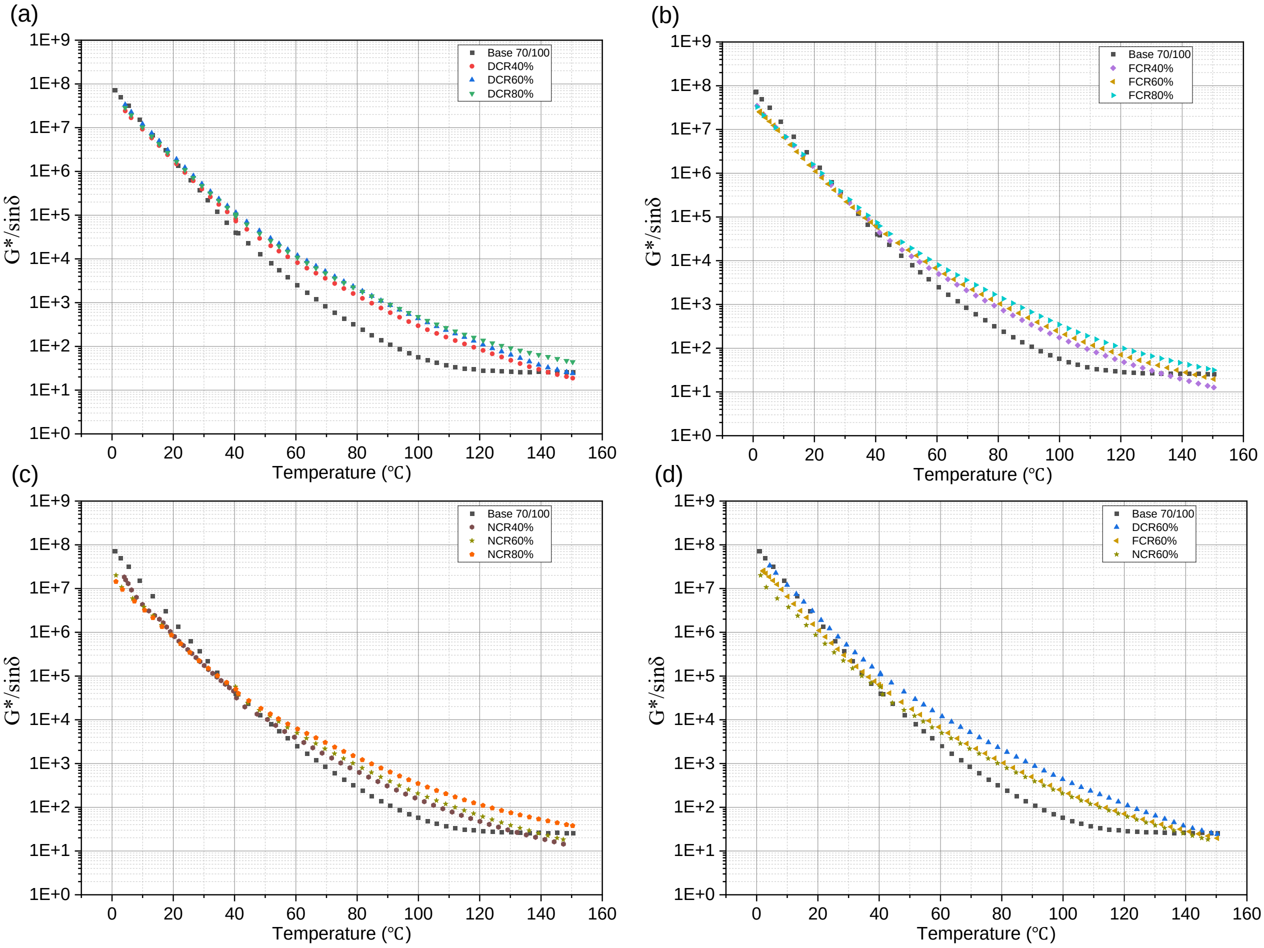


Fig. 3.10 Effect of temperature on G*/sinδ parameter

The asphalt binder with higher G* and lower phase angle will be more rut resistance[102]. Effect of temperature on G*/sinδ is shown in Fig. 3.10. The Superpave parameter G*/sinδ has been designated as the stiffness indicator for assessing the rutting resistance of binders. Rutting, characterized by the gradual accumulation of permanent deformations within each layer of a pavement structure under repetitive loading, is a critical concern. A higher G*/sinδ value is indicative of superior rutting performance in binders. As depicted in Fig.3.7, RAB consistently exhibits commendable rutting resistance at elevated temperatures. However, its rutting resistance is deteriorated compared to base bitumen under lower temperature conditions. Furthermore, it is noteworthy that both NCR and FCR exhibit weaker rutting resistance performance in comparison to DCR, emphasizing the superior rutting resistance capabilities of the latter.

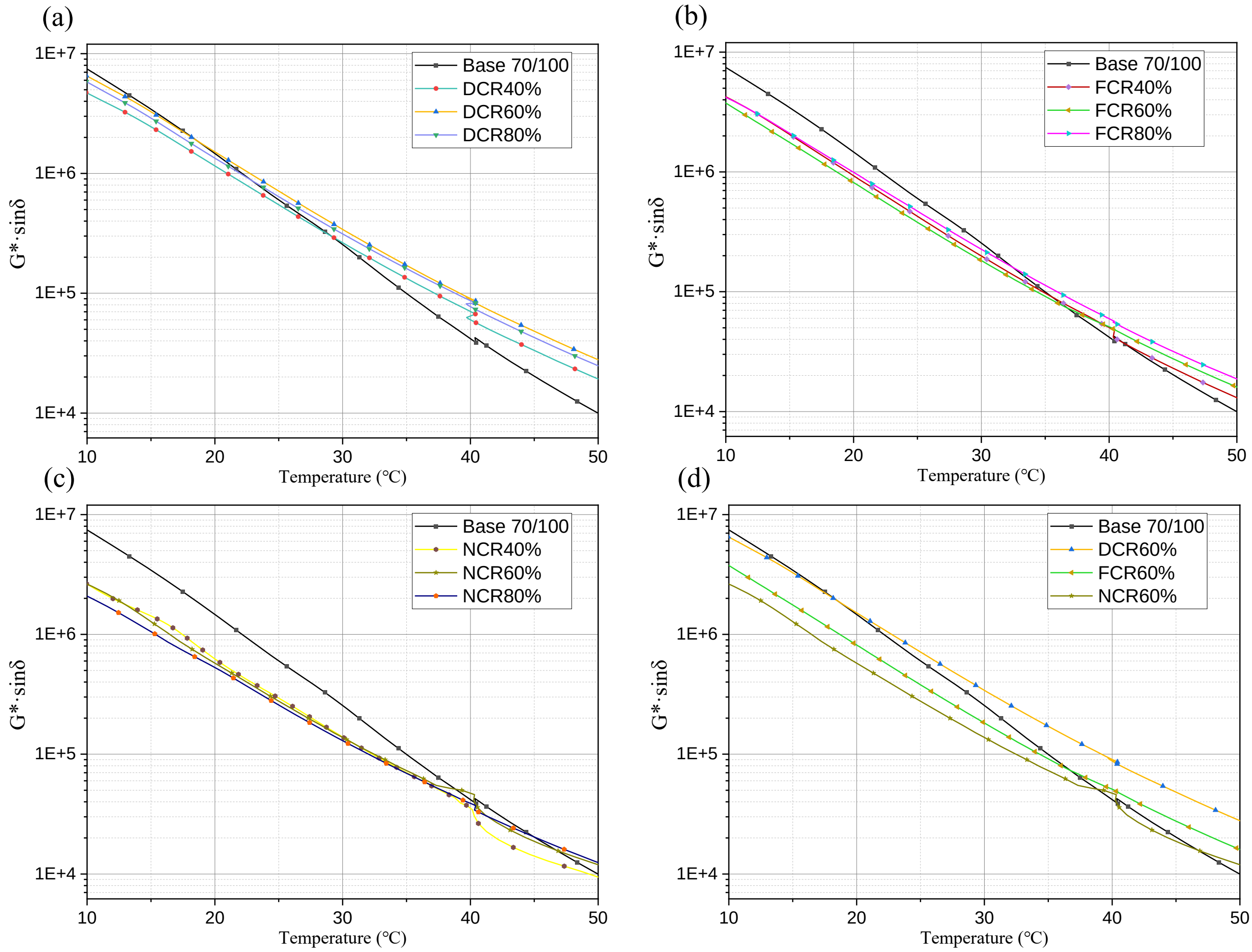


Fig. 3.11 Effect of temperature on $G^*\cdot\sin\delta$ parameter

Effect of temperature on $G^*\cdot\sin\delta$ has been shown in Fig. 3.11. Fatigue damage within asphalt pavements is a multifaceted phenomenon arising from repetitive bending, leading to micro-damage within the asphalt pavement structure. This micro-damage represents a dynamic interplay between micro-crack formation and healing processes, ultimately resulting in a reduction in the stiffness of the asphalt pavement. Consequently, this degradation compromises the load-bearing capacity and resistance to further damage. Over time, these micro-cracks coalesce into macro-cracks, which become visible within the wheel path. The obtained results underscore that, for RAB, $G^* \cdot sin\delta$ exhibits variation across different rubber types. In the case of the NCR alternative binder, $G^*\cdot\sin\delta$ decreases with increasing rubber content within the temperature range of 25-40 °C, consistently remaining lower than that of the base bitumen. Notably, within this temperature interval, the addition of NCR appears to enhance fatigue resistance. Conversely, for the FCR alternative binder, $G^*\cdot\sin\delta$ is lower than that of the base bitumen between 25 and 35 °C, while at higher temperatures, it overs that of the base bitumen. These findings suggest that the addition of rubber content, especially at higher temperatures, adversely affects the fatigue behavior of the FCR alternative binder. In contrast, DCR demonstrates a higher $G^*\cdot\sin\delta$ than the base bitumen, potentially contributing to inferior fatigue performance in this alternative binder.

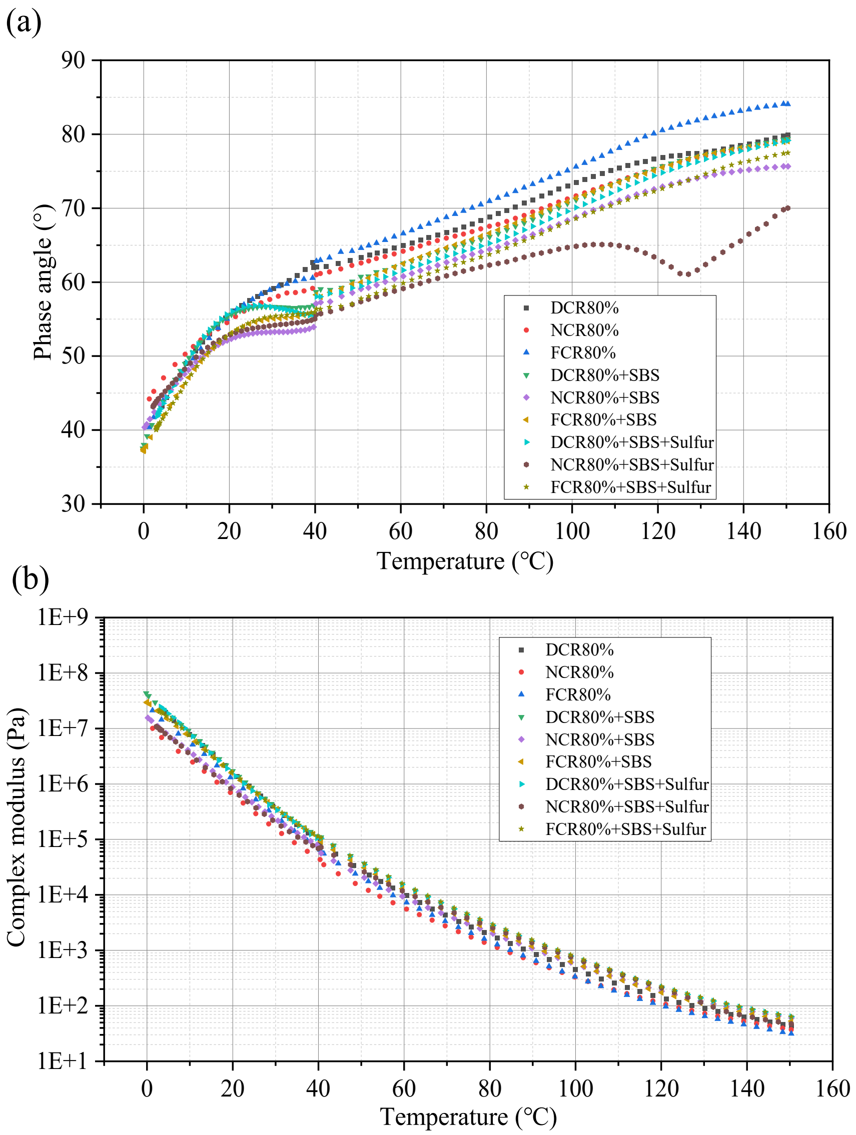


Fig. 3.12 Effect of temperature on rheological parameter of Modified RAB

Furthermore, Fig. 3.12 presents the rheological parameters of the modified RAB. It is evident that following the incorporation of SBS, the phase angle of the modified RAB decreases in comparison to the previous state, indicative of enhanced elastic characteristics.

3.4.2. Frequency sweep

The temperature of 30℃ is chosen as the reference temperature. Fig. 3.13 shows that the complex modulus of the RAB increased as the loading frequency increased. And with the increase of the rubber content in the bitumen, the complex modulus of the RAB increase, which is the same as the conclusion obtained in the previous temperature sweep experiments.

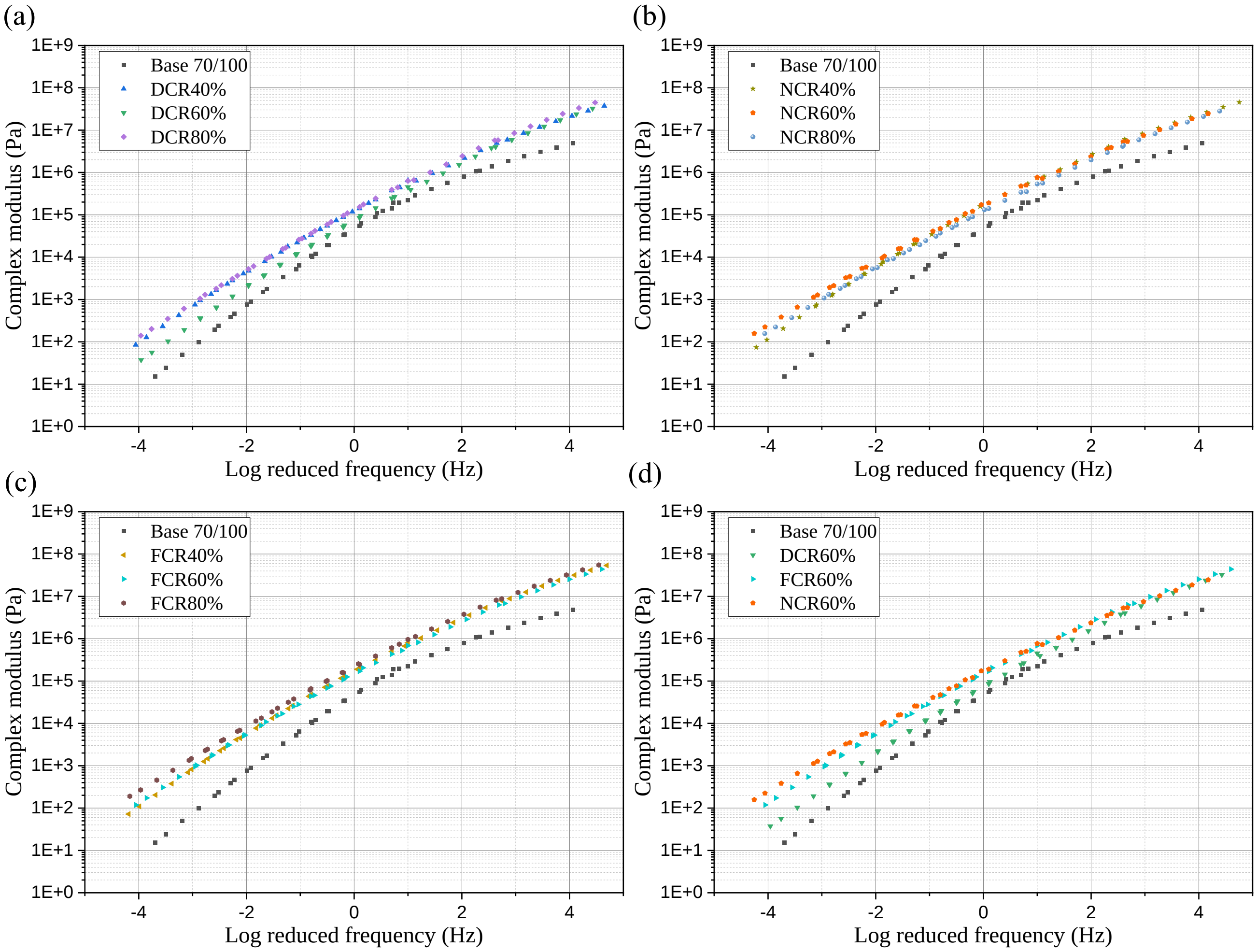


Fig. 3.13 Complex modulus master curve at 30℃

It can be seen that there is a significant increase in the complex modulus of the RAB in the high-frequency region, implying that the RAB is stiffer at low temperatures, which may lead to crack resistance problems. At this point, the black space diagram is quoted to assess the crack resistance. Black space diagram is a graph of complex shear modulus, versus the phase angle, δ without the requirement to perform the Time-temperature superposition principle. It is convenient to use it to provide ‘fingerprints’ for different types of bitumen. Anderson and his team[103] developed a method to fit the master curve of G^* and phase angle with an important parameter R-value, shown in the following equation.

$$R = \frac{(log2) \times log\frac{G^*(\omega)}{G_g}}{\log\left(1-\frac{\delta(\omega)}{90}\right)} \tag{3-1}$$

Where $G^*(\omega)$ is complex modulus at frequency ω, G_g is glassy modulus and assumed to be 1E+09 Pa, $\delta(\omega)$ is the phase angle at frequency ω. With the aid of the regions divided by the R=1, R=2, and R=3 curves, it is interesting to view the results of modification on a Black space diagram about potential damage, as shown in Fig. 3.14.

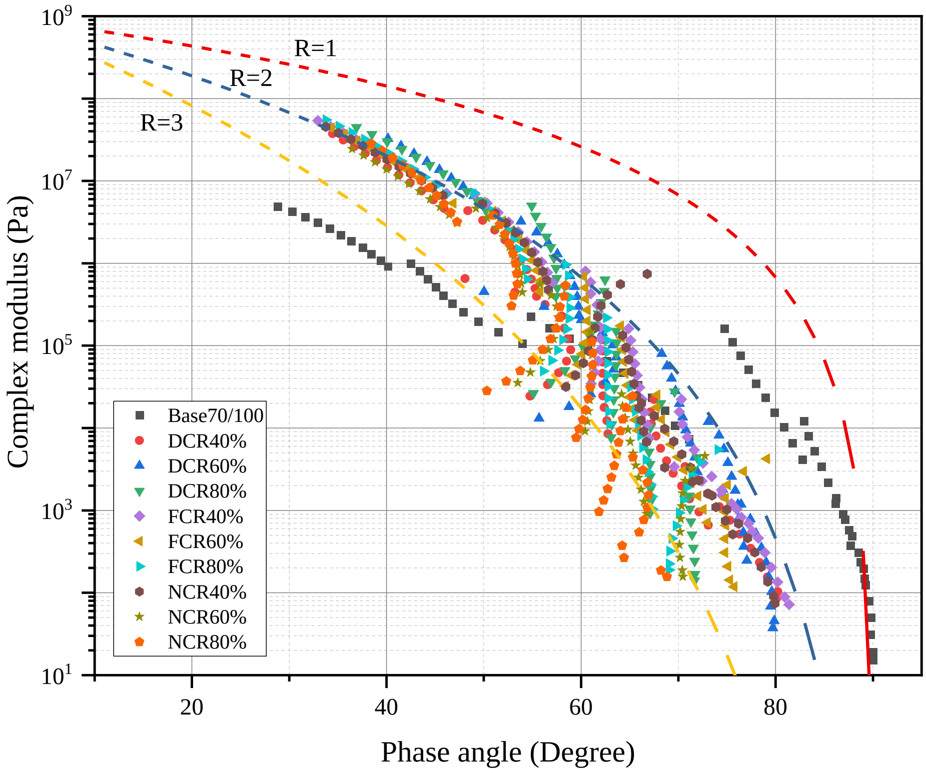


Fig. 3.14 Black space diagram of rheological data for each sample

Based upon ranges in R-value, Higher R-values mean that cracking is more likely to occur, i.e. the area in the lower-left corner of the graph represents the possibility of cracking and the area in the upper right corner represents no cracking. As can be seen in Figure 3.11, the overall shift in the curve after the addition of the rubber means that RAB is closer to the curve for lower R values than base bitumen. This alignment, in turn, indicates that RAB is less prone to cracking. Furthermore, this difference is more pronounced in the lower phase angle region, i.e. in the low-temperature section, indicating that the addition of rubber considerably improves the low-temperature cracking resistance of the bitumen. In contrast, for the groups where rubber were added, all curves almost at same region of R-value, indicating that the difference in the effect of rubber type and content on this properties was not significantly noticeable.

3.4.3. Multiple stress creep recovery (MSCR)

Fig. 3.15, Fig. 3.16, and Fig. 3.17 display the MSCR test results of the RAB and modified RAB at shear stress level of 3.2 kPa at temperature 64 ℃ and 70 ℃, respectively. The test results overall reflected the visco-elastic–plastic property of asphalt binders. After the removal of the creep load, the elastic strain was recovered immediately, while some viscous strain was recovered gradually. The study conducted by FHWA proposed J_{nr} and percent recovery as an indexes of high temperature stability and elasticity. And J_{nrdiff} means the percent difference in nonrecoverable creep compliance between 0.1 kPa and 3.2 kPa.

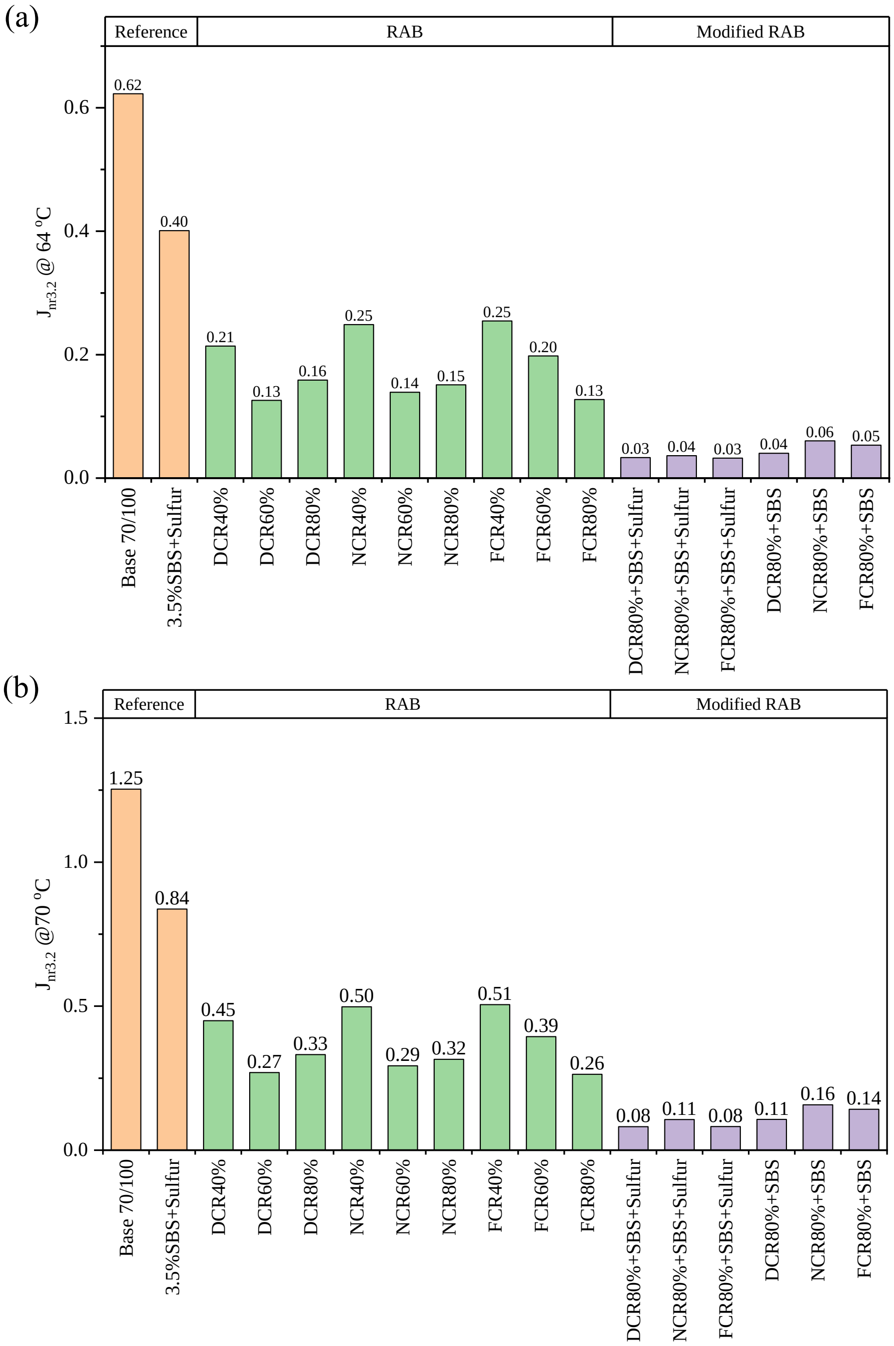


Fig. 3.15 J_{nr} at shear stress level of 3.2 kPa at temperature (a)64℃ and (b)70℃

Higher permanent deformation will be revealed by higher J_{nr} value. As can be observed, the J_{nr} of all RABs is less than base bitumen at two different temperatures. In terms of the three different rubber types, it becomes apparent that the values of J_{nr} of RAB, which is indicative of resistance to permanent deformation, remain quite similar at the same rubber replacement ratio. Particularly noteworthy is that for both NCR and DCR, the J_{nr} of RAB is minimized at a 60% substitution ratio, indicating that permanent deformation is minimized at this specific level of rubber addition. It's also evident that the J_{nr} values for RAB are lower than those for 3.5% SBS modified bitumen, suggesting superior resistance to permanent deformation in RAB. Furthermore, the combination of rubber and SBS results in a significantly lower J_{nr} for RAB, with the combination effect of these components exhibiting more favorable outcomes than the mere stacking of individual elements. This underscores the positive impact of rubber substitution in bitumen on permanent deformation resistance, with an even more pronounced effect when combined with SBS, signifying a synergistic enhancement in performance.

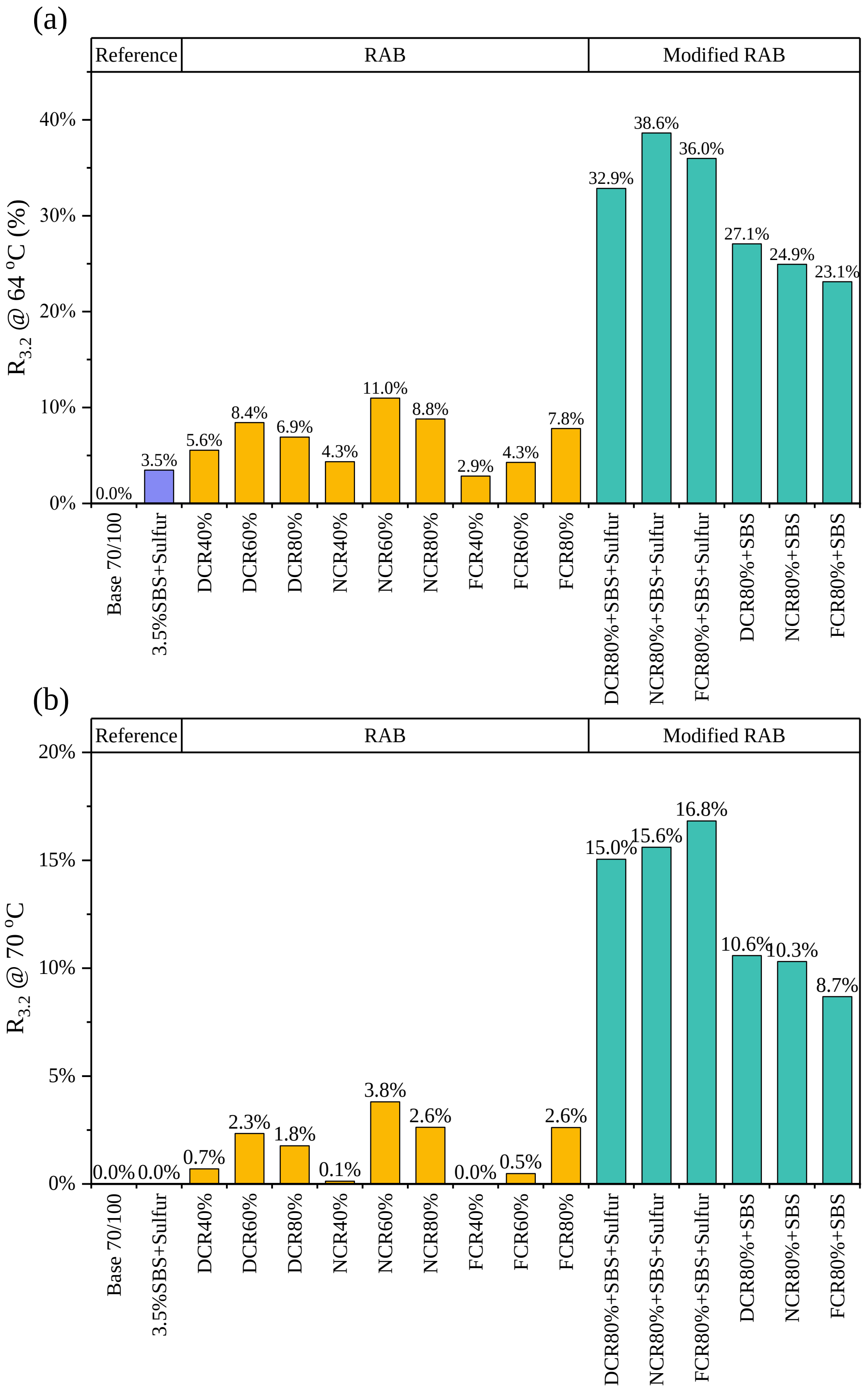


Fig. 3.16 Percent recovery at shear stress level of 3.2 kPa at temperature (a)64℃ and (b)70℃

Percent recovery provides an indication about the delayed elastic response of the asphalt binders. The analysis of percent recovery, as depicted in Fig. 3.16, reveals that RAB exhibits inherent elasticity. Furthermore, consistent with the findings of the prior temperature sweep analysis, the base bitumen loses its elasticity at 64°C, transitioning solely to a viscous state. Moreover, in comparison to SBS modified bitumen, RAB maintains a degree of elasticity even at higher temperatures, suggesting that the elasticity of RAB is more resilient to high-temperature conditions. Within the scope of modified RAB, it becomes evident that the addition of sulfur yields improved elasticity performance, underscoring sulfur's influence on enhancing the dispersion of the polymer network. Notably, the percent recovery of modified RAB better than that of the corresponding unmodified RAB by a factor of four and exceeds that of 3.5% SBS modified bitumen by tenfold. This outcome strongly implies the formation of a polymer network between rubber and SBS within the modified RAB. Additionally, upon contrasting the performance of FCR in modified RAB with the other two rubber types, the differences in results appear relatively insignificant, indicating that the catalyst employed in FCR has limited effect on facilitating crosslinking with SBS.

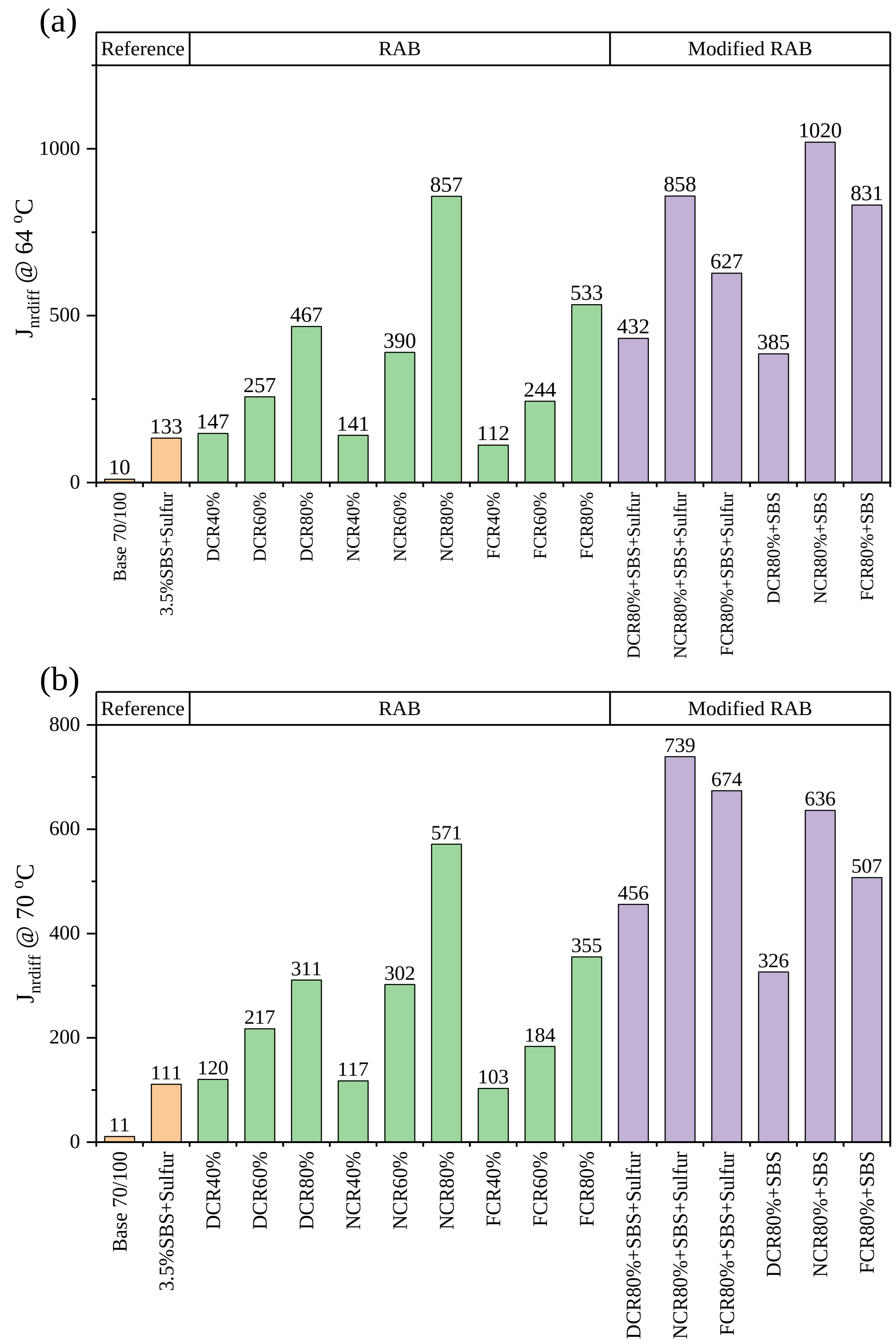


Fig. 3.17 J_{nrdiff} at shear stress level of 3.2 kPa at temperature (a)64℃ and (b)70℃

However, regarding J_{nrdiff}, the addition of rubber led to an increase in stress sensitivity and the result was the exact opposite of the improvement in rutting resistance, i.e. the stress sensitivity of the alternative binder increased significantly with increasing rubber content. At shear stress level of 0.1 and 3.2kPa, it was observed that a higher creep loading level also resulted in a higher J_{nr} . This was mainly due to the higher permanent deformation and lower percent recovery when the creep loading level increases. This may be caused because although the cross-linking of rubber molecules creates a network that enhances the stiffness of the material, yet it is not able to resist larger strain amplitudes, which leads to an increase in the gap in its performance in response to changes in stress level.

3.4.4. Linear Amplitude sweep (LAS)

The shear stress response as the increased strain for RAB and modified RAB at 20℃ is shown in Fig. 3.18. In the initial phase, there is a linear relationship between shear stress and the increment in loading strain, reflecting a gradual rise in the material's response to applied stress. As the strain amplitude continues to increase, this rate of shear stress augmentation decelerates, marking the transition of the binders into nonlinear regions. It is noteworthy that each binder type attains its peak shear stress at distinct strain amplitudes. Subsequently, following the attainment of the peak shear stress, the material experiences a continuous reduction in shear stress as the strain level further intensifies. This decline signifies the initiation of significant damage within the material, characterized by a loss of structural integrity and mechanical strength[104]. It can be observed that the addition of rubber resulted in increased failure strains and lower maximum stresses in comparison with the base bitumen. Nonetheless, it is noteworthy that at identical replacement ratios, distinct rubber types can yield varying patterns of influence. Furthermore, in the context of modified RAB, the increasement of stiffness resulting from the presence of SBS exerts a heightened shear stress effect, with the introduction of sulfur contributing to the formation of a stronger polymer network. This enhanced network formation amplifies the impact on shear stress, further underscoring the complex interactions between rubber, SBS and sulfur in the modified RAB composition.

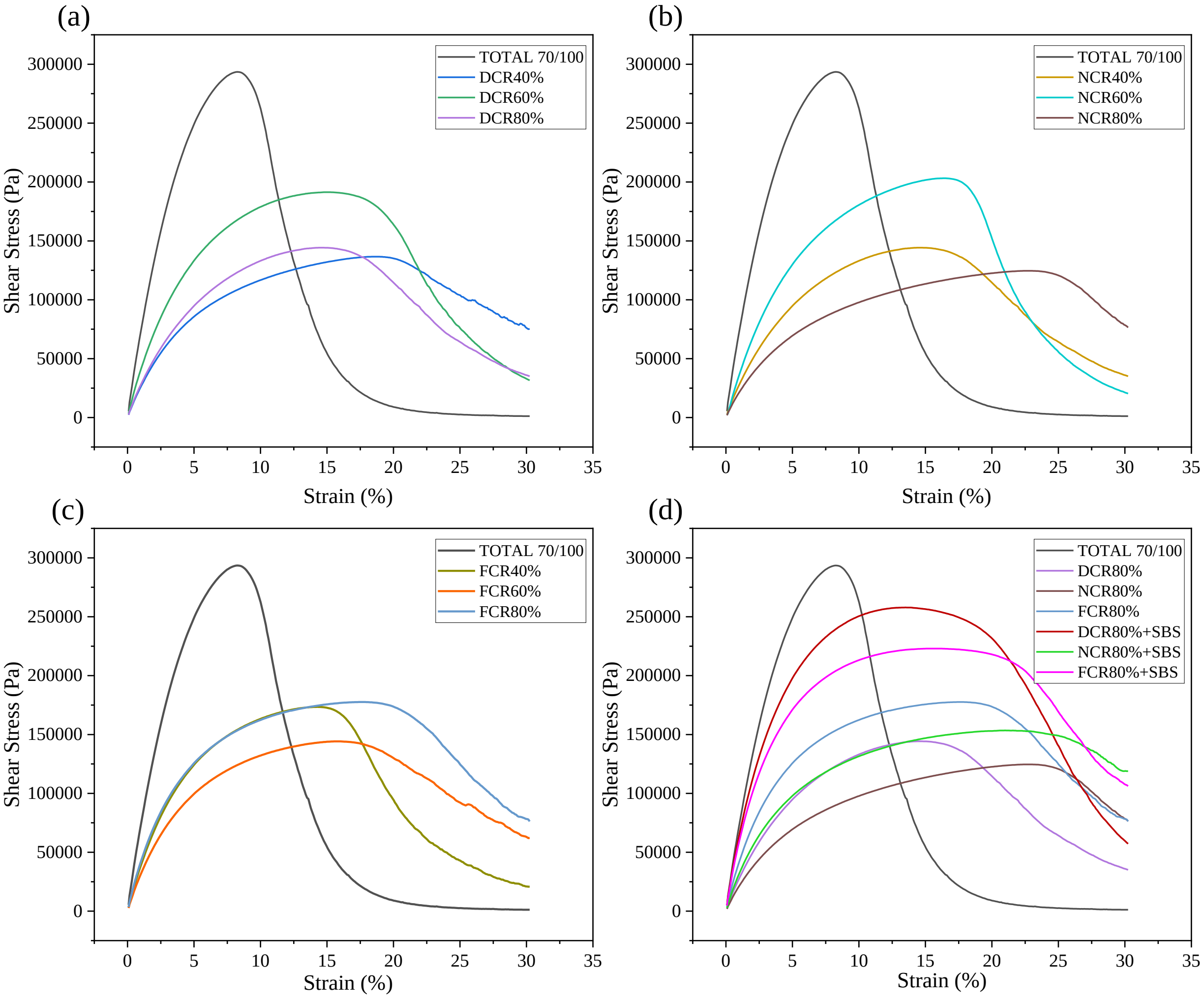


Fig. 3.18 Stress-stain curves from LAS test for (a)DCR, (b)NCR, (c)FCR, and (d)modified RAB

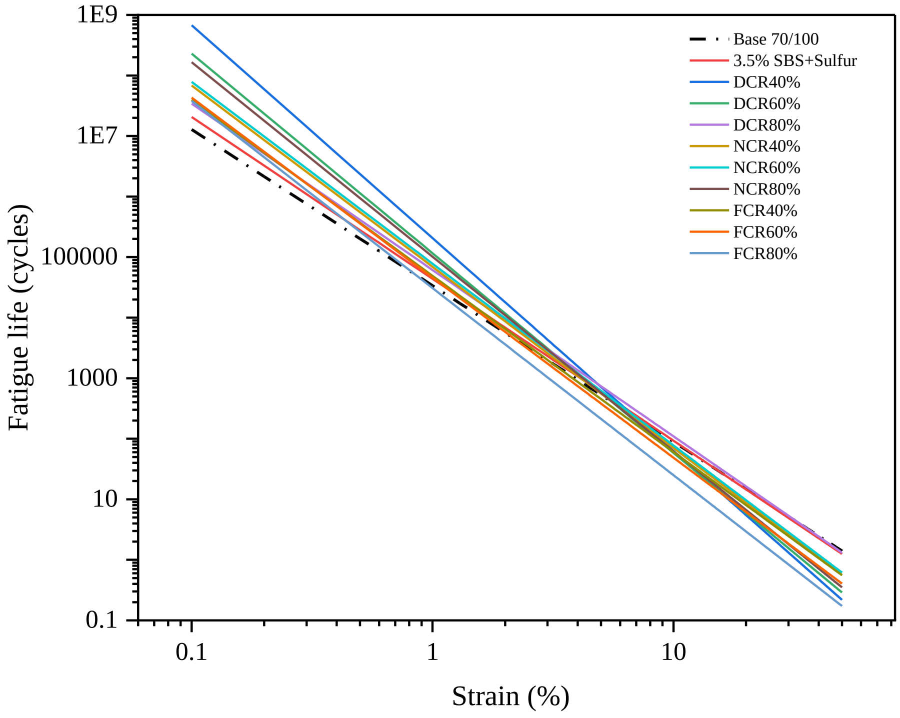


Fig. 3.19 Fatigue life at different strain level

Fig. 3.19 provides a depiction of the fatigue life at various strain levels. Broadly, it is observed that RAB exhibits an extended fatigue life, particularly at lower strain amplitudes. However, as the strain amplitude increases, the fatigue life of RAB experiences a more substantial reduction compared to that of the base bitumen, ultimately falling below that of conventional binders when the strain amplitudes exceed approximately 5-7%. Remarkably, DCR stands out with superior fatigue life when compared to the other RAB variants.

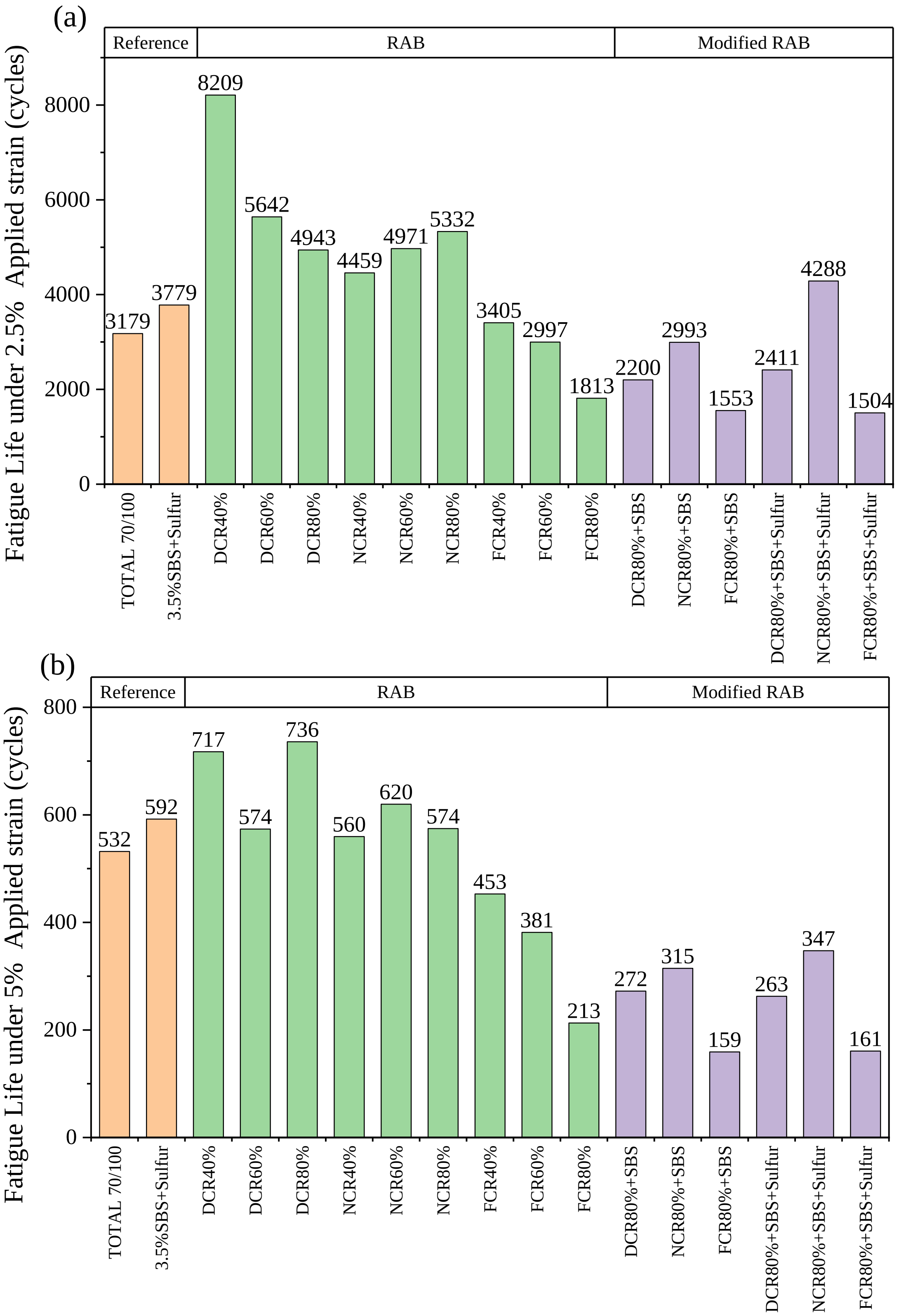


Fig. 3.20 Predicted fatigue lives at (a) 2.5% and (b)5% strain amplitudes

To facilitate a more detailed comparison, the fatigue life at strain levels of 2.5% and 5% have been extracted from the fatigue life curves and are presented in Fig. 3.20. Under a 2.5% applied strain, both DCR and the NCR alternative binder demonstrate significantly improved fatigue life compared to the base bitumen and even outperform SBS modified bitumen. Interestingly, for DCR, the fatigue life declines as the quantity of added rubber increases, whereas NCR exhibits the opposite trend, with improved fatigue life corresponding to higher rubber content. Conversely, the introduction of FCR results in decreased fatigue life, and this trend worsens with increasing rubber content. Furthermore, the combination of SBS with rubber in SBS modified RAB leads to compromised fatigue performance. When the strain level is elevated to 5%, the fatigue life of DCR and the NCR alternative binder does not exhibit substantial improvement compared to the base bitumen. In the case of FCR, the situation is notably worse. Moreover, for modified RAB, the fatigue life deteriorates further at elevated stress levels, indicating the intricate relationship between strain levels, rubber type, and fatigue behavior in these asphalt binders.

3.4.5. Relaxation

Considering the continuous traffic loading conditions experienced by pavement, it is imperative that bitumen exhibits a relatively short relaxation time to prevent the accumulation of stress within the pavement structure. Fig. 3.21 illustrates that both RAB and modified RAB variants consistently exhibit shorter times required for stress to recede to 50% compared to the base bitumen and SBS modified bitumen. The performance of the FCR alternative binder, while relatively modest, still surpasses that of the base bitumen. In the context of modified RAB, it is notable that the relaxation time is slightly extended in comparison to unmodified RAB, although this difference is not particularly pronounced when considering the time required for stress to recede to 50%.

However, when assessing the time needed for stress to recede to 10%, as shown in Fig. 3.21b, a distinct trend emerges: both the DCR and NCR alternative binders exhibit notably accelerated residual stress release times, approximately half that of the base bitumen. In contrast, the FCR alternative binder needs a longer duration than the base bitumen, potentially attributable to the influence of the catalyst present in FCR, which appears to hinder the process of residual stress release. For modified RAB, there is an overall increase in relaxation time relative to unmodified RAB. Nevertheless, it is noteworthy that, in the case of FCR, the incorporation of SBS exerts a positive influence on relaxation performance, further emphasizing the multifaceted impact of various additives on relaxation behavior. Overall, RAB exhibits better residual stress relaxation than base bitumen and SBS-modified bitumen, and also outperforms modified RAB. This observation underscores the advantageous relaxation behavior of RAB, rendering it a favorable choice for pavement applications subjected to dynamic and sustained traffic loading.

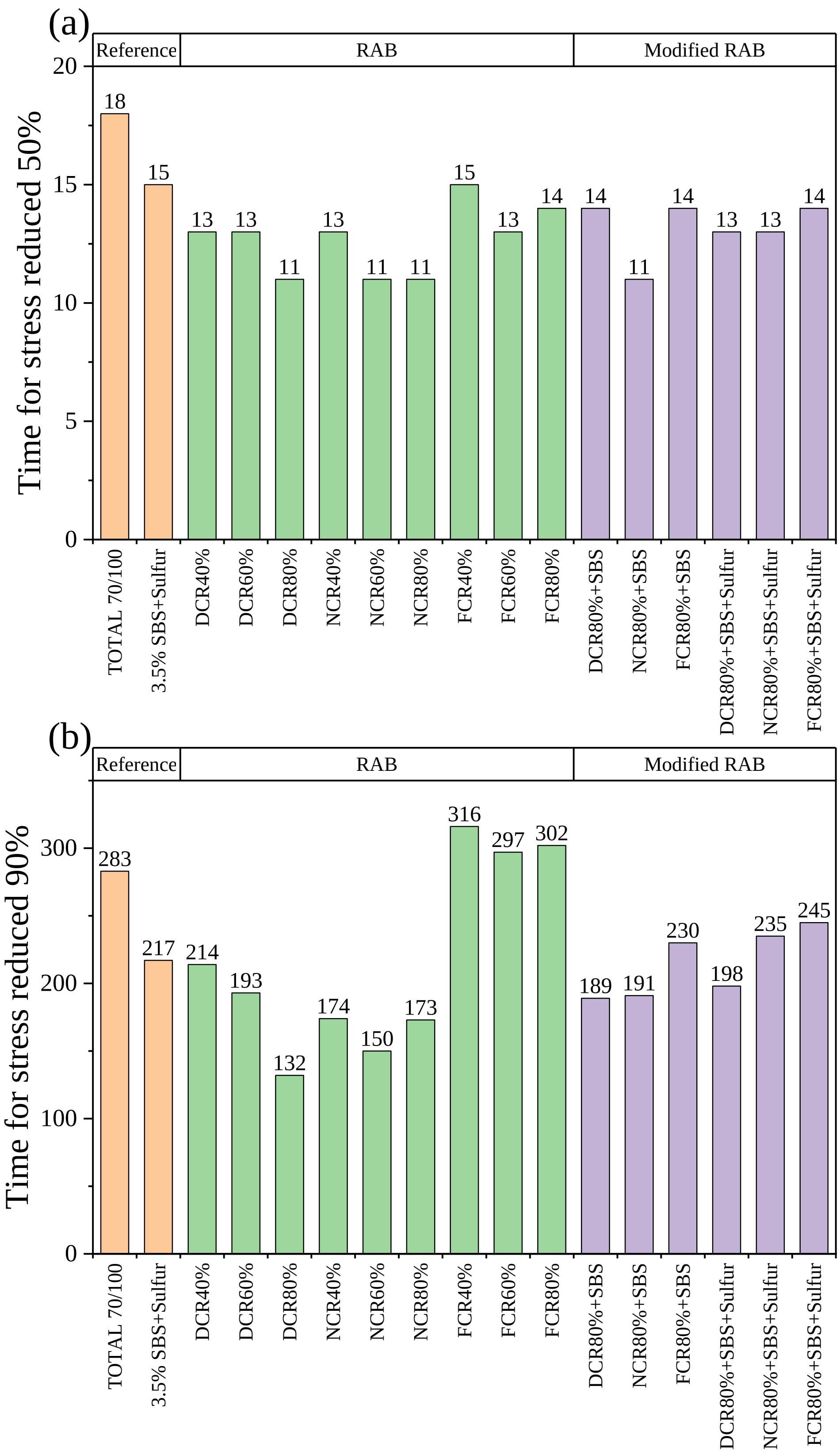


Fig. 3.21 Relaxation time required for the stress to reduce (a) 50% and (b)90%

3.5. RANKING

On the basis of the tests discussed earlier, a simple ranking method is introduced to select the most applicable rubber replacement ratio and type to be used in RAB. First, the specimen studied were ranked for each test. The highest ranked material receives a ranking value (RV) of 17 point and the last material is ranked at 1 point. The scores were then converted to a ten-point scale, i.e., multiplied by 10 on a scale of 17 to obtain a final score. Additionally, for workability ranking, the specimen that exceed the requirement of viscosity can be considered impractical pavement construction materials. Therefore, such materials are ranked as 0 points in this regard. Finally, the RVs for each binder were summed up to give the Total Ranking Value (TRV) for that material. The RV and TRV results for RAB and the reference bitumen are shown in Table 3.1.

Table 3.1 Ranking values of RAB and reference bitumen

	Workability	**High Temperature Properties**		**Stress sensitivity**	**Fatigue Life**		**Low Temperature Properties**		**Total Ranking Point**
	Viscosity	**$R_{3.2}$**	**$J_{nr\ 3.2}$**	**$J_{nr\text{-}diff}$**	**Fatigue life-5% strain**	**Fatigue life-2.5% strain**	**Relaxation to 50% stress (T_{50})**	**Relaxation to 10% stress (T_{10})**	
	10.0	0.6	0.6	0.6	4.7	5.9	0.6	2.4	**25.3**
3.5% SBS+Sulfur	9.4	1.8	1.2	1.2	5.9	8.2	2.4	4.7	**34.7**
DCR40%	7.1	3.5	2.9	2.9	10.0	9.4	1.8	5.3	**42.9**
DCR60%	6.5	5.3	6.5	6.5	9.4	7.6	7.6	6.5	**55.9**
DCR80%	5.3	4.1	4.1	4.1	8.2	10.0	10.0	10.0	**55.9**
NCR40%	8.8	2.9	2.4	2.4	7.1	6.5	7.6	8.2	**45.9**
NCR60%	5.9	6.5	5.3	5.3	7.6	8.8	10.0	9.4	**58.8**
NCR80%	4.7	5.9	4.7	4.7	8.8	7.6	10.0	8.8	**55.3**
FCR40%	8.2	1.2	1.8	1.8	5.3	5.3	2.4	0.6	**26.5**
FCR60%	7.6	2.4	3.5	3.5	4.1	4.7	7.6	1.8	**35.3**
FCR80%	4.1	4.7	5.9	5.9	1.8	1.8	4.7	1.2	**30.0**
DCR80%+SBS	3.5	8.2	8.2	8.2	2.4	2.9	4.7	7.6	**45.9**
DCR80%+SBS+Sulfur	2.9	8.8	9.4	9.4	2.9	2.4	7.6	5.9	**49.4**
NCR80%+SBS	0.0	7.1	7.1	7.1	3.5	3.5	10.0	7.1	**45.3**
NCR80%+SBS+Sulfur	0.0	10.0	8.8	8.8	6.5	4.1	7.6	3.5	**49.4**

FCR80%+SBS	2.4	7.1	7.6	7.6	1.2	1.2	4.7	4.1	**35.9**
FCR80%+SBS+Sulfur	0.0	9.4	10.0	10.0	0.6	0.6	4.7	2.9	**38.2**

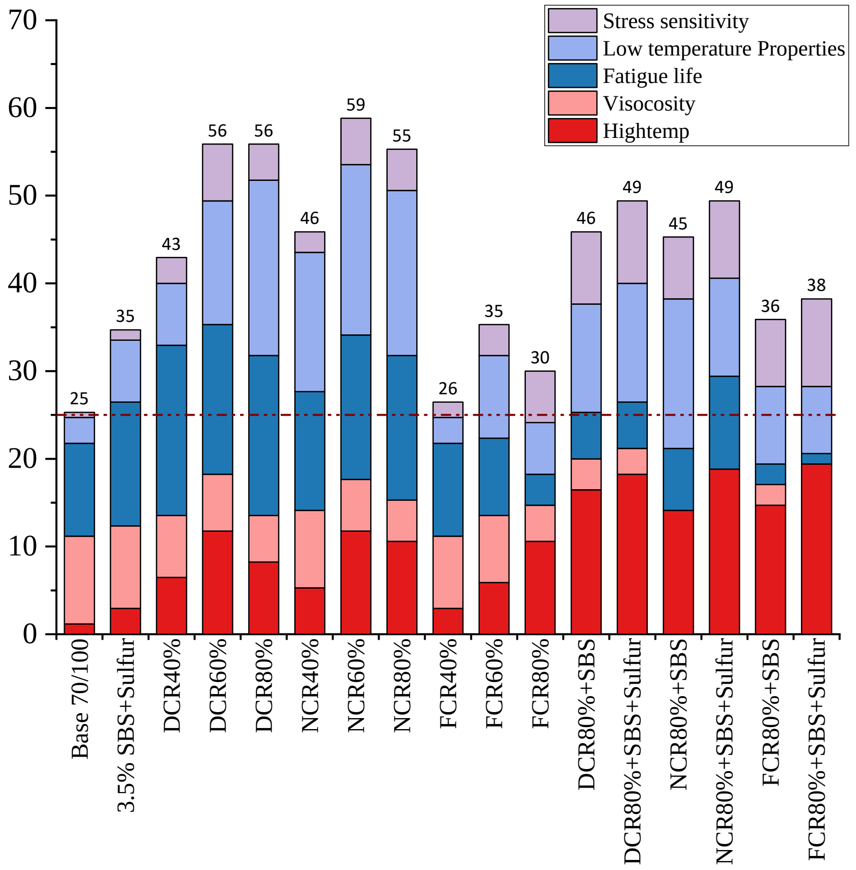


Fig. 3.22 Ranking values of RAB and reference bitumen

The test results have been categorized into low-temperature, high-temperature, workability, and fatigue performance assessments. As depicted in Fig. 3.22, RAB with a 60% replacement of NCR emerges as the optimal choice for overall performance. Furthermore, a noteworthy observation is that the majority of RAB perform better than both the base bitumen and SBS modified bitumen counterparts. This implies that rubber replacement for bitumen not only fails to compromise the base bitumen's performance but contributes positively to the overall performance. Conversely, the performance of the FCR alternative binder appears notably inferior compared to other RAB, and there even a gap in performance compared to that of the base bitumen. Considering the higher cost associated with FCR in comparison to common rubber, it becomes apparent that FCR may not be a cost-effective raw material for alternative binders. Additionally, it's worth noting that modified RAB does not exhibit performance better than that of unmodified RAB. Given the potential deterioration of performance due to the need for further processing to reduce viscosity, the cost of SBS, and its environmental impact, it raises questions about the competitiveness of modified RAB in practical applications.

In conclusion, a 60% substitution ratio appears to be the most practical choice, taking into account overall performance and the energy consumption involved in the preparation process. The following section will focus on conducting aging resistance assessments specifically for DCR60% and NCR60%.

3.6. AGING RESISTANCE

In this study, Thin Film Oven Test(TFOT) in accordance with E12607-2 was conducted to simulate short term aging of the bitumen. The long term aging of the bitumen was simulated using the Pressure Aging Vessel (PAV) in accordance with EN 14769[105]. The short term aging was conducted at 163 °C for 5h while long term aging was conducted at 100 °C for 80 h. The rheological performance of the virgin and the aged bitumen was assessed.

Fig. 3.23(a) shows the master curve of complex modulus of virgin and aged binders. Upon comparing the enclosed area within the complex modulus master curve change between virgin bitumen and aged bitumen, notable observations come to light. Firstly, the complex modulus of the base bitumen undergoes a significant increase following aging, signifying a hardening effect that could potentially lead to issues such as cracking. Furthermore, while the DCR alternative binder exhibits a smaller change compared to the base bitumen, it still registers a larger modulus value after aging. This outcome is partly attributed to the inherently larger complex modulus of DCR in its unaged state. Conversely, the complex modulus of NCR undergoes a notably lesser change after aging, as shown in Fig. 3.23(b). Moreover, given its initial modulus proximity to that of the base bitumen in its unaged state, the modulus remains within an acceptable range post-aging. These findings collectively suggest that the incorporation of NCR plays a beneficial role in mitigating the aging process.

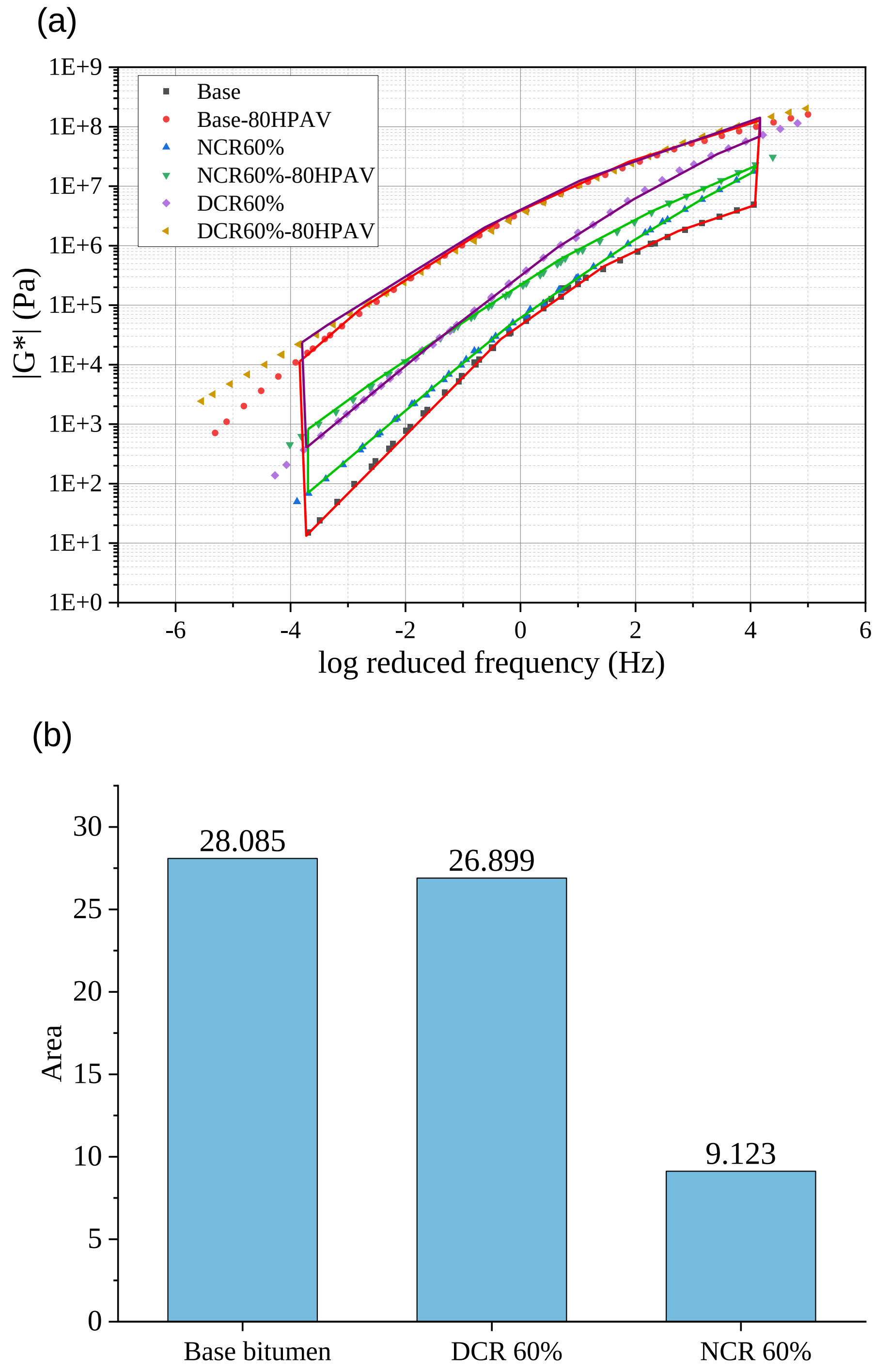


Fig. 3.23 (a) Complex modulus of Frequency sweep test (b) Area change of Complex modulus

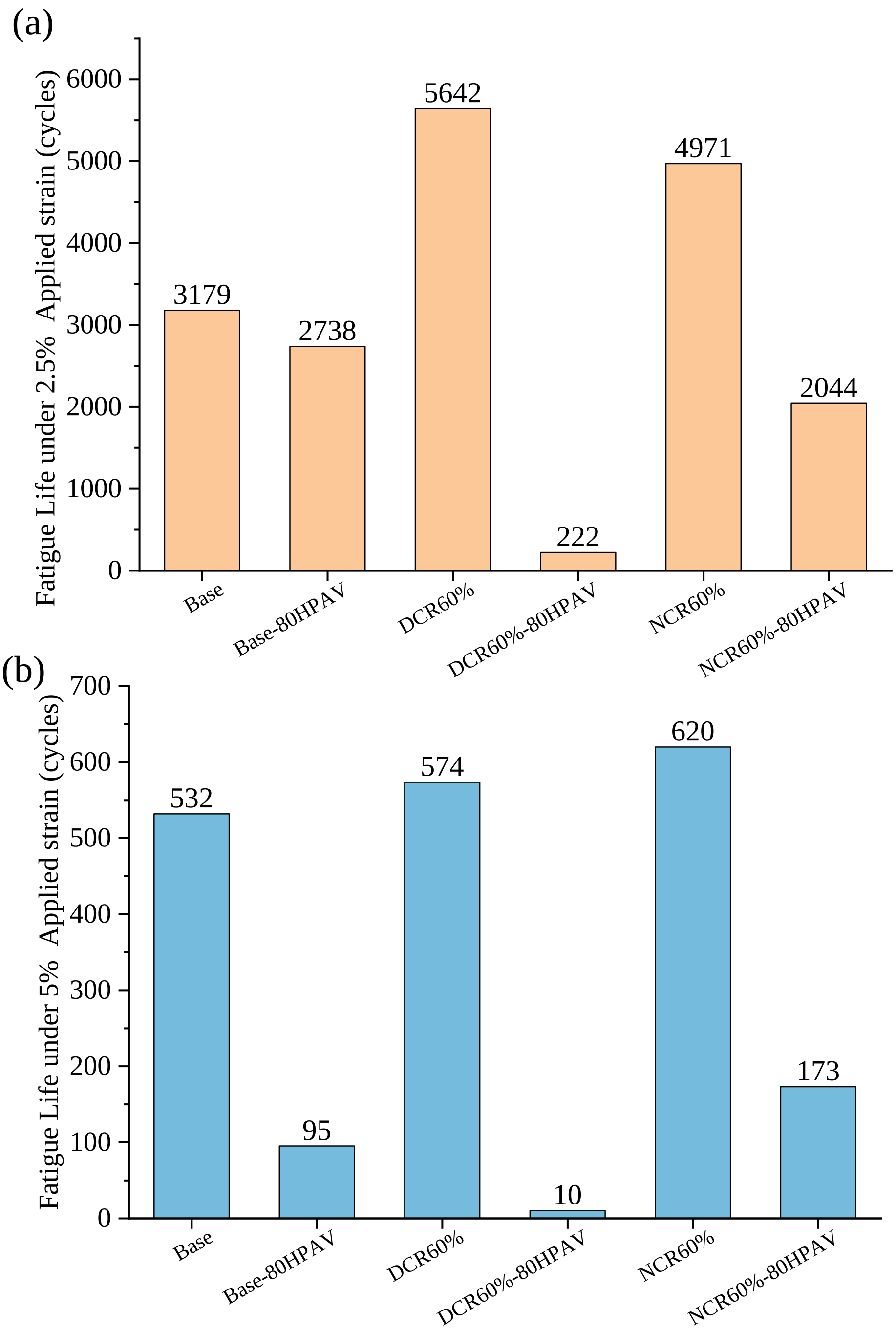


Fig. 3.24 Predicted fatigue lives at (a) 2.5% and (b)5% strain amplitudes

Fig. 3.24 shows the fatigue life of bitumen after aging. It is worth noting that the effect of aging on the fatigue life of DCR is fatal. The fatigue life of DCR with 2.5% strain amplitude applied has a difference of about 25 times before and after aging. In addition, the fatigue life is also reduced for the NCR, by about 60%. In contrast, the fatigue life of base bitumen decreases by only 10% with this applied strain. It is possible that segregation between the rubber and bitumen may have occurred after aging, which adversely affected the fatigue performance of the RAB. At 5% applied strain, the aging performance of base bitumen was worse than that of NCR, which may be due to the loss of ductility of bitumen after aging and brittle fracture under large strains, thus affecting the fatigue performance. However, the rubber of RAB still provides elasticity to RAB after aging, which makes its fatigue performance under large strains outperform that of base bitumen.

The MSCR test was employed in this work to characterize the high temperature performance of aged bitumen, the results of which are presented in Fig. 3.25. Percent recovery, which gives a measure of the relative value for the elastic response of the binder at different temperature, and J_{nr}, a value related to nonrecoverable creep compliance, are two critical parameters in the MSCR test to evaluate the high temperature performance of bitumen. For base bitumen, the aging process led to the decline in J_{nr} and the rise in R, which demonstrated that the high temperature performance was significantly improved based on both absolute and relative evaluation parameters. Furthermore, it is noteworthy that DCR exhibited a substantial improvement in high-temperature performance following aging. However, it's essential to emphasize that while NCR displayed a similar trend to other bitumen samples after aging, characterized by a decrease in J_{nr} and an increase in percent recovery, the extent of these changes was relatively minor. Both the relative change and the absolute value of these parameters were less pronounced compared to those of the base bitumen. This observation implies that the presence of NCR has had a mitigating effect on the high-temperature performance of bitumen after aging, which is regarded as the side-effects of the primitive softening effect by the dissolved rubber: the degradation of high temperature performance[106].

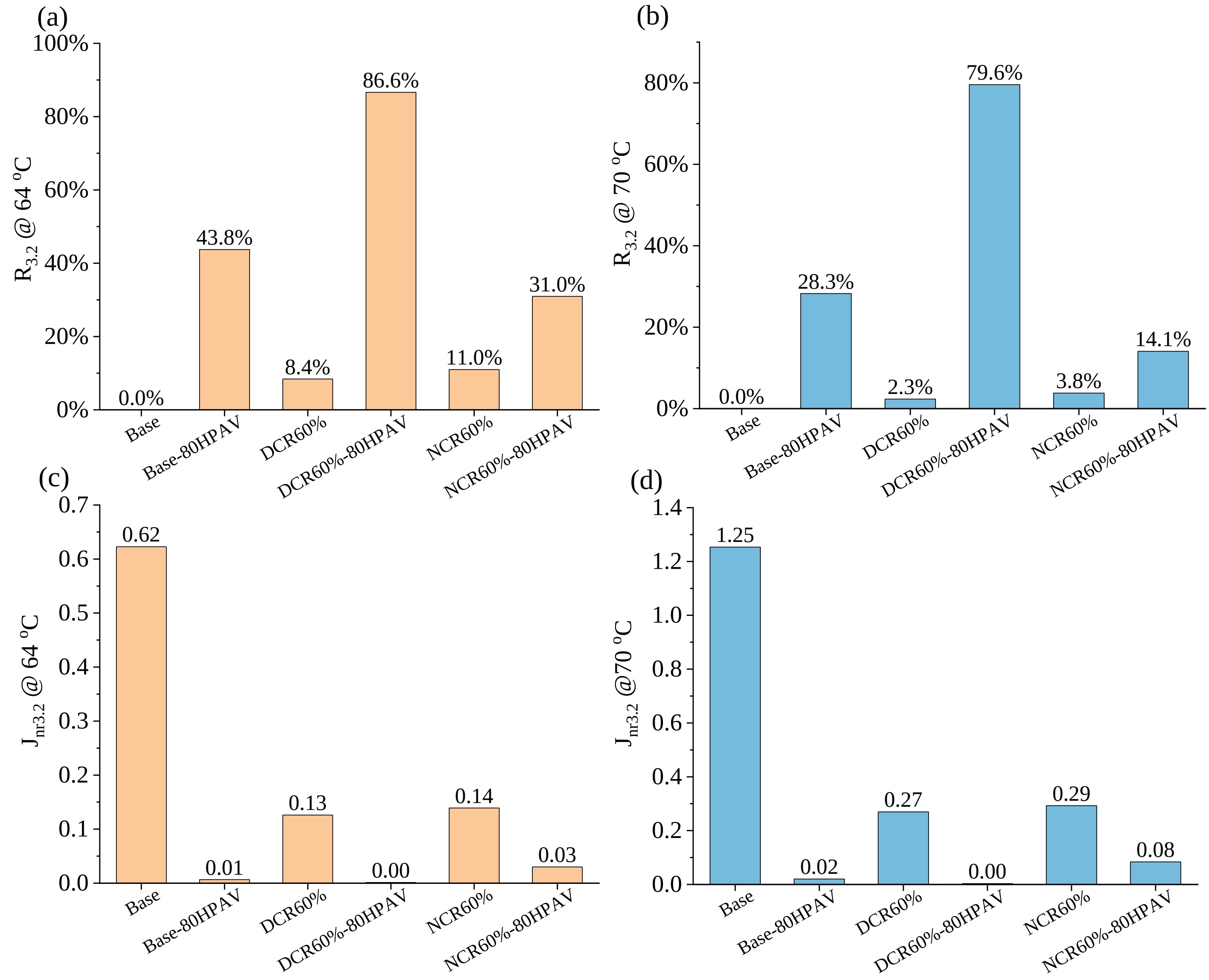


Fig. 3.25 Percent recovery at shear stress level of 3.2 kPa at temperature (a)64°C and (b)70°C
J_{nr} at shear stress level of 3.2 kPa at temperature (c)64°C and (d)70°C

Fig. 3.26 presents an insight into the low-temperature performance of aged bitumen, specifically its ability to dissipate residual stresses at low temperatures. When considering the duration required for stress to reduce to either 50% or 10% of the initial stress level, it becomes evident that base bitumen exhibits the longest residual stress application time post-aging. This observation strongly suggests that base bitumen loses its elasticity at low temperatures following the aging process. In the case of DCR, there is a noticeable degree of elastic degradation, but when compared to base bitumen, DCR serves as a protective element in preserving the bitumen's elasticity during aging. It is noteworthy, however, that NCR does not display significant alterations in the timing of residual stress release before and after aging, both in absolute and relative terms. This compelling finding implies that the substitution of bitumen with NCR allows RAB to maintain outstanding low-temperature performance throughout the aging process.

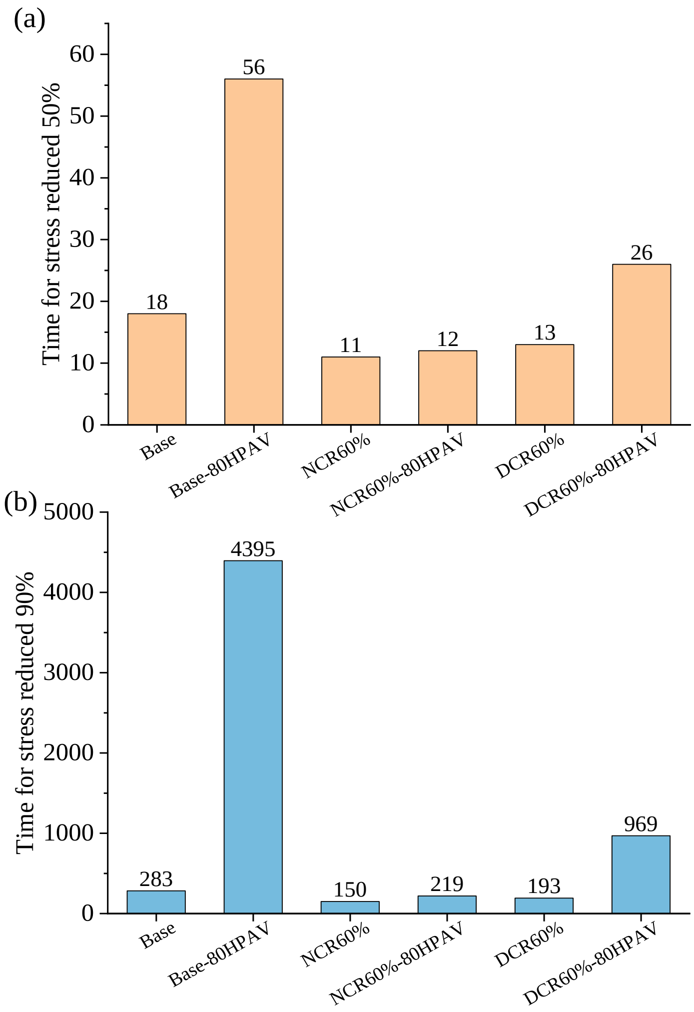


Fig. 3.26 Relaxation time required for the stress to reduce (a) 50% and (b)90%

Taking into account the aforementioned rheological performance of aged bitumen, it becomes evident that the anti-aging performance of Rubberized Asphalt Binders (RAB) is better than that of base bitumen, with NCR exhibiting particularly pronounced anti-aging properties. This underscores the effectiveness of NCR as a resilient and cost-efficient alternative. Given the considerably higher cost associated with DCR, along with the additional desulfurization treatment it necessitates, which consumes more energy and poses environmental concerns, it becomes clear that NCR stands out as the more suitable candidate for utilization as the raw material for RAB in subsequent research and practical applications. In the upcoming section, this study will delve into the verification of the storage stability of NCR60%, marking the further step in fully realizing the potential of NCR in real engineering applications.

3.7. STORAGE STABILITY

According to NEN-EN 13399, to determine the stability of RAB during storage at high temperature, stability test was performed in which in the beginning the aluminum tubes filled with bitumen were vertically paced at the temperature of 180℃ for 72h. After cooling, the aluminum coating is removed. The samples in the form of cylinders are divided into three equal parts. Upper and lower parts of cylinders are taken to determine their rheological properties. The results are shown in Fig.3.24 and Fig.3.25.

Fig. 3.27 provides a visual representation of the complex modulus and the phase angle in the temperature sweep test of virgin NCR as well as the specimen after undergoing the storage stability test. It is easy to see that the curves for both the complex modulus and phase angle closely align with one another. This convergence suggests that bitumen that has undergone significant rubber replacement does not segregate even after prolonged static storage at high temperatures. This result is in perfect agreement with the predictions of previous studies, emphasizing that the dissolution of rubber in asphalt after devulcanization and dissolution greatly improves the thermal stability of RAB[107].

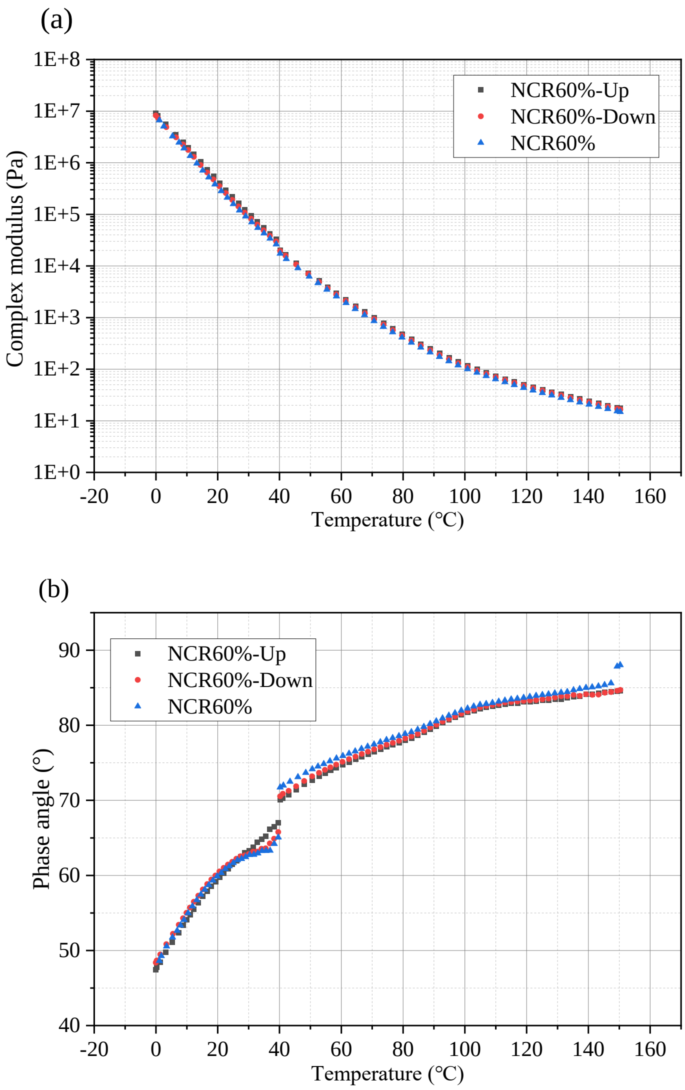


Fig. 3.27 Temperature sweep results of storage stability (a)complex modulus (b)phase angle

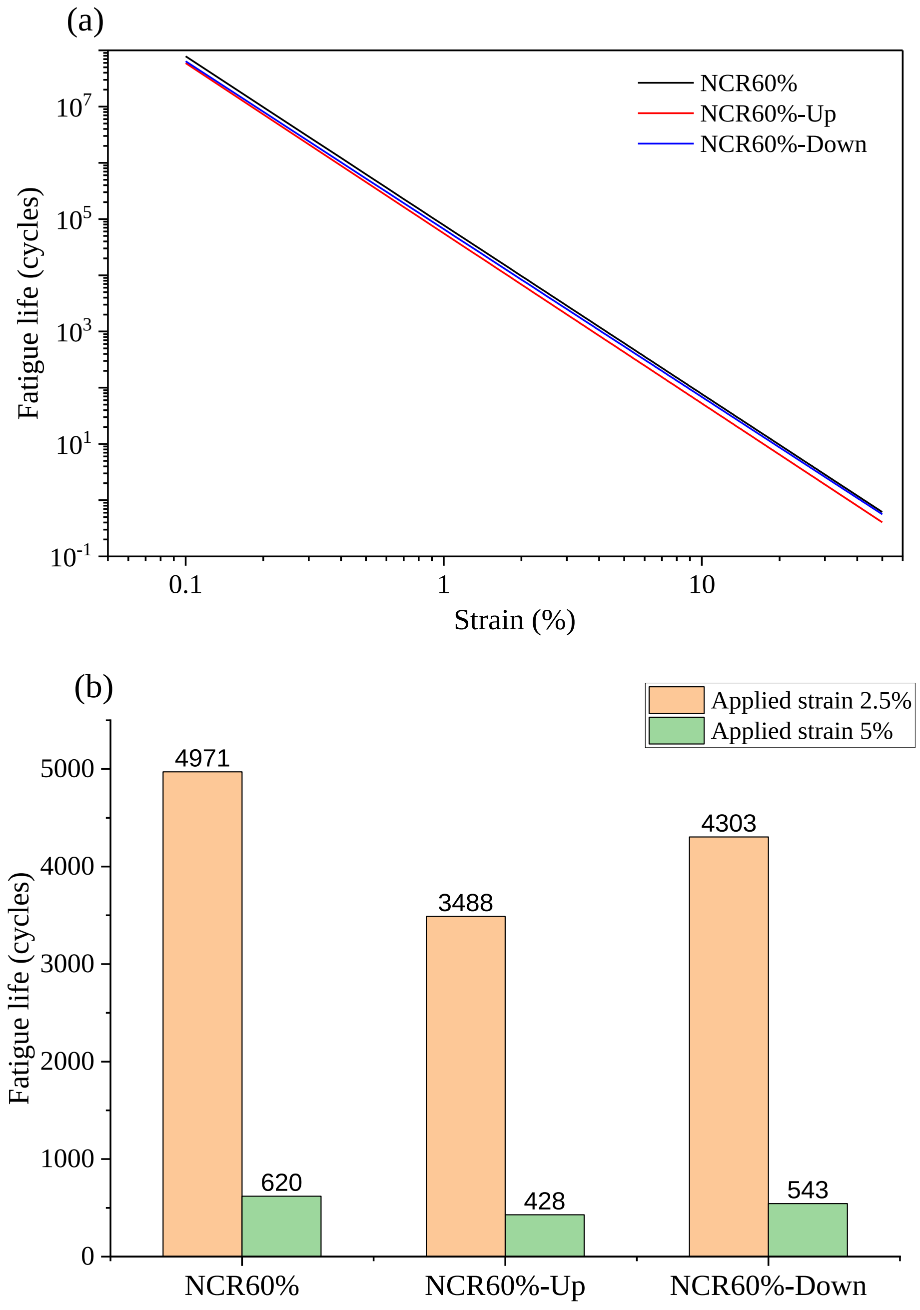


Fig. 3.28 Fatigue life (a)at different strain level (b)at applied strain 2.5% and 5%

In addition, the fatigue life test was conducted on the NCR after storage stability test, and the results showed that the fatigue curve of the NCR appeared to shift downward as a whole after a long time of high temperature heating and storage as shown in Fig. 3.28(a), and the upper part of the NCR showed a greater degree of fatigue life. This can also be seen in the fatigue life of a specific applied strain, as shown in Fig. 3.28(b). Further degradation of the rubber in the RAB occurs after prolonged heating at elevated temperatures. This leads to a reduction in the overall performance of the RAB, including fatigue performance[107]. Furthermore, it's worth noting that there is a difference in fatigue life between the upper and lower sections. Over an extended period of high-temperature storage, the polymer network from rubber gradually settles towards the lower part, resulting in a dilution of the polymer concentration in the upper sample. This phenomenon contributes to a more favorable fatigue life in the lower section compared to the upper sample.

3.8. MIXTURE VERIFICATION

Mixture laboratory experiments were conducted to evaluate the strength, moisture damage resistance and raveling resistance of RAB mixture used in porous asphalt.

3.8.1. Indirect tensile strength test

The Force-displacement data from the indirect tensile strength test is shown in Fig. 3.29. It's evident that NCR demonstrates comparable strength to the base bitumen, but it achieved maximum force at a lesser deformation. In light of these observations, the analysis will now incorporate fracture energy for further examination.

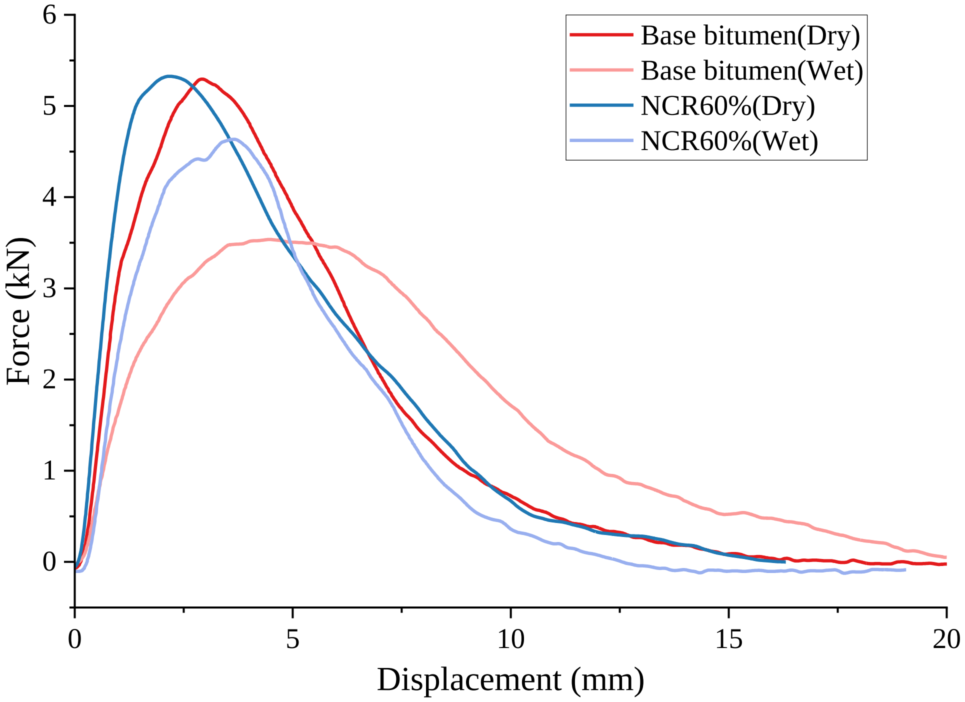


Fig. 3.29 Force-displacement curve of base bitumen and NCR

The fracture energy is equal to the area under the force-displacement curve up the maximum failure load, which can correlate with the field performance of asphalt mixture. The fracture energy of a mixture is the sum of the elastic energy and dissipated energy due to structural change, and the resistance of asphalt mixture to fatigue cracking is controlled by the resistance to deformation and damage. This parameter could be used to analyze the fatigue performance of asphalt mixture[108]. Further, the fracture energy density, which is defined as the fracture energy divide the volume of mixture, has been proven a linear relation between fatigue life of asphalt mixture. The fracture energy can be calculated according to the following equation[109]:

$$FE = \frac{\int_0^{\delta_{max}} P(\delta)d\delta}{V} \tag{3-1}$$

Where:

FE = fracture energy density, MPa
P = applied load, N
V = volume of asphalt mixture, mm^3
d = deformation

The results of fracture energy density of base bitumen mixture and NCR mixture is shown in Fig. 3.30. As with the load-displacement curves, the fracture energy density of NCR mixtures is lower than that of the base bitumen. Mixtures with higher fracture energy exhibit reduced energy dissipation due to damage extension, consequently resulting in improved fatigue life[109]. Consequently, in the field performance assessment of bitumen mixtures, the fatigue life of the NCR alternative binder is notably inferior to that of the base bitumen.

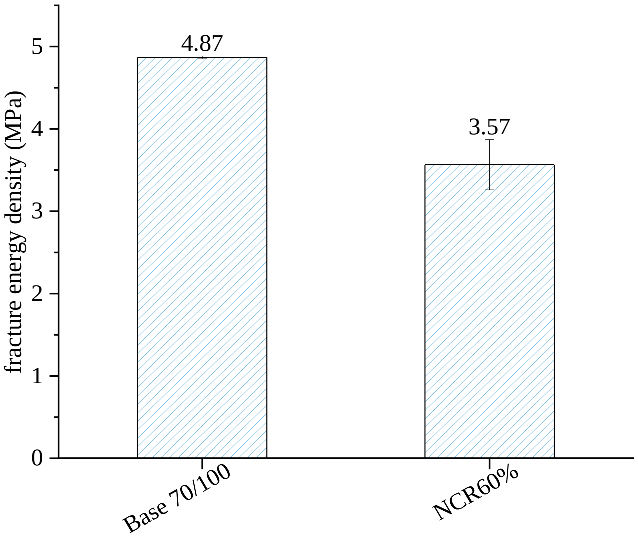


Fig. 3.30 Fracture energy density

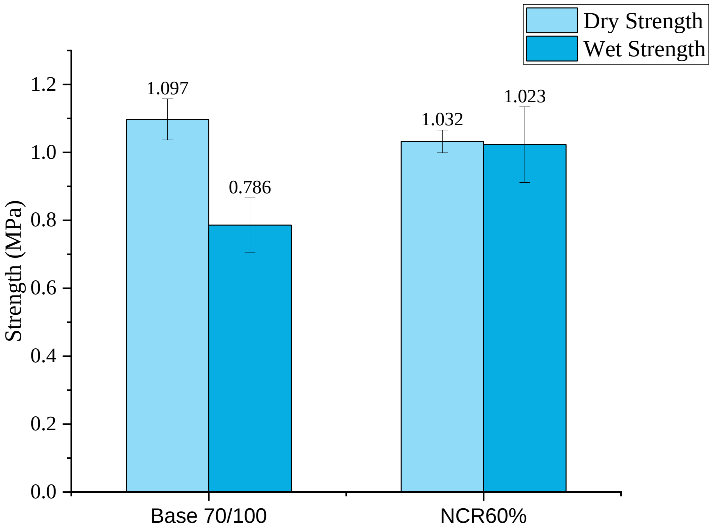


Fig. 3.31 Indirect tensile strength of dry and wet specimen

Water sensitivity of base and NCR binder is evaluated by indirect tensile strength ratio. The test results according to NEN-EN 12697-12 are presented in Table 3.2. Compared to base bitumen, which has an ITSR of about 70%, NCR shows excellent resistance to water damage. Considering the sample variation and the measurement accuracy, the strength deterioration because of moisture damage of NCR can be neglectable.

Table 3.2 ITSR of base and NCR asphalt mixture

	NCR60%	**Base 70/100**
Dry Strength, Mpa	1.0323	1.0972
Wet Strength, Mpa	1.0227	0.7860
ITSR,%	99.07%	71.64%

3.8.2. Cantabro test

The Cantabro test is commonly used for open-graded asphalt mixtures to evaluate cohesion and durability. Fig. 3.32 shows the Cantabro mass loss results for the base and the NCR binder. It can be seen that the NCR alternative binder exhibits lower mass loss, indicating that the NCR has better durability than the base bitumen This better performance may be related to the high viscosity of the NCR. In general, the higher the dynamic viscosity of the binder, the lower the mass loss of the porous bitumen.[110].

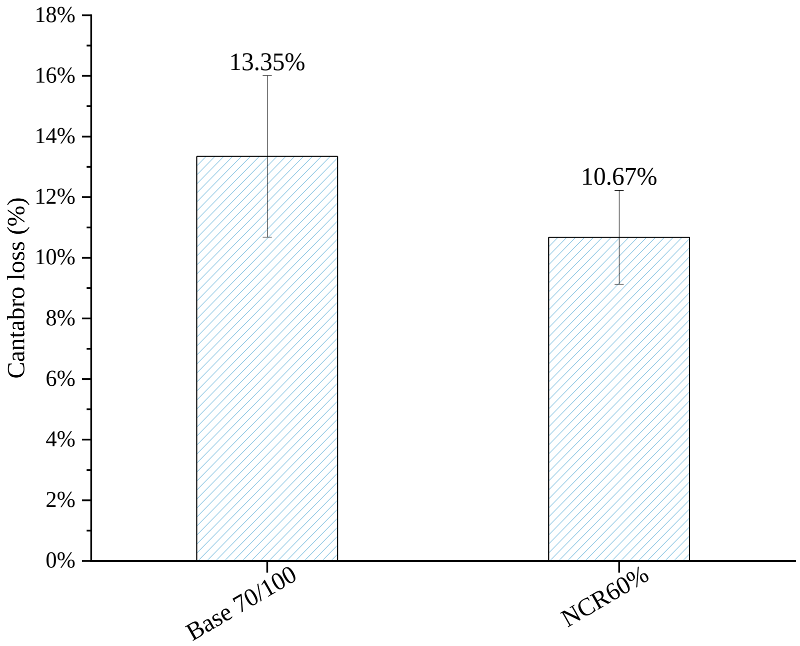


Fig. 3.32 Cantabro loss

3.9. CONCLUSION

In this chapter, a comprehensive evaluation of rubber alternative binder (RAB) with different rubber types and replacement content was conducted. The finding in this study revealed the potential of RAB as an alternative to conventional bitumen binders.

First and foremost, it is evident that both DCR and NCR exhibit substantial advantages over base bitumen in terms of performance. These rubber types enhance various key attributes of the binder, making them promising candidates for future development and application. However, the same cannot be said for FCR, which, in contrast, appears to have a negative impact on bitumen performance. Considering the high cost associated with FCR, it may not be a viable material for RAB in future endeavors. Additionally, we delved into further assessments in aging resistance evaluations, focused on DCR and NCR. Among these rubber types, NCR demonstrated superior performance, showcasing its potential for use in aging-resistant RAB formulations.

Exploration extended to storage stability and mixture-level evaluations, with a specific focus on NCR. The storage stability test revealed that NCR exhibited minimal segregation tendencies, though it did exhibit some rubber degradation during prolonged high-temperature storage, resulting in a reduction in fatigue life. In terms of mixture-level performance, NCR displayed comparable strength to base bitumen. However, an analysis of fracture energy density indicated that the field performance of NCR in terms of fatigue life may be slightly weaker than that of base bitumen. Nevertheless, it's worth noting that the ITSR test confirmed the excellent water damage resistance of NCR, adding another dimension to its suitability for certain applications.

CHAPTER 4.

FULL-ALTERNATIVE BINDER

4.1. INTRODUCTION

Building upon the promising revelations of the previous chapter, where rubber showcased its potential to substantially replace bitumen, Chapter 4 further attempts to utilize a combination of waste materials to achieve a waste full-alternative binder (FAB).

Previous studies have reached into the field of bio-based and waste-based alternative binders, providing valuable insights[78–80]. While there is an investigation revealed a remarkable resemblance between the behavior of the bio-oil blends and conventional bitumen binders[78], their large-scale application poses serious challenges. High production costs and ethical dilemmas that may compete with food production for vital resources are formidable barriers. Employing waste materials presents a potential route to circumvent some of these challenges. However, there is a lack of research on the use of waste materials for bitumen replacement. In light of this situation, this chapter will explore the potential of waste materials as a viable route to address these limitations.

Within the following sections, a waste-based FAB will be developed through the combination of waste tire rubber, waste plastic, resin, and oil. Following preliminary experimental validation and data analysis, the FABs exhibiting superior performance will be singled out. Subsequently, these select formulations will undergo further modifications, followed by comprehensive assessments of their rheological properties. For the most promising group, comprehensive evaluations involving aging and mixture level tests will be conducted to measure its practical applicability. A visual representation of the workflow for this section is depicted in Fig. 4.1.

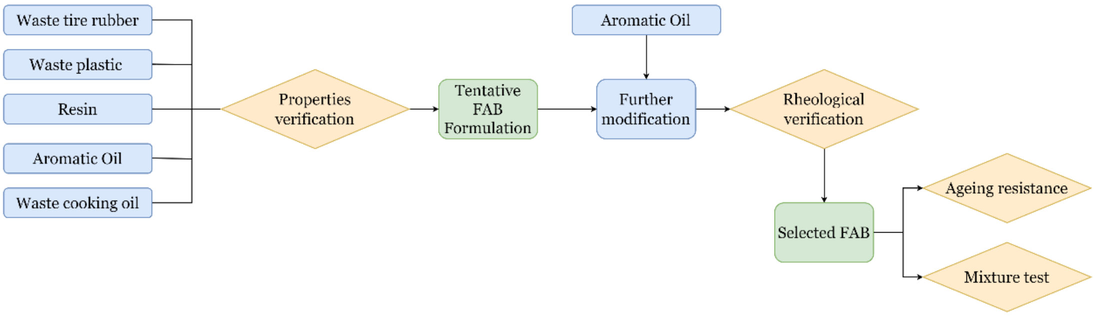


Fig. 4.1 Flow Chart of Chapter 4

4.2. FORMULATION DETERMINATION

4.2.1. Preliminary addition range

The preliminary formulation of FAB is determined by the flowchart shown in Fig.2.4. In order to determine the initial range of addition of each material to the alternative binder, physicochemical and rheological properties of bitumen components were investigated. Based on SARA components, the physical appearance of bituminous components have been investigated. The results showed that physical appearance of each component was different. Saturates, aromatics, resins and asphaltenes were colorless liquid, yellow or red viscous liquid, brown viscous semi-solid and black brittle powder, respectively[111]. This is similar to the chosen raw materials, and WCO, AO, resin as well as waste tire rubber. In addition, the contribution of the bitumen components to the bitumen properties is also presented. The findings revealed that resins, aromatics, and asphaltenes exerted the most substantial influence on bitumen's high-temperature performance, low-temperature performance, and viscosity variations, both before and after aging. Particularly, asphaltenes played a pivotal role in conferring stiffness and elasticity to bitumen, characteristic of its viscoelastic behavior[112]. FTIR results for saturates as well as aromatics show that the saturates and aromatics contained similar chemical bonds and functional groups[111].

In addition, due to the incorporation of waste plastic, FAB components introduce polymer compared to base bitumen. Polymer modified bitumen could be described as a colloidal dispersion of high-molecular-weight(HMW) polymer in the low-molecular-weight-maltenes (saturates, aromatics, resins)[74]. Building upon this theoretical foundation, our research group conducted an analysis of the molecular weight of materials and their distribution using GPC Chromatogram in prior studies. Furthermore, the curves of SBS-modified bitumen were subjected to fitting by adjusting the quantities of various components added. Fig. 4.2 illustrates this process, with the black curve representing the GPC curve of SBS-modified bitumen, while the red dashed line signifies the curve fitted through mathematical analysis.

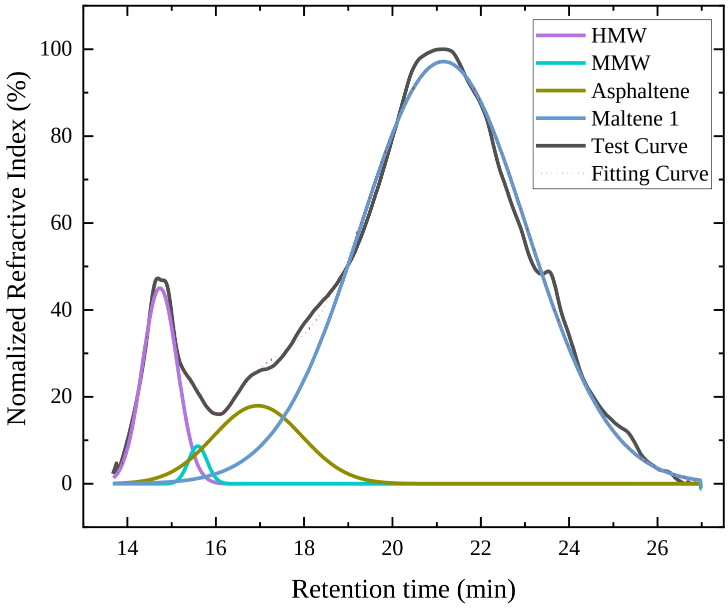


Fig. 4.2 GPC Chromatogram of SBS-modified bitumen simulation

Combining the above theoretical and experience base, for the materials used in this case, the rough additions of each material are shown in Table 2.8.

4.2.2. Rubber Oil selection

The subsequent key phase is the choice of rubber oil (RO), wherein the rubber is dissolved within a liquid component. This procedure is given priority because it is necessary to degrade rubber at high temperatures and high shear rates; if waste plastic is added thereafter, the polymer network may become damaged. In addition, the long duration of rubber oil preparation, mostly attributed to the necessary length for sufficient rubber dissolution, makes it advantageous to initiate this step as the initial stage. This approach can significantly reduce the time cost associated with potential repeats of the experiment. Given the aforementioned factors, the primary aim is to ascertain the most favorable mix of rubber oil. Based on the observations made in Chapter 3 concerning the Rubber Alternative Binder (RAB), it is apparent that the best performance of the binder is achieved when the weight of rubber is 60% in relation to bitumen, which corresponds to around 37% of the total binder weight. Nevertheless, considering the notably raised viscosity seen in prior modified RAB subsequent to the incorporation of polymer, it becomes imperative to decrease the quantity of rubber included into the FAB. Four possible formulations for the RO problem are suggested, labeled as RO1, RO2, RO3, and RO4, based on the starting range and theoretical concerns discussed before.

Furthermore, the initial comprehensive formulation was necessary to set up the FAB for testing, since the ultimate formulation was chosen based on performance evaluations of many formulations conducted by DSR. According to the previous investigation, the quantity of Resin included was d_2%. The selection of polystyrene (PS) as the waste plastic was based on its shown ability to enhance the stiffness of the binder as well as improve resistance to rutting and fatigue[113]. Furthermore, due to its foam-like structure, PS has enhanced solubility compared to other forms of particulate plastic waste.

The initial allocation of waste plastic included into the mixture was established at a rate of e_1%. The selection of RO was decided using two methods. Firstly, visual viscosity judgment was employed during the stirring process. Secondly, the DSR was utilized to conduct MSCR and LAS tests. The RO with the most favorable performance in terms of high temperature performance and fatigue life was selected. The RO2 sample, including a significant quantity of rubber, exhibited the formation of a very viscous gelatinous material upon the addition of PS and subsequent stirring at a temperature of 180°C. This observation suggests that the viscosity of the solution exceeded the desired useable condition. Consequently, this particular solution was chosen for further processing. The preparation procedure for this scheme was abandoned. Fig. 4.3 displays the findings for the last three schemes, including the MSCR and LAS outcomes.

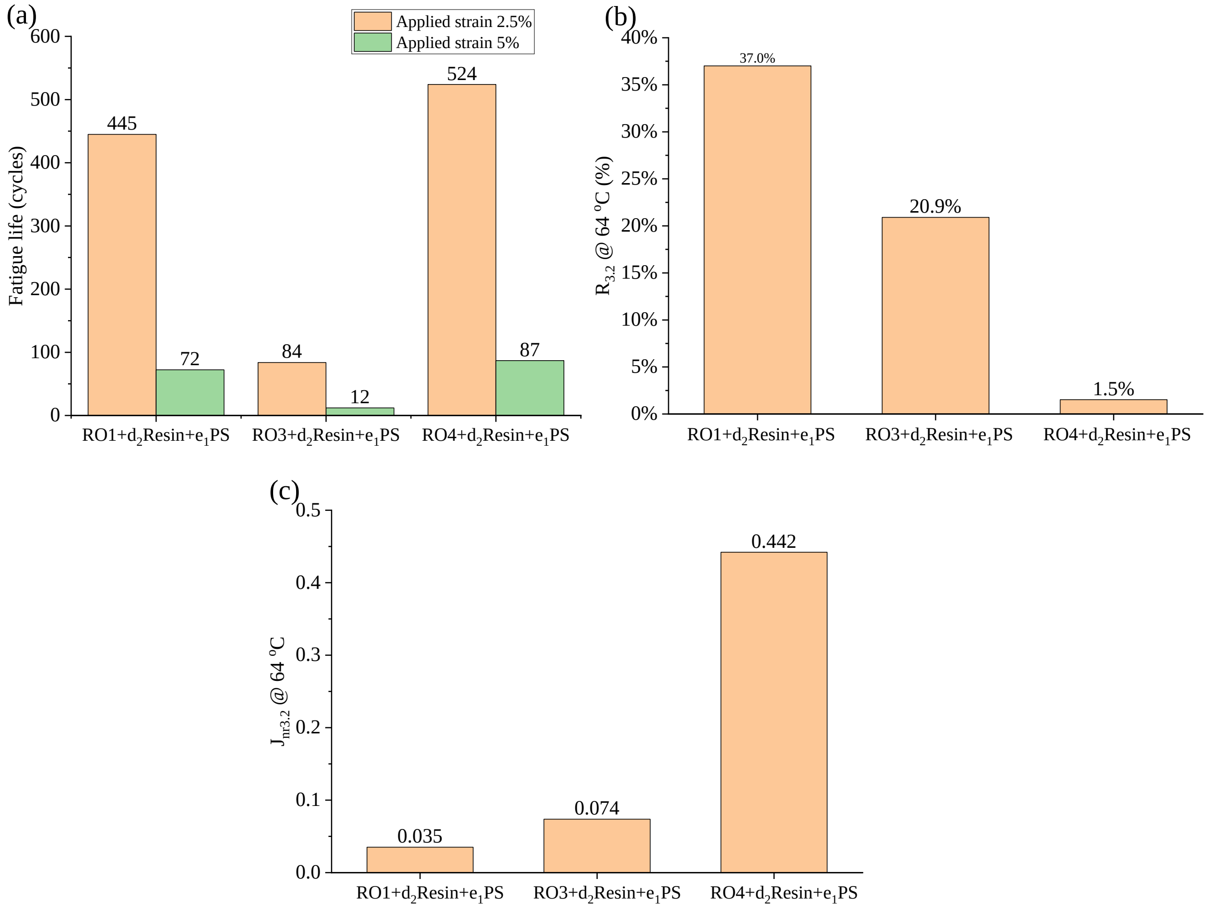


Fig. 4.3 DSR test results for RO selection (a)fatigue life (b)percent recovery (c)J_{nr}

When comparing the fatigue life and high temperature performance, it is evident that RO1 exhibits superior fatigue life and the highest performance in high temperatures. On the other hand, RO4 demonstrates the best fatigue life among the three ROs, but its high temperature performance is average. Nevertheless, it still outperforms the base bitumen in terms of high temperature performance, as observed in previous findings. Conversely, RO3 exhibits poor performance, rendering it unsuitable for further investigation in this formulation. In general, it may be said that RO1 has more potential for enhancement in comparison to RO4. However, in further experimental trials, repeatability of the performance exhibited by RO1 proved to be challenging, but RO4 demonstrated superior repeatability. The unpredictable outcomes seen may be attributed to the incorporation of undesirable chemical constituents by the WCO into RO1[38]. In conclusion, RO4 was ultimately selected as the foundation for the further research.

4.2.3. Resin ratio determination

According to the resin range given in Table 2.8, the upper, middle and lower ratios are taken, i.e. d_1%, d_2% and d_3%, similarly the FAB is fabricated using e_1% PS and the performance is verified by DSR test LAS as well as MSCR. The results are shown in Fig. 4.4.

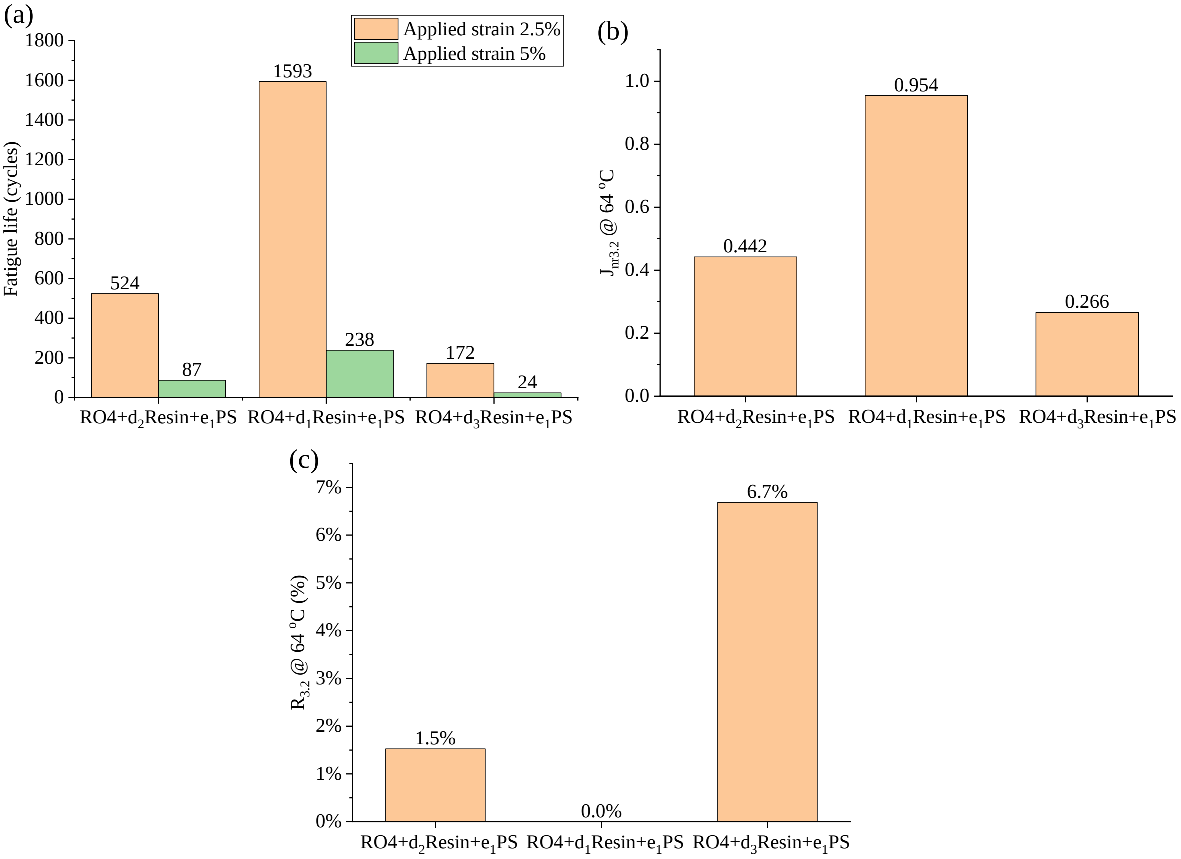


Fig. 4.4 DSR test results for resin ratio selection (a)fatigue life (b)*Jnr* (c)percent recovery

According to the data shown in Fig. 4.4, it can be observed that the fatigue life of FAB with a resin content of d_1% exhibits the highest performance. The subsequent best fatigue life performance is observed with a d_2% resin content, which is approximately one-third of that at the d_1% resin level. Compared to that, the fatigue life performance is notably worse when the resin percentage reaches d_3%, since the observed fatigue life is just one-tenth of that recorded at the d_1% resin level. However, it is essential to acknowledge that the performance at high temperatures demonstrates a contradictory arrangement, wherein the incorporation of d_1% resin displays the poorest performance, while the addition of d_3% resin yields the most favorable outcomes.

Given the divergent outcomes seen, it is imperative to conduct a comprehensive assessment of both attributes in combination. Firstly, in terms of the MSCR results, when comparing the experimental outcomes with the base 70/100 bitumen, it becomes evident that although the d_1% resin addition level demonstrates the worst performance among the three, it aligns more closely with the high-temperature performance of the base bitumen. Moreover, the fatigue life of the underlying bitumen under a 2.5% applied load is estimated to be around 3000. Although none of the three FAB formulations satisfy this condition, the notable gap in fatigue life performance between the d_2% and d_3% resin additions makes it unlikely for them to fulfill this need. As a result, a resin addition of d_1% was selected for subsequent experiments.

4.2.4. Polymer ratio

According to the polymer range given in Table 2.8, the upper, middle and lower ratios are taken, i.e. e_1%, e_2% and e_3%. Similarly, the polymer type is still chosen for PS. The results are shown in Fig. 4.5.

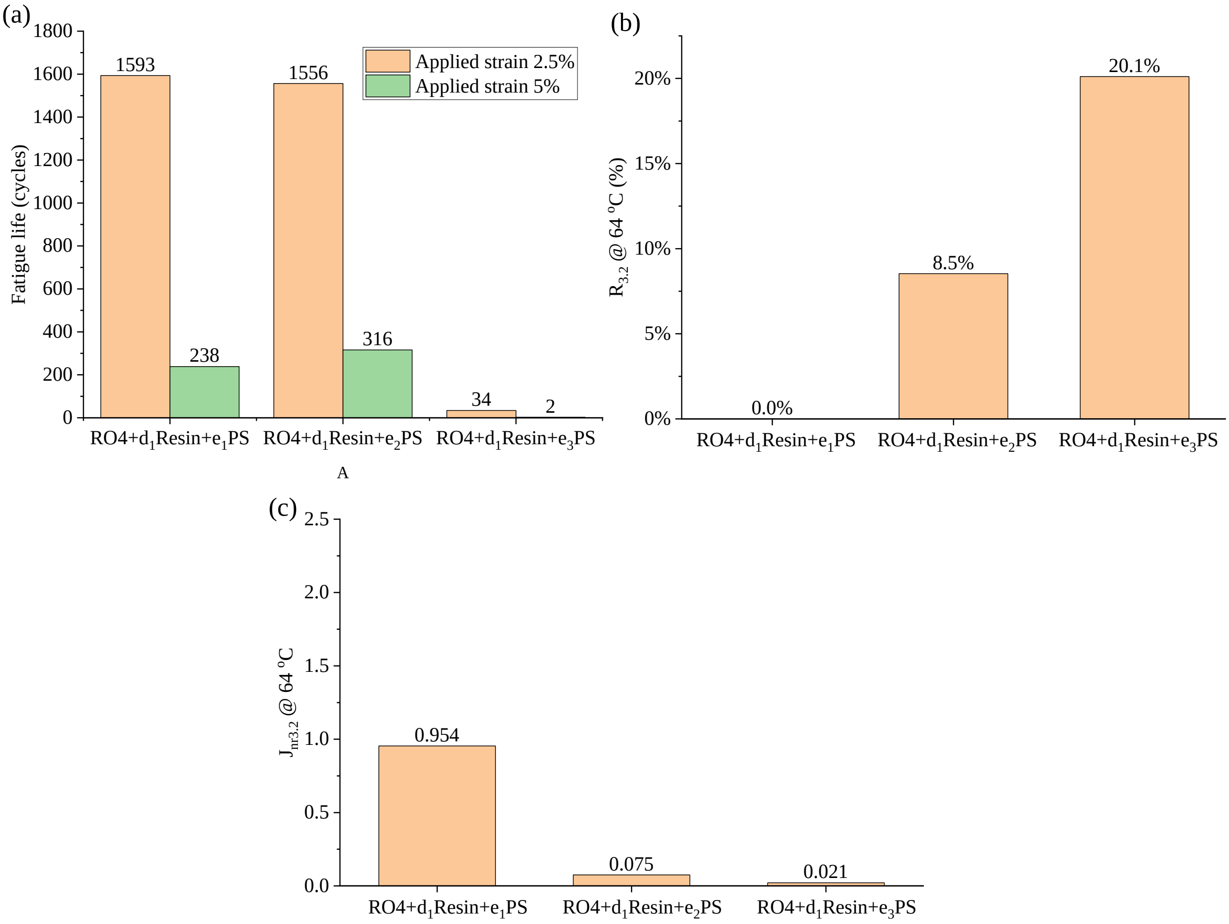


Fig. 4.5 DSR test results for polymer ratio selection (a)fatigue life (b)percent recovery (c)J_{nr}

Fig. 4.5(a) provides a clear depiction of the significantly decreased fatigue life seen in FAB with a e_3% polymer addition, therefore declaring the addition of this amount of polymer as unacceptable. By contrast, the fatigue life of the e_1% and e_2% additions demonstrate a similar performance, with one outperforming the other at varying strain levels. Nevertheless, upon further analysis of Fig. 4.5(b) and (c), a notable improvement in the performance at high temperatures is shown when the polymer addition amount is increased to e_2% as compared to e_1%. Considering all of these data, a polymer ratio of e_2% was chosen for subsequent analysis in order to assess the polymer type.

4.2.5. Polymer type

Building upon the aforementioned analysis, five distinct waste plastics—PS, PE, PP, LDPE, and EVA—were incorporated into FAB using the same rubber oil (RO), resin addition, and polymer addition. In addition to the MSCR and LAS tests detailed earlier, their viscosities at 135°C and 170°C were assessed to validate their workability.

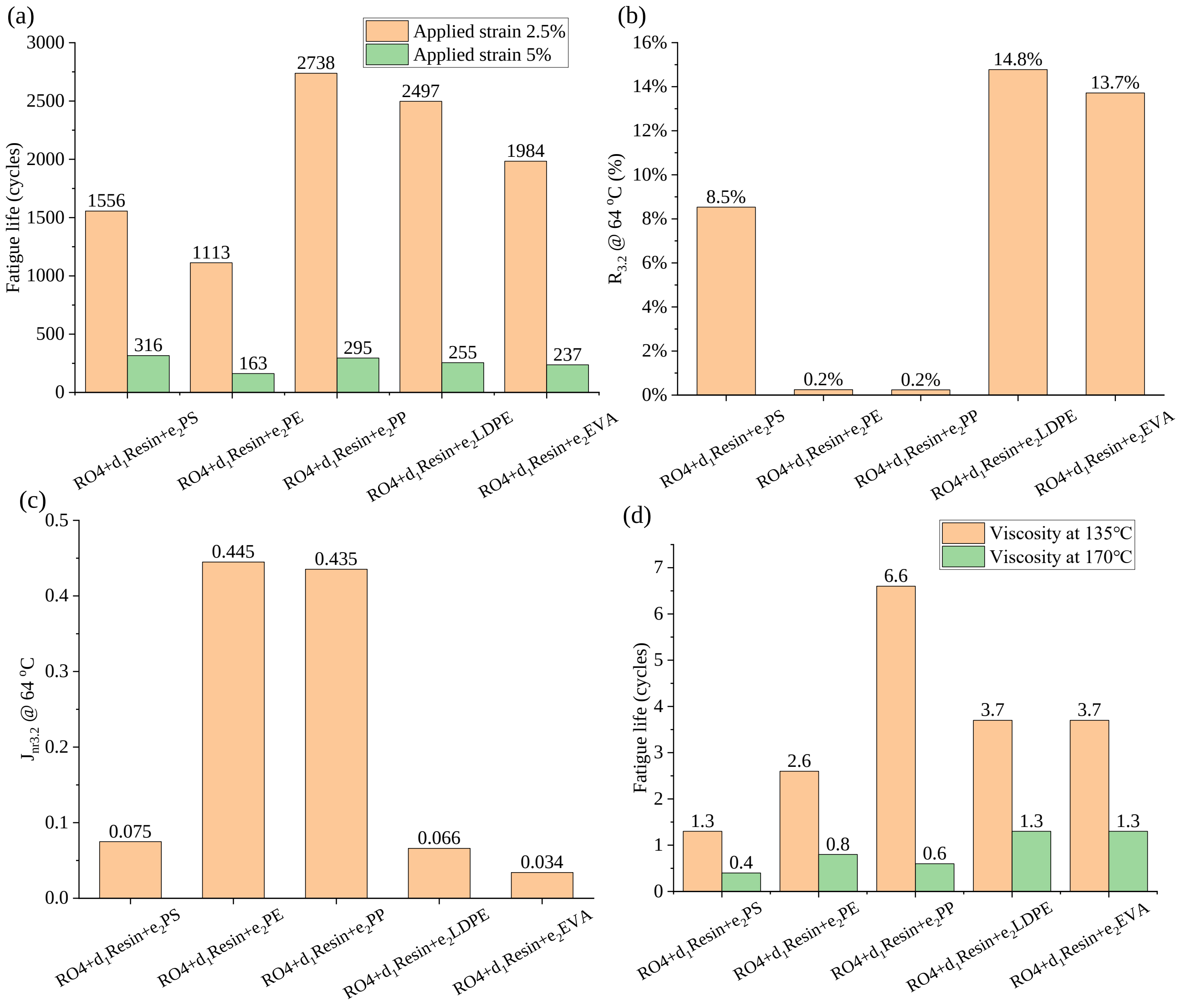


Fig. 4.6 DSR test results for polymer ratio selection (a)fatigue life (b)percent recovery (c)J_{nr} and (d) viscosity result

Based on the findings of the LAS analysis, it was observed that FABs made on PP, LDPE, and EVA exhibited superior performance. Regarding the outcomes pertaining to high temperature performance, as depicted in Fig. 4.6(b) and (c), it is evident that FABs made from LDPE and EVA exhibit superior performance. Furthermore, the findings obtained from MSCR indicate a comparable performance for both LDPE-based and EVA-based FABs. However, PP-based FAB performs poorly in high-temperature performance and is even one of the worst performers among the five materials. In the viscosity test, it was observed that the PS-based FAB exhibited the least viscosity, whilst the LDPE and EVA-based FAB had comparable viscosity characteristics, slightly beyond the specified threshold of 3 Pa·s at a temperature of 135°C. But the level of exceeding is not significant, and given the comparatively outstanding performance at high temperatures, more investigation may be conducted to explore viscosity reduction. It is important to highlight that the viscosity of PP-based FAB at 135°C is measured to be 6.6 Pa·s, significantly above the specified requirement of 3 Pa·s. In addition to its poor performance at high temperatures in the MSCR test, this property severely limits the potential for later treatments aimed at reducing viscosity. After a thorough review, it was determined that EVA and LDPE would be the most suitable materials for conducting the final verification of rheological characteristics and modification.

4.3. MODIFIED FAB

4.3.1. Modification of FAB

After conducting a series of validations as described earlier, LDPE and EVA were selected as the preferred polymer types, along with the validated RO type, resin, and polymer ratios. However, it was observed that the viscosities of LDPE-based and EVA-based FABs slightly exceeded the specified requirements. Additionally, the fatigue life performance of these FABs was slightly lower than that of the base 70/100 bitumen. To address these performance disadvantages, further modifications were made to the FABs by adding additional additives to the validated ratios.

The results of complex viscosity and flow activation energy demonstrated that aromatics exhibited better fluidity compared to base 70/100 bitumen[111]. Furthermore, it was established that the addition of aromatic oil could enhance fatigue resistance[83]. The advantages of aromatic oil in these two aspects could mitigate the current challenges faced by FAB. Therefore, two FABs were modified using aromatic oil. Given that all other variables had been previously established, the only factors influencing what came out were the type of polymer and the amount of extra aromatic oil. As a result, the subsequent naming was shortened as LDPE/EVA+xAro. Here, x represents the weight ratio of the added aromatic oil to the weight of each previously added component material. The specific list of modified FAB samples is provided in Table 4.1.

Table 4.1 Sample list of modified FAB

	AO	**Rubber**	**C9 Resin**	**Waste Plastic(polymer)**		**additional AO**
				LDPE	**EVA**	
LDPE+3Aro	b_4	a_3	d_1	e_2	-	3
LDPE+5Aro	b_4	a_3	d_1	e_2	-	5
LDPE+7Aro	b_4	a_3	d_1	e_2	-	7
LDPE+8Aro	b_4	a_3	d_1	e_2	-	8
LDPE+10Aro	b_4	a_3	d_1	e_2	-	10
EVA+4Aro	b_4	a_3	d_1	-	e_2	4
EVA+5Aro	b_4	a_3	d_1	-	e_2	5
EVA+6Aro	b_4	a_3	d_1	-	e_2	6

In next step, a comprehensive evaluation of the rheological performance of modified FAB is conducted, employing a dynamic shear rheometer (DSR). A full range of tests, including the Temperature Sweep Test, Multiple Stress Creeps Recovery (MSCR) Test, Linear Amplitude Sweep (LAS) Test, and Relaxation Test, has been carefully utilized to thoroughly assess important characteristics related to temperature sensitivity, high-temperature elastic response, fatigue life, and the ability to relax residual stress at low temperatures. The combination of these evaluating methodologies provides a comprehensive understanding of the complex rheological dynamics and performance characteristics inherent in FAB. Such assessment offers invaluable insight into the suitability of a material for particular applications within the field of pavement engineering.

4.3.2. Temperature sweep

Effect of temperature on DSR parameters including G^*, phase angle δ, $G^*/sin\delta$ and $G^*\cdot sin\delta$ have been shown in Fig. 4.7, Fig. 4.8, and Fig. 4.9.

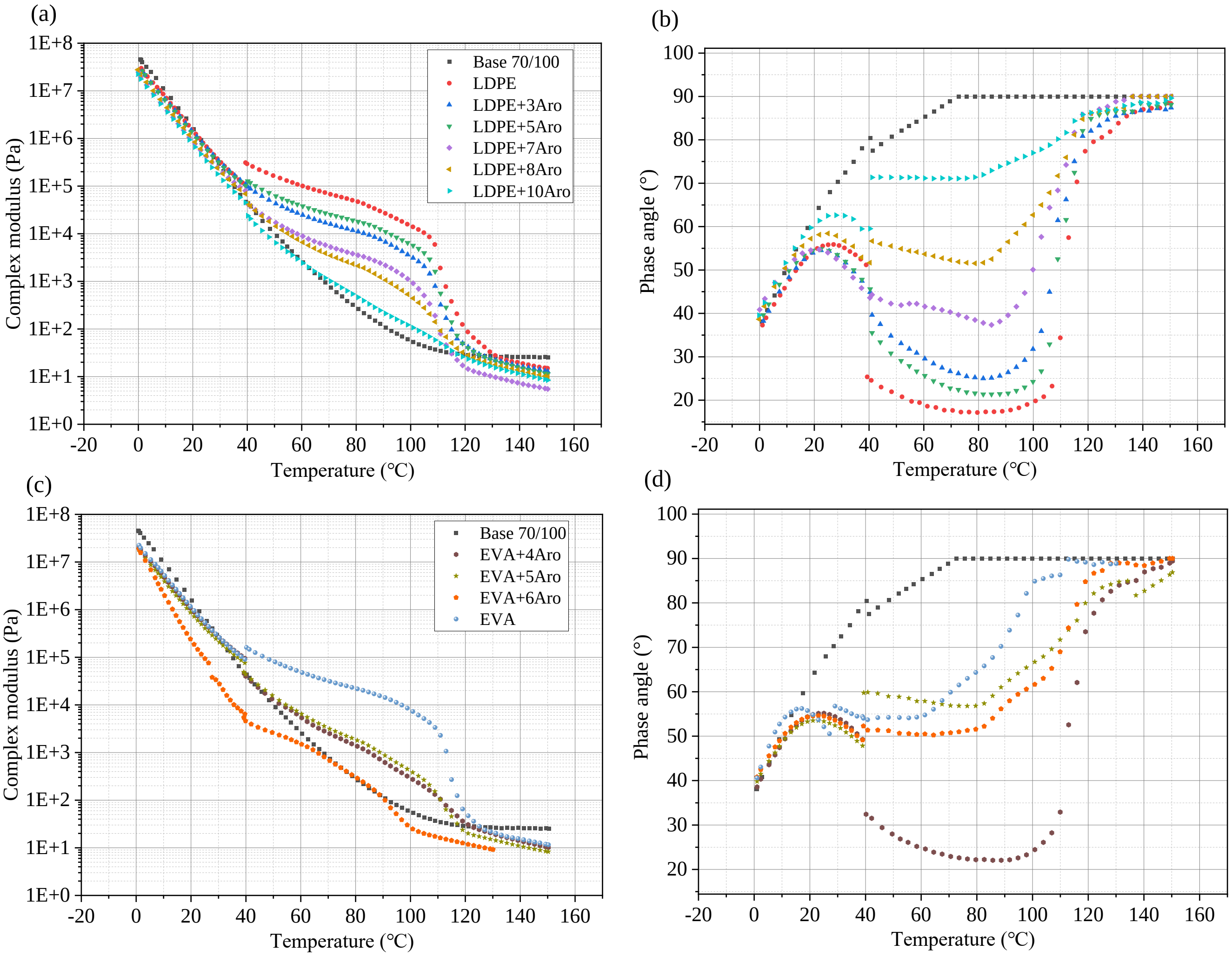


Fig. 4.7 Effect of temperature on G^* and phase angle parameter

As seen in Fig. 4.7, The behavior of FAB displays a notable deviation from the typical pattern found in base bitumen at certain temperature ranges. This deviation is primarily defined by a decrease in the phase angle as the temperature increases. This unique occurrence, as seen in Fig. 4.7(b) and (d), is characterized by the phase angle undergoing a transition into a rather stable platform zone at around 20°C, followed by a gradual decrease as the temperature continues to rise. The observed behavior can be ascribed to the impact of the polymer network present inside the FAB system. The appearance of the phase angle platform area can be ascribed to the existence of a polymer elastic network or polymer chain entanglement. As temperature rises, the phase angle progressively declines, indicating the growing influence of the polymer phase on the rheological properties. This discovery suggests that the inclusion of waste plastic has a similar role to a polymer network, approximating the effects of SBS.

Regarding the complex modulus curve, FAB exhibits a gradual decrease in comparison to base bitumen within the temperature range of 40 to 110°C, ultimately falling below the complex modulus of base bitumen beyond 130°C. This signifies FAB's superior high-temperature performance, ensuring better flowability during construction at elevated temperatures. Additionally, the introduction of AO imparts a softening effect on FAB, as evidenced by the gradual decrease in complex modulus with increasing AO content. The reduction in phase angle within the platform region is also less pronounced, even in the case of EVA-based FAB, where the complex modulus falls below that of base bitumen when AO is added in quantities exceeding 6 units.

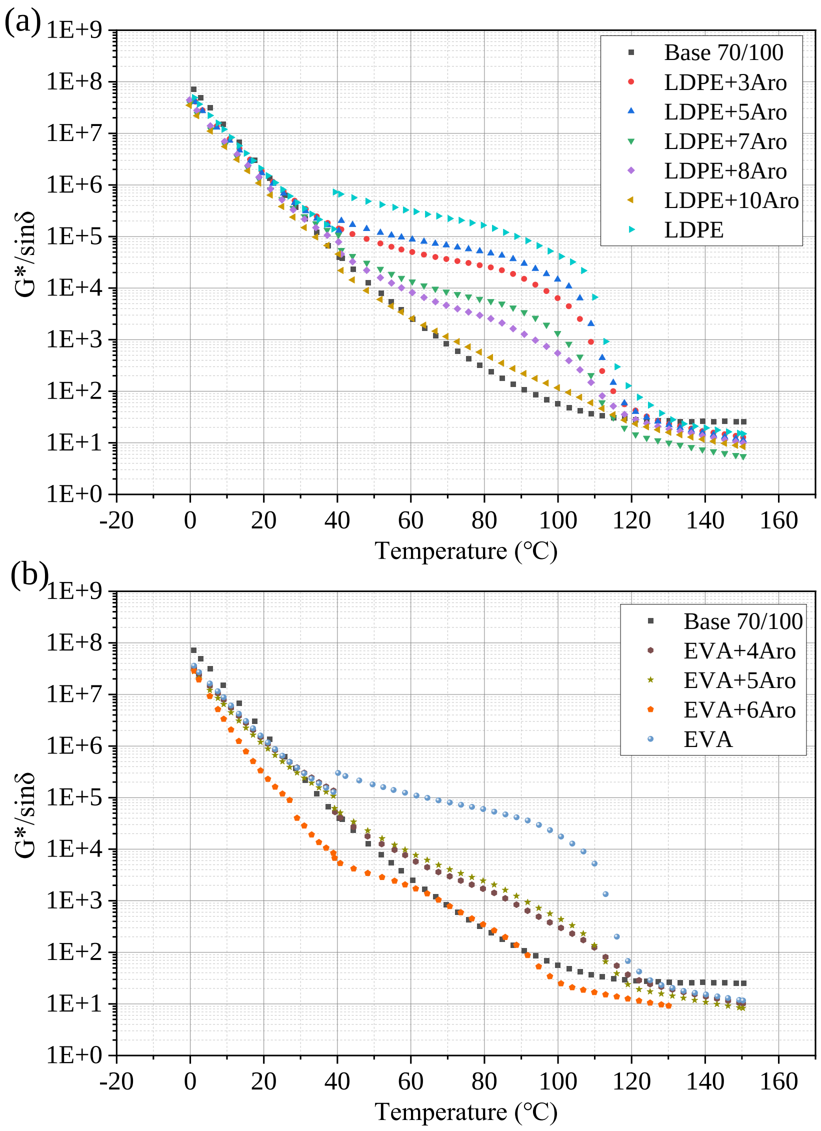


Fig. 4.8 Effect of temperature on $G^{*}/sin\delta$ parameter

$G^{*}/sin\delta$ can be an indicator for assessing the rutting resistance of binders. A higher $G^{*}/sin\delta$ value is indicative of superior rutting performance in binders. As shown in Fig. 4.8(a), LDPE-based FAB consistently exhibits commendable rutting resistance at elevated temperatures. In the lower temperature region, it also shows similar behavior to base bitumen. Moreover, it is important to highlight that the additional AO had an incremental effect, and the LDPE-based FAB demonstrated a consistently high value of $G^*/sin\delta$, even when 10 AO were applied. In contrast, the behavior shown by EVA-based FAB demonstrated some divergences. When AO was not present, the EVA-based FAB had similarities to the LDPE-based FAB. Yet, with the implementation of AO, even when used in small amounts, there was a noticeable decrease in the resistance to rutting at high temperatures. At the addition level of 6AO, the EVA-based FAB exhibited significantly worse performance compared to the base bitumen throughout different ranges of temperature.

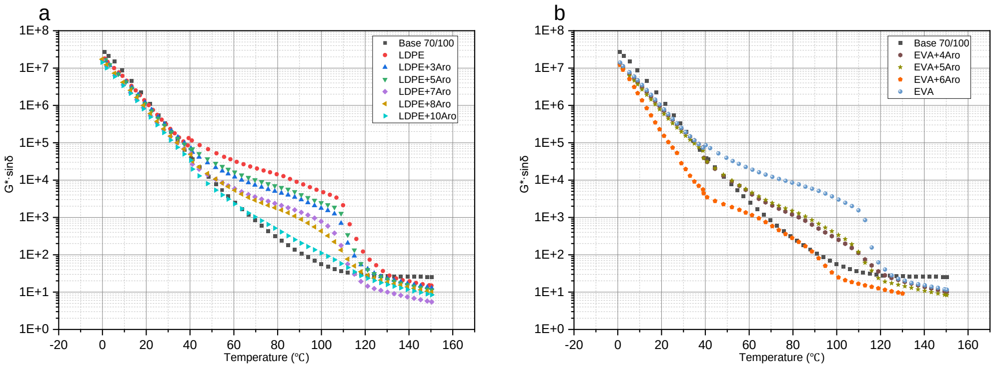


Fig. 4.9 Effect of temperature on $G^*{\cdot}sin\delta$ parameter

$G^*{\cdot}sin\delta$ can be an indicator for assessing the fatigue resistance of binders. As shown in Fig. 4.9, for LDPE-based FAB, it can be seen that its fatigue resistance is better than that of base bitumen in the temperature region of 40-100°C, i.e., at higher temperatures, but slightly worse at temperatures lower than 40°C. For EVA-based bitumen, similar to the previous analysis of rutting resistance, there is a substantial decrease in fatigue resistance after the addition of AO. In relation to EVA-modified bitumen, similar to previous investigations on rutting resistance, the incorporation of AO also results in a notable decrease in fatigue resistance. Moreover, by examining the differences between LDPE-based and EVA-based FAB in relation to base bitumen at low temperatures, it becomes evident that EVA-based FAB demonstrates a lower level of fatigue resistance in such circumstances.

4.3.3. MSCR

Fig. 4.10 display the MSCR test results of the FAV at temperature 64℃ shear stress level of 0.1kPa and 3.2 kPa.

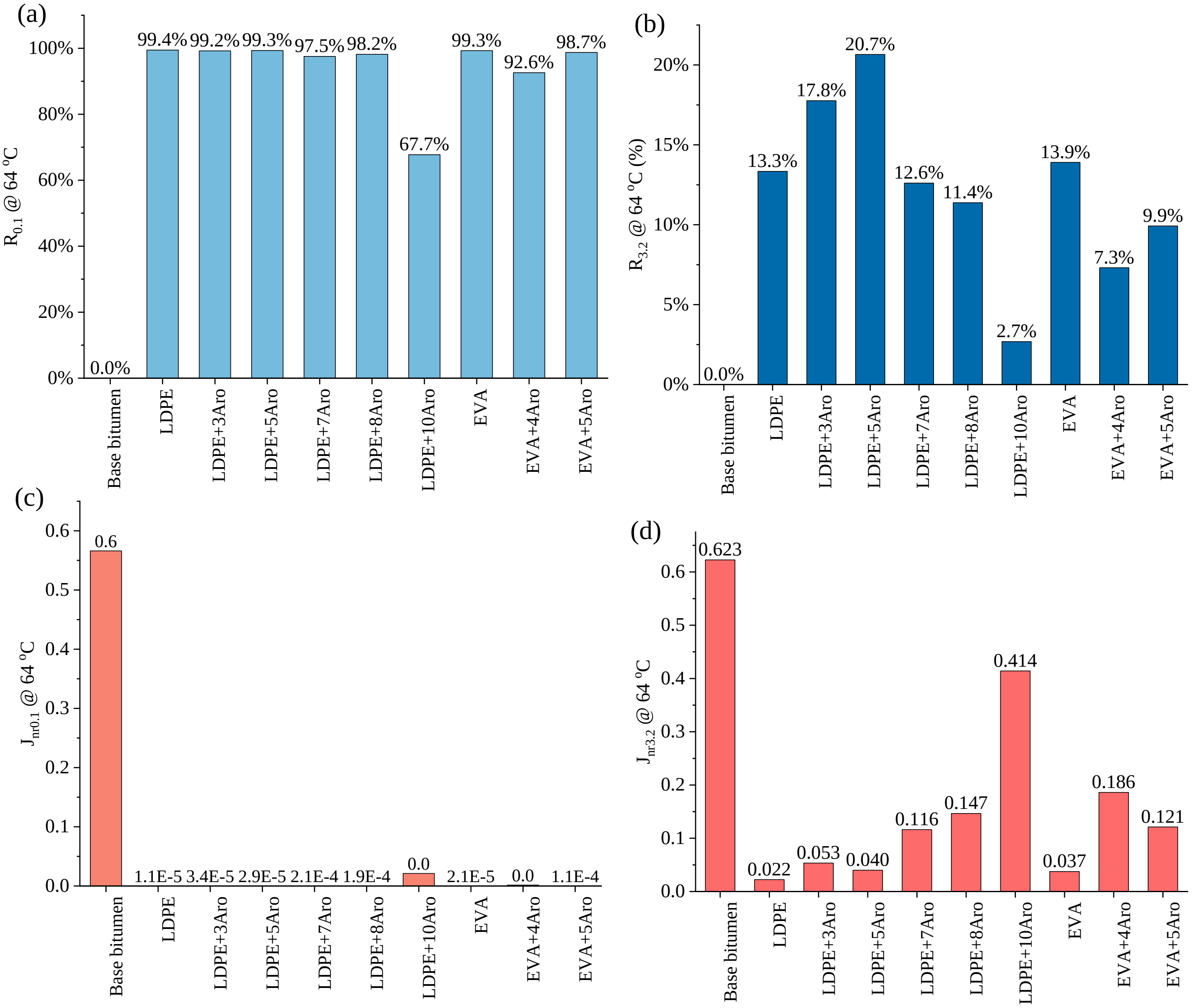


Fig. 4.10 Percent recovery at temperature 64℃ at shear stress level of (a)0.1kPa, (b)3.2 kPa J_{nr} at temperature 64℃ at shear stress level of (c)0.1kPa, (d)3.2 kPa

At a stress level of 0.1 kPa, it is apparent that all FABs have remarkable elasticity and ability to withstand permanent deformation, with the exception of LDPE+10Aro, as seen in Fig. 4.10(a) and (c). As the applied stress reaches a value of 3.2 kPa, the high-temperature performance of LDPE+10Aro exhibits a more pronounced deterioration. Fig. 4.10(b) and (d) illustrate that the high-temperature performance of LDPE-based FAB initially improves and then diminishes with increasing AO addition. Conversely, the high-temperature performance of EVA-based FAB initially declines and subsequently improves with AO addition, yet the final high-temperature performance remains lower than that without additional AO, aligning with the earlier findings from the Temperature Sweep Test.

In conclusion, it can be observed that all FABs exhibit superior performance compared to base bitumen in terms of percent recovery and unrecoverable deformation, regardless of the stress levels used (0.1 kPa and 3.2 kPa). This implies that the incorporation of AO does not compromise the thermal stability of FAB too much as compared to the original bitumen. The mitigating impact of AO on FAB is considered to be within an acceptable range.

4.3.4. LAS

One of the primary objectives of the supplemental AO addition is to enhance the fatigue life of the binder, aiming to achieve a performance similar to that of the base bitumen. Fig. 4.11 presents the fatigue life of FABs and base bitumen under 2.5% and 5% applied strain.

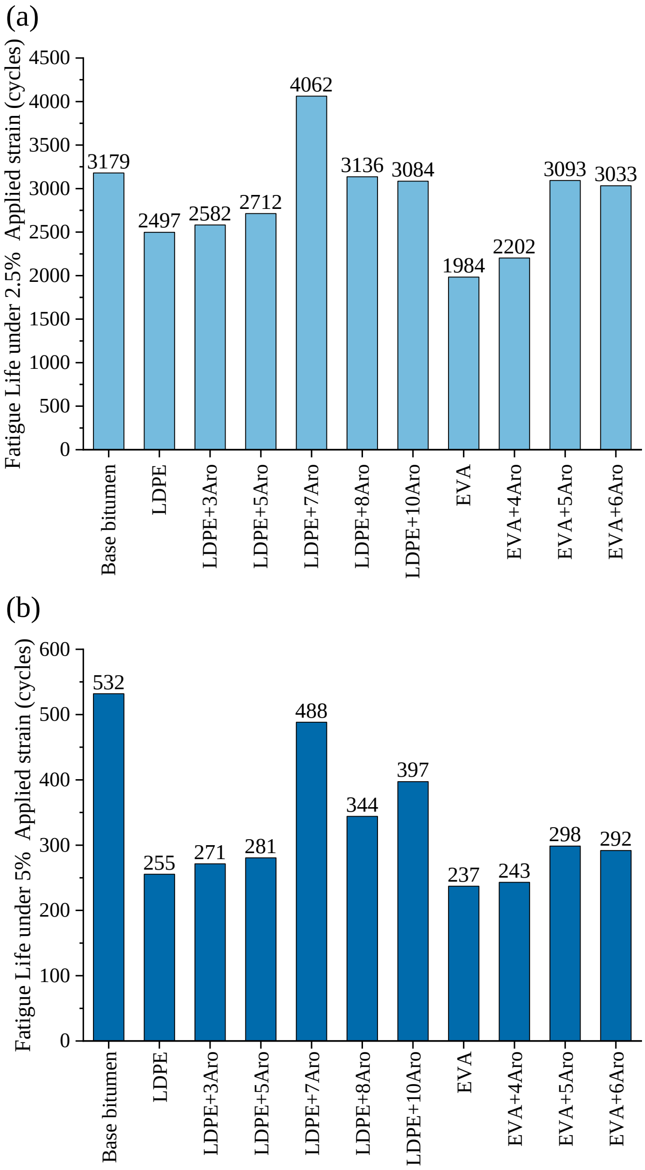


Fig. 4.11 Predicted fatigue lives at (a) 2.5% and (b)5% strain amplitudes

It is evident that the inclusion of AO has a positive impact on the fatigue life of the binder. Under a 2.5% applied strain, a total of five FABs achieved fatigue performance levels similar to those of the base bitumen, with LDPE+7Aro even surpassing the fatigue life of the base bitumen. However, at a 5% applied strain, although AO addition improved the fatigue life of FAB, only LDPE+7Aro exhibited a comparable fatigue life. It's important to note that the LAS test condition was conducted at 20°C, and the fatigue performance at this temperature aligns with the previous findings from the temperature sweep test, indicating that FAB's fatigue performance is inferior to that of base bitumen at lower temperatures.

4.3.5. Relaxation

The utilization of AO also helps to an improvement in performance at low temperatures, as seen by the expedited release of residual stresses. The significantly reduced relaxation durations serve to mitigate the accumulation of stresses within the pavement structure. Fig. 4.12 illustrates the time required for stress to reduce to 50% for FAB, which is notably faster than that for base bitumen. The aforementioned improve becomes particularly evident when taking into account the timerequired for stress levels decrease to 10%. To summarize, the duration required for stress relaxation as the quantity of AO increases. When comparing FABs to basic bitumen, it is observed that all FABs demonstrate enhanced residual stress release capabilities at low temperatures. This advantage is further enhanced by the use of AO.

Taking into account the rheological properties mentioned above, AO-modified FAB exhibits superior performance compared to base bitumen in areas such as rutting resistance and low-temperature relaxation. However, there are still some limitations in terms of fatigue life, with only LDPE+7Aro demonstrating similar performance to base bitumen. For the subsequent aging and mixture-level validation in this study, LDPE+7Aro was selected to comprehensively assess the potential for replacing petroleum bitumen with FAB. To simplify presentation in the following sections, LDPE+7Aro FAB will be referred to as LDPE.

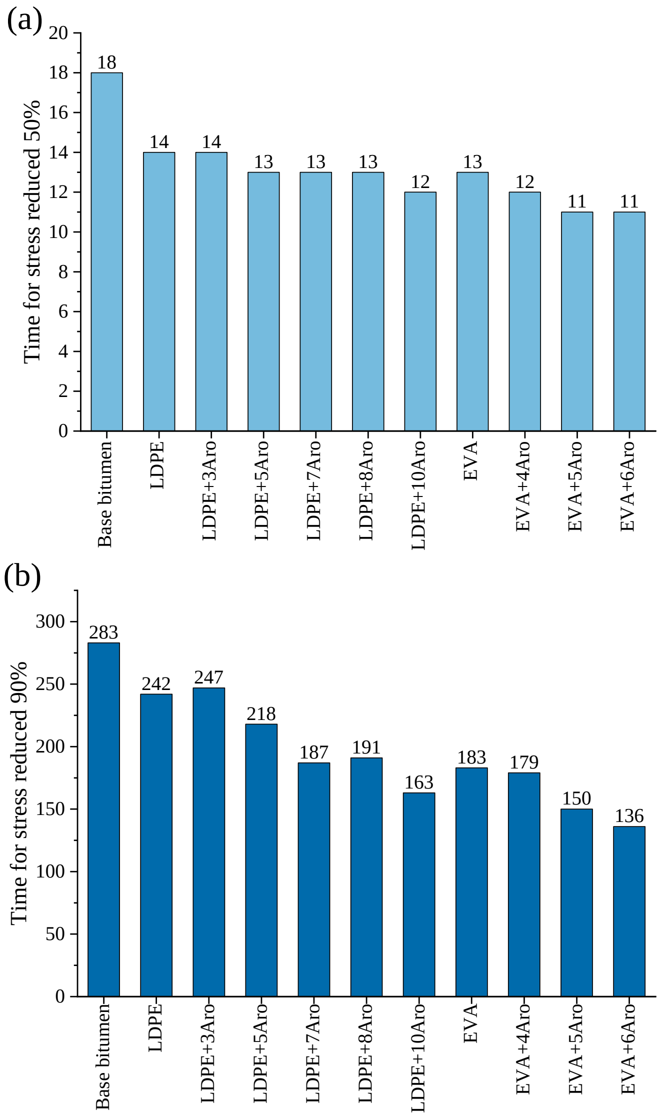


Fig. 4.12 Relaxation time required for the stress to reduce (a) 50% and (b)90%

4.4. AGING RESISTANCE

In order to have a full understanding of the changes in FAB characteristics during the aging process, LDPE was subjected to aging for 20 hours PAV and 80 hours PAV correspondingly. Following that, the characteristics of the properties were compared to those of the basic bitumen that experienced same aging circumstances. The rheological parameters of the aged samples are graphically shown in Fig. 4.13, Fig. 4.14, Fig. 4.15, and Fig. 4.16.

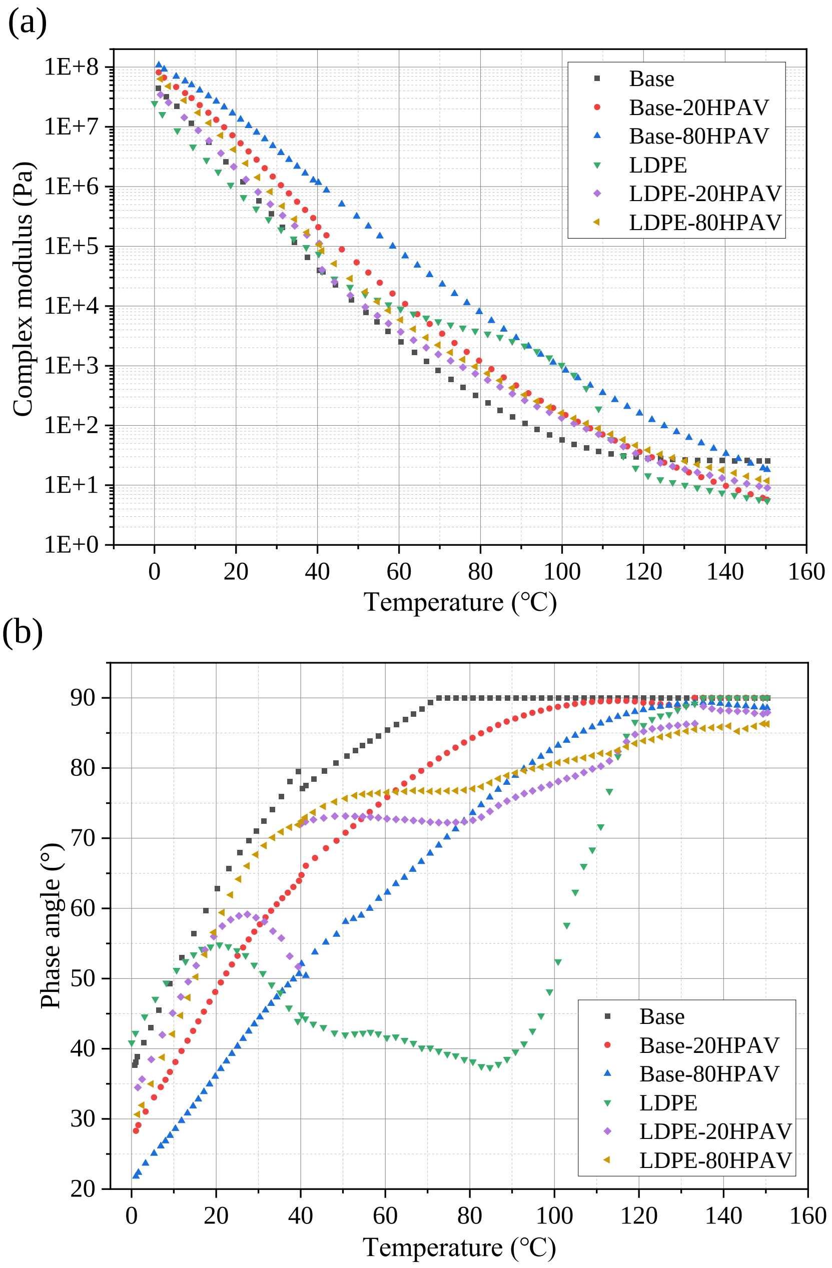


Fig. 4.13 Effect of temperature on (a) G^* and (b) phase angle parameter

The analysis of the complex modulus curve throughout the temperature sweep demonstrates an apparent absence of the platform area in LDPE during the aging process, particularly as the temperature increases. The aforementioned phenomena becomes more evident when analyzing the phase angle curve, as it demonstrates a notable rise in phase angle within the temperature range that corresponds to the initial platform region following to the aging process. The prior findings suggest that the polymer network inside the LDPE has seen deterioration, leading to a reduction in its ability to enhance the strength of the FAB. In contrast to base bitumen, which exhibits a tendency to undergo hardening with time, the complex modulus of aged LDPE demonstrates a decrease from its initial value throughout the temperature range of 60 to 110°C, as shown in Fig. 4.13. This reduction can be attributed to the degradation of the polymer network that previously contributed to the reinforcement of bitumen. Furthermore, while analyzing the rheological characteristics of bitumen at various stages of aging, it becomes apparent that there is no substantial difference in the properties of LDPE at both 20 HPAV and 80 HPAV stages. This finding is consistent with the findings made regarding earlier alternative binder created from rubber. This observation implies that the incorporation of rubber may potentially improve the ability of FAB to resist aging.

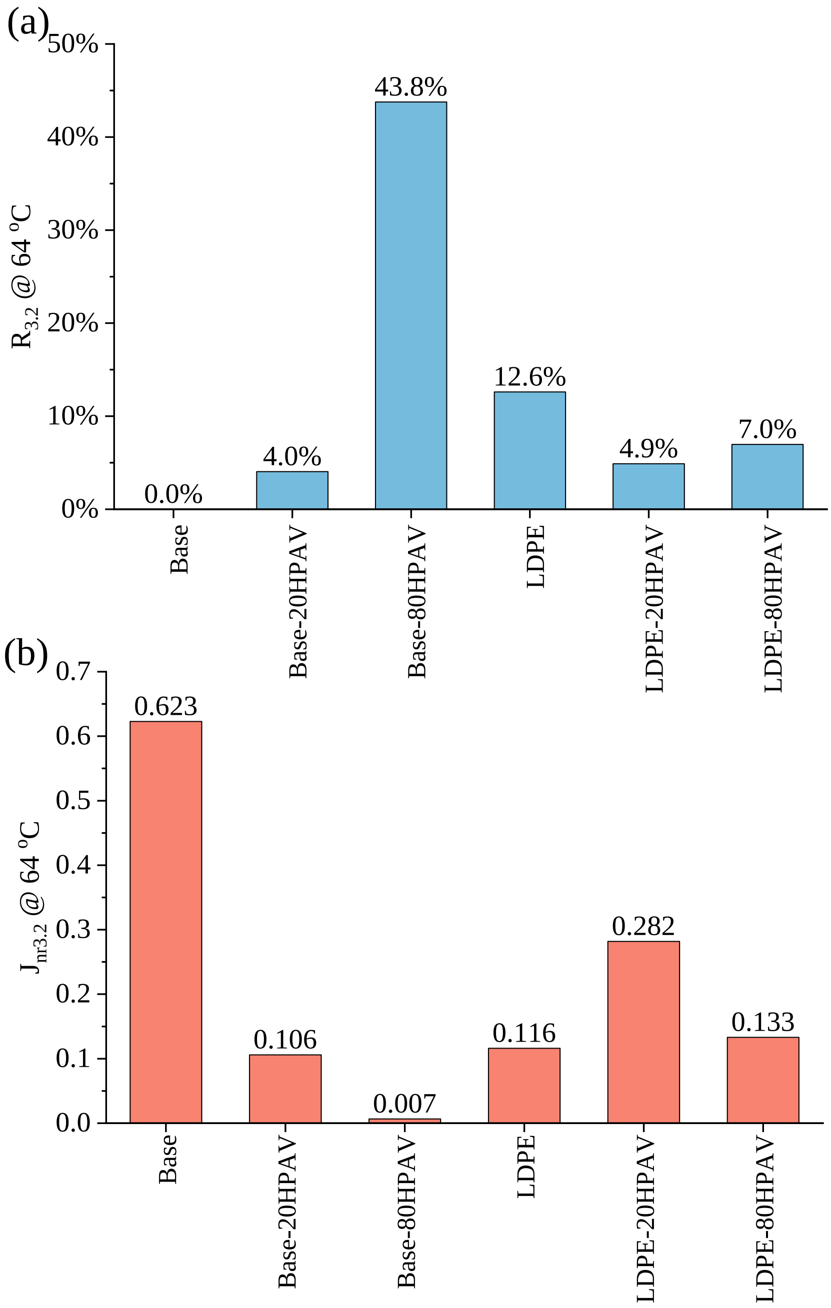


Fig. 4.14 (a)Percent recovery and (b) J_{nr} at temperature 64°C and shear stress level of 3.2 kPa

Consistent with the findings from the temperature sweep experiments, the conclusions of the MSCR evaluations also indicate a deterioration in the performance of the material at elevated temperatures as a result of the degradation of the polymer structure after age, as shown in Fig. 4.14. In general, the aging process of bitumen is associated with an increase in stiffness, which therefore leads to improved performance at high temperatures. The aforementioned trends is observable in the MSCR outcomes related to the base bitumen following to the process of aging. However, when considering LDPE, the process of aging initially results in a certain level of deterioration in the performance at high temperatures after undergoing 20 HPAV aging. This degradation is mostly attributed to the breakage of the polymer network. As the aging process advances, there is a steady enhancement in high-temperature performance. Nevertheless, it still falls short of the performance exhibited by LDPE in its original condition.

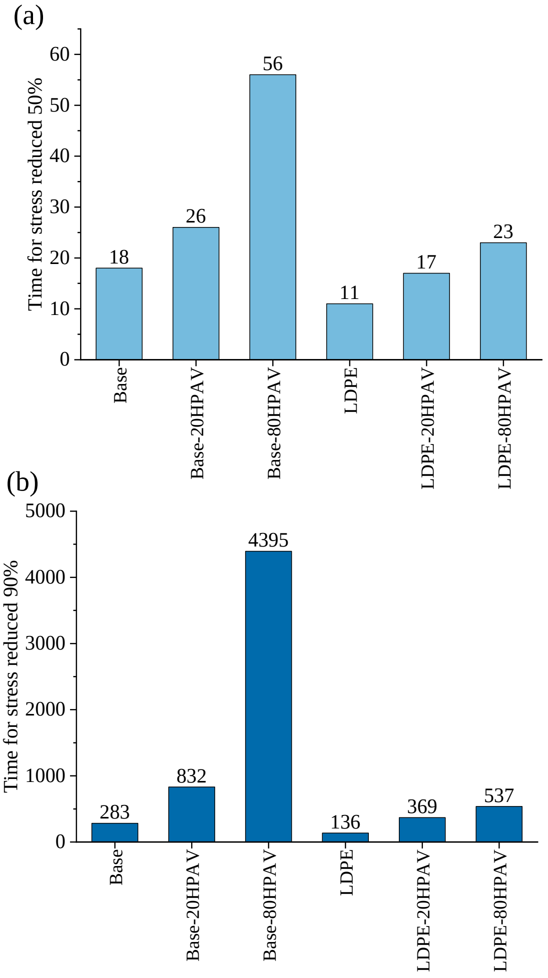


Fig. 4.15 Relaxation time required for the stress to reduce (a) 50% and (b)90%

Fig. 4.15 illustrates an attractive comparison between LDPE and base bitumen concerning their low-temperature properties following aging. This observation strongly suggests that base bitumen loses its elasticity at low temperatures following the aging process. On the other hand, the duration for relaxation of residual stress in LDPE during the aging process stays within a range that is considered acceptable. It is worth noting that the relaxation period of LDPE at 80 HPAV is comparatively lower than that of base bitumen following 20 HPAV. The results mentioned above suggest that FABs made from LDPE exhibit the ability to retain their elasticity even after undergoing the aging process. This characteristic has great potential for enhancing their performance in environments with low temperatures.

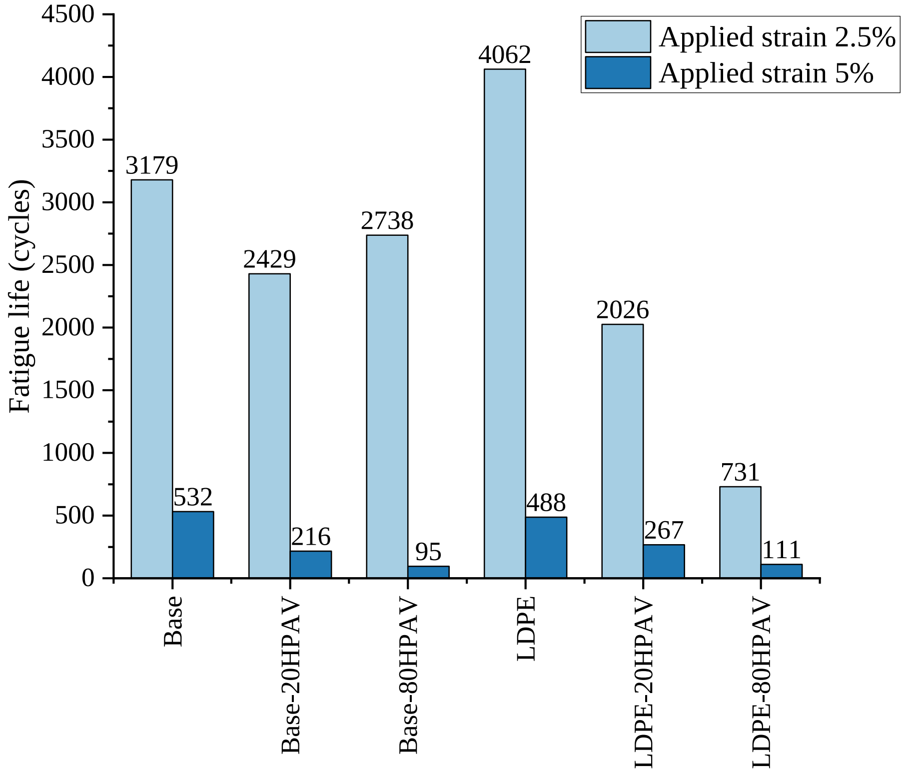


Fig. 4.16 Predicted fatigue lives at 2.5% and 5% strain amplitudes

4.5. MIXTURE LEVEL EVALUATION

Mixture laboratory experiments were conducted to evaluate the strength, moisture damage resistance and raveling resistance of LDPE-based FAB mixture used in porous asphalt.

4.5.1. Indirect tensile strength test

4.5.2. Cantabro test

Fig. 4.17 illustrates the Cantabro mass loss results for both the base bitumen and the LDPE mixture. These results clearly demonstrate the outstanding performance of LDPE in the Cantabro test, with LDPE exhibiting only a quarter of the mass loss compared to the base bitumen. This outcome underscores the excellent adhesion of LDPE-based FAB to aggregates, leading to improved resistance against raveling.

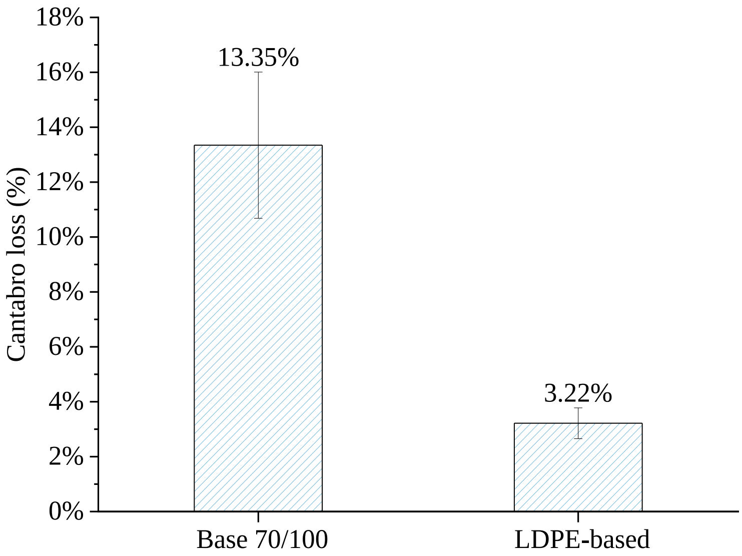


Fig. 4.17 Cantabro loss

4.6. CONCLUSION

This section presents a complete process for the validation of full-alternative binder (FAB) formulations, which is based on previous theoretical and practical research. A range of FAB formulations, comprising diverse waste materials and varying amounts, were created. Following this, a sequence of thorough assessments of rheological characteristics was carried out. Through a comprehensive testing procedure, LDPE and EVA have been identified as the optimal polymer types for FAB modification. A well-balanced FAB formulation was devised, primarily comprising recycled LDPE, waste tire rubber, aromatic oil, and resin. Subsequent aging tests and assessments at the mixture level were conducted to thoroughly examine its performance. The FAB based on LDPE demonstrated remarkable resilience to aging and shown robust adherence to aggregates.

CHAPTER 5.

ENVIRONMENTAL IMPACT

The focus of this chapter is to examine the environmental impacts of selected Rubber Alternative Binder (RAB) and Full-Alternative Binder (FAB), as described in previous parts. The Environmental Cost Indicator (ECI) is utilized to evaluate the financial consequences of the environmental impact associated with both RAB and FAB. The findings of this research study highlight the potential environmental benefits associated with alternative binders when compared to traditional petroleum bitumen.

5.1. INTRODUCTION

One of the primary imperatives underlying the exploration of alternative binders is the mitigation of the environmental repercussions associated with petroleum-based bitumen, spanning its lifecycle from production and application to ultimate disposal. Preceding chapters in this thesis have delineated the formulation and performance evaluation of rubber alternative binder(RAB) and full-alternative binder(FAB). Although those evaluation has illuminated the viability of RAB and FAB from a performance standpoint, the absence of a thorough examination of their environmental impacts is plainly evident. The lack of research in this area necessitates thorough investigation, especially considering the significant environmental impact of the pavement industry throughout history.

Concurrently, the concept of Life Cycle assessment(LCA) has gained currency in the discourse surrounding bituminous materials[116,117]. The Environmental Cost Indicator(ECI), which is derived from LCA, is an indicator expressed in euros to represents the cost of the environmental impact of a product or project[118]. This indicator could provide crucial insights into their environmental footprints. However, the existing research mostly centers around conventional bitumen generated from petroleum, resulting in an absence in the assessment of alternative binders.

The purpose of this chapter is to provide a multifaceted environmental analysis for the RAB and FAB by engaging in environmental analysis: the Environmental Cost Indicator (ECI) within the context of Life Cycle Assessment (LCA) for RAB and FAB. The overall objective is to estimate the environmental impacts of semi-alternative and full-alternative asphalt based on data from the existing literature, and to make a preliminary estimate of the environmental impacts of alternative binder relative to petroleum bitumen.

5.2. ENVIRONMENTAL COST INDICATOR

Environmental cost indicator (in Dutch Milieukosten indicator, or the MKI-score) of RAB and FAB will be calculated to estimate the costs incurred to prevent the environmental burden, the shadow price. In this section, the cost are calculated over the binder production periods, i.e. based on raw materials and the environmental impacts generated by the production process. Within these processes, certain raw material resources may be consumed, or toxic substances may be emitted. The ECI summarizes all impacts into a single value, expressed in euros. The statistics used in this section are sourced from existing literature and are only estimations of environmental impact. It is important to note that owing to differences in material sources and manufacturing processes, these estimations may not fully reflect actual circumstances.

5.2.1. ECI of RAB

The Environmental Cost Index (ECI) is initially calculated for the constituent elements of RAB, which include petroleum-based bitumen and waste tire rubber.

For petroleum bitumen, the potential environmental impacts were derived from an Eurobitume report which defined the inventory associated to extraction, transport and refinement of crude oil[120]. The potential environmental impact for production of 1 ton of paving grade bitumen is shown in Table 5.1 The Potential Environmental Impact for production of 1 ton of bitumen.

Table 5.1 The Potential Environmental Impact for production of 1 ton of bitumen

Impact category	Unit	Total	ECI(€)
Climate change - IPCC 2013	kg CO2 eq	255.38	12.77
Ozone depletion	kg CFC-11 eq	3.79E-05	0.00
Acidification terrestrial and freshwater	mol H+ eq	3.03	12.12
Resource use, Abiotic depletion fuel	kg Antimone	26.37	4.22
TOTAL ECI [€]			**29.11**

The utilization of crumb rubber obtained from waste tires holds promising prospects for environmental conservation, as it involves the recycling of waste materials. The production of one metric ton of Crumb Rubber (CR) requires the processing of 1.45 tons of end-of-life tires. This process demands an energy input of 384 kilowatt-hours of electrical power and 2.99 liters of diesel fuel. Additionally, various ancillary materials are used, including 1.85 kilograms of big-bags, 0.29 kilograms of steel for shredding blades, 0.22 cubic meters of water, and 0.04 kilograms of lubricating oil. The research further considers the future allocation of co-products, namely 0.29 metric tons of steel and 0.16 metric tons of textiles. Due to its high market value, steel was hypothesized to have a recycling rate of 90%. In contrast, textiles were given a comparatively lower recycling rate of 50% due to their possible use as alternative fuel sources in cement kilns[116]. Based on the above analysis, it is converted to ECI and calculated as shown Table 5.2 below.

Table 5.2 The Potential Environmental Impact for production of 1 ton of CR from waste tire

	Gross Energy Requirement [MJ/ton]	**Global Warming Potential [kg CO_2/ton]**
Diesel	145	9.65
Lubricanting Oil	3.19	0.004
Steel blades	10.3	0.669

Big bag	165	5.05
Water	0.305	0.0185
Electricity	3740	223
Textile output	-4890	-39.6
Steel output	-3410	-302
SUM	-4236.205	-103.208
ECI [€]	-0.326	-5.160
Total ECI [€]	**-5.486**	

The energy demands associated with RAB encompass more than just the production of crumb rubber powder and virgin bitumen. They also contain the energy consumption required for the dissolution of rubber in bitumen. Haoran’s studies have established that the manufacturing of one ton of RAB requires an electricity consumption ranging from 3.5 to 5 kwh, as well as a fuel oil demand of 6 to 8 kg[117]. For the sake of analytical precision, average values have been utilized. Since the environmental impact of RAB preparation in Haoran's report includes petroleum bitumen, to avoid duplication of calculations, this data was reduced by the environmental impact of the petroleum bitumen it contained. Based on the above analysis, it is converted to ECI and calculated as shown Table 5.3 below.

Table 5.3 The Potential Environmental Impact for production of 1 ton of RAB

	Unit		**ECI(€)**	**Total ECI(€)**
Energy consumption	kg CO_2 eq	221.01	11.050	11.129
GHG emission	kg Antimone	0.494	0.253	

According to Chapter 3, the selected RAB is NCR60%. For one ton of NCR60%, 370kg of CR and 630kg of bitumen are consumed, and together with the ECI calculated above for the RAB at the production stage, the total ECI for one ton of NCR60% is shown in Table 5.4.

Table 5.4 ECI of production of 1 ton of NCR60%

	CR	**Bitumen**	**Production**
ECI[€]	-2.029	18.339	11.129
Total[€]		27.43	

The Environmental Cost Indicator (ECI) for RAB is €27.43, which is less than the €29.11 attributed to petroleum bitumen, based on the results reported in Table 5.4.

Drawing from the statistics presented above, it is possible to conclude that RAB has a lower environmental effect than petroleum bitumen, indicating its relative eco-friendliness. Furthermore, a comparison of Tables 5.4 and 5.1 demonstrates that the ECI difference between RAB and petroleum bitumen about equals to the environmental benefits achieved by the use of recycled waste tire rubber. This shows that replacing waste tire rubber for petroleum bitumen might have a favorable environmental impact.

It is essential to recognize that the statistics used are based on previous literature and may not entirely correlate with the unique conditions of the current study owing to differences in material sources and manufacturing processes. Even so, preliminary studies show that RAB may offer more environmental benefits than petroleum bitumen.

5.2.2. ECI of FAB

As described in Chapter 4, the most practical Full-Alternative Binder (FAB) is the LDPE-based FAB, which is composed of crumb rubber, recycled LDPE, aromatic oils, and C9 resin, as shown in the formulation table. According to the data presented in Table 5.2, the ECI associated with waste tire crumb rubber is recorded as -€5.48 per metric ton. In the specific context of recycled LDPE, the quantification of carbon dioxide emissions amounts to 29 kg CO_2e/t[121]. This measurement corresponds to an ECI estimate of €1.45 per ton. Upon reviewing the data sheet provided by VENTRACO, it is shown that the ECI for aromatic oils and resins are recorded as €0.159 perkg and €1.197 per kg, respectively. Considering that the phase of the FAB fabrication process that requires the most energy is similar to the corresponding stage in RAB preparation, it is hypothesized that the ECI resulting from FAB production is equivalent to that of RAB. By integrating the previously given data, the associated ECI values have been computed and are systematically displayed in Table 5.5.

Table 5.5 The Potential Environmental Impact for production of 1 ton of FAB

Component	ECI per ton(€)	ECI of FAB(€)
Crumb Rubber	-5.15	**257.4**
Recycled LDPE	1.45	
Aromatic Oil	159.72	
Resin	1197.3	
Production	18.878	

In comparison to petroleum-based bitumen, the ECI of FAB exhibits a significant increase, roughly nine times more than that of its petroleum-based equivalent. As indicated in Table 5.5, the primary factors responsible for the increased ECI of FAB are costs related to Aromatic Oil and Resin materials. Due to the constraints of time and limited options for obtaining supplies in this research, no waste-derived or bio-based alternatives were chosen to replace these two basic ingredients. The use of recyclable materials with a lower ECI would result in a much lower ECI for FAB.

Cashew shell oil, a kind of bio-oil derived from cashew nut processing, is considered to be a sustainable resource. The primary components of this oil consist of cashew phenol, cardol, and 2-methyl cardol, which exhibit similarities to the aromatic portion found in bitumen[122]. Prior research has indicated the effectiveness of cashew shell oil in modifying bitumen, resulting in noticeable improvements in many evaluations of bitumen[123]. Data from Composite Technology Services, Inc. provide a measure of the quantification of CO2 emissions generated during the production of cashew nutshell oil. In Table 5.6 it shows the ECI from the production of 1.62 kg of cashew nutshell oil.

Table 5.6 ECI from the production of 1.62 kg cashew shell oil

	Absorbance	**Shell waste**	**Kernels waste**	**Oil Heat Duty**	**Emission**
kg CO_2 eq	-56.88	34	11.33	0.21	11.33
ECI(€)	-2.844	1.7	0.5665	0.0105	0.5665
Total ECI(€)			**-0.0005**		

Also, in the same report, a bio-resin derived from cashew nutshell oil was developed. In Table 5.7 it shows the ECI from the production of 1.0 kg of bio-resin.

Table 5.7 ECI from the production of 1.0 kg bio-resin derived from cashew shell oil

	Absorbance	**Residol**	**Column Heat Duty**	**Emission**	**Reactor Heat Duty**
kg CO_2 eq	-11.33	3.96	0.008	5.78	1.58
ECI(€)	-0.5665	0.198	0.0004	0.289	0.079
Total ECI(€)			**-0.0791**		

If the same formulation of FAB is prepared based on the above bio-based material, the ECI results are shown in Table 5.8.

Table 5.8 ECI from the production of 1 ton of FAB with bio-based material

Component	**ECI per ton(€)**	**ECI of FAB(€)**
Crumb Rubber	-5.15	**-1.767**
Recycled LDPE	1.45	

Aromatic Oil	-0.308
Resin	-79.1
Production	11.129

As shown in the above table, after replacing the aromatic oil as well as resin with environmentally friendly materials, the ECI of FAB shows a significant reduction, even negative, which indicates that FAB has a great potential in terms of environmental impact.

5.3. CONCLUSION

This chapter performed a tentative observation on environmental impact of rubber alternative binder(RAB) and full-alternative binder (FAB). The environmental impact was quantified through the Lens of Environmental Cost Indicator (ECI). When compared to its petroleum-based alternative, data show that RAB has showed environmental benefits. While one should exercise prudence in extrapolating these results to broader applications, it is provisionally suggestive that RAB could be an environmentally advantageous choice. For FAB, the ECI measurements suggest that, despite its promise as a recycled resource, its current formulation may be more environmentally damaging than petroleum bitumen. The possibility of further modifying the composition of FAB by substituting bio-based or waste-based materials for its present components is a significant mitigating factor. As an outlook for FAB, similar bio-based material was hypothesized to be used in FAB, and the results showed that FAB has great potential for environmental benefits.

The ECI assessments provide an approximated guide for navigating the environmental elements of semi-alternative and full-alternative binders, even if they are not comprehensive. While RAB appears to set a promising precedent for sustainable engineering practices, FAB serves as a cautionary example whose potential eco-friendliness lies latent, awaiting further advancements in material science.

CHAPTER 6. CONCLUSION

This thesis has undertaken an examination and assessment of semi-alternative and full-alternative binders as potential substitutes for bitumen, with the aim of promoting environmental sustainability. This thesis has undertaken an examination and assessment of semi-alternative and full-alternative binders as potential substitutes for bitumen, with the aim of promoting environmental sustainability. The semi-alternative binder section centered on the investigation of Rubber Alternative Binder (RAB). This section conducted a thorough evaluation of RAB, encompassing an extensive analysis of different rubber types and the extent of replacement. Notably, it was discerned that Not-functionalized Crumb Rubber (NCR) from waste tire with a 60% replacement rate exhibited significant advantages over conventional bitumen, particularly in terms of rutting resistance and stress relaxation performance. Furthermore, at the mixture level, NCR demonstrated comparable strength to conventional bitumen while showcasing superior resistance to water-induced damage. Impressively, storage stability tests confirmed minimal segregation tendencies in NCR. The subsequent exploration delved into full-alternative binders, presenting a thorough process for validating Full-Alternative Binder (FAB) formulations, founded on prior theoretical and practical research. A range of FAB formulations with diverse compositions were developed, including a variety of waste materials in different ratios. A comprehensive assessment of rheological properties was conducted, resulting in the determination that LDPE and EVA are the most suitable polymer types for FAB modification. A balanced-performance FAB formulation, predominantly comprising recycled LDPE, waste tire rubber, aromatic oil, and resin, emerged as a frontrunner. The subsequent aging tests and analyses conducted at the mixture level yielded convincing data regarding its ability to withstand the effects of aging and its strong adherence to aggregates. Nevertheless, it is important to recognize that the strength of the mixture remained inferior to that demonstrated by traditional bitumen.

Regarding the impact on the environment, Environmental Cost Indicator (ECI) values were estimated using information from already available literature for both Rubber Alternative Binder (RAB) and Full-Alternative Binder (FAB). The environmental benefits of using used rubber tires instead of petroleum bitumen are supported by preliminary evaluations that show RAB to have a smaller environmental impact than petroleum bitumen. In contrast, the ECI attributed to FAB was higher than that of petroleum bitumen, partly because it contained elements made of non-recycled materials. Notably, FAB showed improved environmental prospects after hypothetical replacement of these non-recycled components with bio-based ones. This emphasizes the necessity of a more thorough investigation of ways to improve the FAB composition, maybe by including waste- or bio-based components.

The results of this study demonstrate that alternative binder has the potential to replace petroleum bitumen in terms of performance. The inherent advantages of lower cost and environmental friendliness associated with waste materials position these alternative binders as strong contenders for future pavement applications. As we look to the horizon of forthcoming research endeavors, there is a compelling case for further exploration of alternative binders, with a pronounced focus on replacing components with even more waste or bio-based materials. For example, the C9 resin and automatic oil used in this FAB study could be replaced with more environmentally friendly materials.

Furthermore, it is imperative to acknowledge the time limitations inherent in this study, which constrained the extent of adjustments made to the formulations. In the future, a more comprehensive optimization of the formulations could be pursued to deal with the identified shortcomings effectively. While the results of this study show potential, it is important to emphasize that this is only a preliminary evaluation of the performance of alternative binders and further rheological and mechanical analysis is required.

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