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Theme

An experimental study on the impact of adding coffee waste powders on the properties of hydrocarbon binders.

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Dedication

We would heartily thank our parents for supporting us and believing in what we have proudly become today. We also thank our precious siblings for being our reliving companions along the way, and we will always appreciate their unconditional love.

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Abstract:

Hydrocarbon binders, derived from oil refining, are essential in road construction to create durable bituminous surfacings. They offer excellent adhesion, flexibility, and waterproofing properties, ensuring their longevity and performance in various conditions. There is a need to improve their subjective properties and the use of agricultural waste by-products in this area is becoming increasingly widespread in developing countries.

Several research projects on bitumen and hydrocarbon binders have been initiated to improve their quality and consequently the performance of roads in terms of durability, safety, and environmental impact, either by using bio-sourced or recycled materials in the composition of hydrocarbon binders.

In this context, we have carried out this experimental study which aims on the one hand to produce a modified bitumen and modified bitumen emulsion by adding food by-products, and on the other hand the possibility of reducing coffee powder waste by making the environment less polluted.

We experimentally studied the modification of bitumen and bitumen emulsion by adding percentages of ground coffee waste to deduce the properties of these two materials concerning pure bitumen, which is 40/50 bitumen, and pure bitumen emulsion, which is 65% cationic emulsion.

The preliminary results obtained are encouraging and will be very useful for more in-depth research in the future.

Key-words: Hydrocarbon binders, road construction, coffee powder waste, bitumen, bitumen emulsion

Résumé :

Les liants hydrocarbonés, dérivés du raffinage du pétrole, sont essentiels dans la construction routière pour créer des revêtements bitumineux durables. Ils offrent d'excellentes propriétés d'adhésion, de flexibilité et d'imperméabilisation, garantissant ainsi leur durabilité et leur performance dans diverses conditions. Il est nécessaire d'améliorer leurs propriétés subjectives et l'utilisation de sous-produits de déchets agricoles dans ce domaine spécifique est de plus en plus répandue dans les pays en développement.

Plusieurs recherches sur le bitume et les liants hydrocarbonés ont été entamé pour le but d'améliorer leur-qualités et par conséquence l'amélioration les performances des routes en termes de durabilité, de sécurité et d'impact environnemental, soit en utilisant des matériaux bio sources or recyclés dant la composition du-liants hydrocarbonés.

Dans ce contexte nous avons mené cette étude expérimentale qui vise d'une part la production d'un bitume modifié et émulsion de bitume modifié en ajoutant des sous-produits alimentaires, et d'autre part la possibilité de réduire les déchets des poudrettes du café en rendent un environnement mois pollué.

Nous avons étudié expérimentalement la modification le bitume et émulsion de bitume en ajoutant des pourcentages en déchets de café moulu pour en déduire les propriétés de ces deux matériaux vis a vis le bitume pur qui est bitume 40/50 et émulsion bitume pure qui est émulsion cationiques 65%.

Les résultats préliminaires obtenus sont encourageants et seront très utiles pour des recherches plus approfondies dans le futur

Mots-clés : Liants hydrocarbonés, construction de routes, les déchets des poudrettes du café ,bitume, Émulsion de bitume

الملخص:

تعتبر مواد الربط الهيدروكربونية، المشتقة من تكرير البترول، ضرورية في إنشاء الطرق لإنشاء أسطح بيتومينية متينة. وهي توفر خصائص ممتازة للالتصاق والمرونة والعزل المائي، مما يضمن طول عمرها وأدائها في مختلف الظروف. وهناك حاجة إلى تحسين خواصها الذاتية، وقد أصبح استخدام المنتجات الثانوية للمخلفات الزراعية في هذا المجال

تحديداً منتشراً على نطاق واسع في البلدان النامية.

وقد بدأت العديد من البحوث حول المواد الهيدروكربونية الرابطة بهدف تحسين جودتها وبالتالي تحسين أداء الطرق من حيث المتانة والسلامة والأثر البيئي، إما باستخدام مواد حيوية المصدر أو مواد معاد تدويرها في تركيبة المواد الهيدروكربونية الرابطة.

وفي هذا السياق، أجرينا هذه الدراسة التجريبية التي تهدف من ناحية إلى إنتاج البيتومين المعدل ومستحلب البيتومين المعدل بإضافة منتجات ثانوية غذائية، ومن ناحية أخرى إمكانية تقليل نفايات مسحوق القهوة بجعل البيئة أقل تلوثًا.

قمنا بدراسة تجريبية لتعديل البيتومين ومستحلب البيتومين بإضافة نسب مئوية من نفايات القهوة المطحونة من أجل استنتاج خصائص هاتين المادتين بالنسبة للبيتومين النقي وهو 50/40 بيتومين ومستحلب البيتومين النقي وهو مستحلب كاتيوني نسبة 65 %.

النتائج الأولية التي تم الحصول عليها مشجعة وستكون مفيدة جداً لإجراء المزيد من البحوث المتعمقة في المستقبل.

الكلمات المفتاحية: روابط هيدروكربونية، بناء الطرق، نفايات مسحوق القهوة,البيتومين,مستحلب البيتومين

Table of contents

List of Figures

List of tables

List of photos

Abbreviations:

ECM: Emulsion Cationic Medium

ECR: Emulsion Cationic Rapid

PMB: Polymer-modified bitumen

PVC: Polyvinyl Chloride

BSD: Basaltic stone dust.

CHA: Coffee husk ash.

AASHTO: American Association of State Highway and Transportation Officials.

OBC: Optimum bitumen content.

TSR: Tensile strength ratio.

VA: Air voids.

VMA: Voids in mineral aggregates.

SBS: Styrene-Butadiene-Styrene

X-SBR: Carboxylated Styrene Butadiene Rubber

HMA: Hot Mix Asphalt

SCG: Spent Coffee Grounds

NF: French Standard

EN: European standard

General Introduction

General Introduction

Hydrocarbon binders are essential components in various industries, particularly road construction. These binders, derived from petroleum refining processes, play a crucial role in creating durable and resilient asphalt pavements. By combining hydrocarbon binders with aggregates, such as gravel and sand, engineers create asphalt mixes that withstand heavy traffic, weathering, and environmental factors. Hydrocarbon binders offer excellent adhesive properties, allowing asphalt to adhere to aggregates effectively, resulting in strong pavement structures. Additionally, they contribute to the flexibility and waterproofing characteristics of asphalt pavements, ensuring longevity and performance in diverse conditions; therefore, to ensure that these properties are achieved, it is necessary to improve the subjective properties of hydrocarbon binders.

Several studies have chosen to add leftover organic materials to bonds (hydrocarbon, hydraulic) for two main reasons: first, to strengthen the characteristics of the linkages; and second, to exploit the good of the remains of organic materials to reduce the risks arising from them.

In our study, we chose to add coffee waste after breaking down some of its organic components and converting it into activated carbon, which raises the following questions: Does the addition of carbonated coffee waste enhance the properties of the hydrocarbon link? and does it answer the difference requirement, which will impact positively on the roads in the future?

To answer this question, we present this research project, where carbonized coffee waste was added to the bitumen material and the bitumen emulsion in certain proportions after studying the properties of each of the aforementioned materials. To present our work, this report goes through five chapters as follows:

- **First chapter:** General information on hydrocarbon binder (bitumen, bitumen emulsion) to know all about them, including definition, composition, and fabrication.
- **Second chapter:** The research and modifications made to bitumen and bitumen emulsion. This chapter aims to learn about previous research and changes to hydrocarbon binder and use it as a reference to complete continuous research.
- **Third chapter:** laboratory experiments and tests that have been applied to our materials.
- **Fourth chapter:** Performance and Results includes a comparison between modified bitumen, bitumen emulsion, and pure bitumen and pure bitumen emulsion

Bibliography

I.General information on hydrocarbon binders.

INTRODUCTION:

This study dealt with the modification of the properties of hydrocarbon materials, and this chapter is devoted to introducing the materials that were worked on

I.1.Definition of Bitumen and its components:

It is widely believed that the term 'bitumen' originated in Sanskrit, where the words 'jatu' meaning pitch, and 'jatu-krit' meaning pitch creating, referred to the pitch produced by some resinous trees. The Latin equivalent is claimed by some to be originally 'with-men' (pertaining to pitch) and by others, 'picture-men' (bubbling pitch), which was subsequently shortened to 'bitumen' and then passed via French into English. In the USA the term Asphalt denotes what in the UK is known as Bitumen. [2]

Bitumen is manufactured from crude oil. It is generally agreed that crude oil originates from the remains of marine organisms and vegetable matter deposited With mud and fragments of rock on the ocean bed. Over millions of years, organic material and mud accumulated into layers hundreds of meters thick, the immense weight of the upper layers compressing the lower layers into sedimentary rock. Conversion of the organisms and vegetable matter into the hydrocarbons of crude oil is thought to be the result of the application of heat from within the earth's crust, pressure applied by the upper layers of sediments possibly aided by the effects of bacterial action and radio-active bombardment. As further layers of sediment were deposited on the sedimentary rock where the oil had formed, the additional pressure squeezed the oil sideways and upwards through porous rock. Where porous rock extended to the earth's surface, oil seeped through resulting in the surface seepages described earlier. Fortunately, the majority of oil and gas was trapped in porous rock which was overlain by impermeable forming gas and oil reservoirs. Here the oil remained until its presence was detected by seismic surveys and recovered by drilling through the impermeable rock. [2]

Bitumen, in general, consists of a complex mixture of hydrocarbons and the initial composition largely depends on its origin (the origin of crude oil)

And refining techniques. The most important components are as follows:

Carbon: %80 - %87, hydrogen: %08 - %12, oxygen: %1-%3, sulfur: %1-%6

nitrogen: %0 - %1.5. [1]

and structurally, bitumen consists of three main components, namely:

- **Asphaltenes:** are large black spherical particles with a molecular structure ranging from 1000 to 3000 MOL and take one of the following formulas: x (n2H Cn)-x (CnHn). Asphaltenes are responsible for the hardness and fragility of asphalt and account for up to about 30%. [1]
- **Maltin:** these are brown to black molecules with a density of 0.99–1.09 surrounding asphaltenes and a structure close to it but with a hydrogen ratio greater than carbon and molecular weights ranging from 700–1200 mol. Maltin plays an important role in giving

asphalt the properties of elongation, viscosity, and adhesion. And it even represents about 70%. [1]

- **Oil:** is a viscous hydrocarbon mixture with a light to dark color and a structure of 200–600 MOL, and it also contains paraffin. [1]

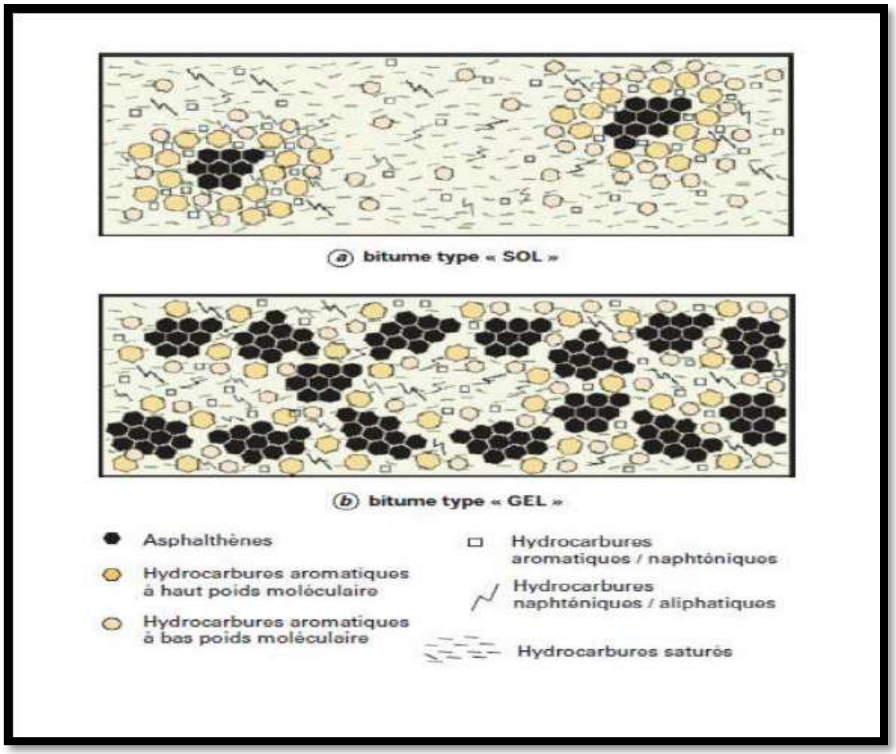

Fig I.1. Schematic representation of two compositions of pure bitumen.[1]

I.2. Uses of bitumen :

Bitumen or asphalt has many applications, but they are primarily limited to the road field; we will discuss the most relevant ones. [1]

- Paving roads, sidewalks, and airport floors.
- Ceiling, subterranean, and pipe protection.
- Use as an insulator to prevent water leaks.
- Enhance water conservation, waste storage, reservoirs, and irrigation channels.
- To strengthen water conservation areas, waste storage areas, reservoirs, and irrigation channels. [1]

I.3. Physical properties of bitumen:

Asphalt has numerous features, the most significant of which are given here:

- Cohesion: Retractable without detachment or cleavage.
- Adhesion to aggregates.
- Viscosity: A measure of liquid mass resistance to deformation, which decreases with increasing temperature.
- Aging causes the loss of some traits, particularly cohesiveness. [1]

I.4. Types of Bitumen:

There are various varieties of bitumen available with varying qualities, specifications, and applications depending on the needs of the consuming industry. The specifications of bitumen vary in terms of safety, solubility, physical qualities, and durability.

I.4.1. Penetration Grade Bitumen:

Penetration grade bitumens are specified by the penetration and softening point tests but are designated by penetration only; eg 100 pen bitumen has a penetration of 100 ∓ 20. [2]

According to the penetration test, we can distinguish several categories:

- Extremely hard bitumen (20/30).
- Hard bitumen (40/50).
- Semi-solid bitumen (80/100).
- Semi-soft bitumen (180/220).
- Soft bitumen (280/300).
- Very soft bitumen (300/350).

Fig I.2. Penetration Grade bitumen. [4]

	Units	Bitumen 40/50	Bitumen 60/70	Bitumen 80/100	Bitumen 100/120	Test Methods
Specific Gravity @25°C	-	1.01-1.06	1.01-1.06	1.01-1.05	1.01-1.04	ASTM D-70
Penetration @25°C, 100gm, 5sec	0.1MM	40-50	60-70	80-100	100-120	ASTM D-5
Softening Point, Ring & Ball	°C	52-60	49-56	45-52	42-49	ASTM D-36
Ductility @25°C, after TFOT, Min	CM	100	100	100	100	ASTM D-113
Loss on Heating, Max	%Wt	0.2	0.2	0.5	0.5	ASTM D-6
Drop in Penetration after Heating, Max	%	20.0	20.0	20.0	20.0	ASTM D-6 & D-5
Flash Point Cleveland open cup, Min	°C	250.0	250.0	232.0	250.0	ASTM D-92
Solubility in CS2, Min	%Wt	99.5	99.5	99.5	99.5	ASTM D-4
Organic Matter Insoluble in CS2, Max	%Wt	0.5	0.5	0.5	0.5	ASTM D-4

Fig I.3: Penetration Grade Bitumen Specification. [4]

I.4.2.Oxidized Bitumen :

The refinery bitumen is further treated by adding processed air. This will result in oxidized bitumen. Air is introduced under pressure into soft bitumen while keeping a controlled temperature. The reaction between the supplied oxygen and bitumen components produces compounds with greater molecular weights. As a result, the concentration of asphaltenes and maltenes increases, resulting in a tougher mix. This tougher mixture has lower ductility and temperature sensitivity. [4]

The oxidized bitumen is used in industrial applications such as roofing and coating for pipes.[4]

Fig I.4: Oxidized Bitumen [4]

	GRADES					TEST METHOD
	BITUMEN R 85/25	BITUMEN R 85/40	BITUMEN R 95/25	BITUMEN R 95/40	BITUMEN R 115/15	
Relative Density at 25 deg C, g/ml	1.00-1.06	1.00-1.05	1.00-1.05	1.00-1.05	1.00-1.06	ASTM D70
Softening Point (Ring and Ball), dec C	80-90	80-90	90-100	90-100	110-120	ASTM D36
Penetration at 25 °C, 0.1 mm	20-30	35-45	20-30	35-45	10-20	ASTM D5
Flash Point (Cleveland open Cup), °C, Min	200	200	200	200	200	ASTM D92
Loss on heating % by mass	0.2	0.5	0.2	0.5	0.2	ASTM D6
Ductility at 25 °C cm, min	2.0	2.0	2.0	2.0	2.0	ASTM D113
Solubility in toluene % wt min	99.0	99.0	99.0	99.0	99.0	EN12592:2000

Fig I.5: Specification for oxidized grade bitumen [4]

I.4.3.<u>Cutback Bitumen (Hydrated asphalt):</u>

To lessen its viscosity, asphalt is mixed with light petroleum distillation fractions such as kerosene or some light oils. This technique, in particular, permits it to be employed at temperatures significantly lower than those required for pure bitumen. When exposed to weather conditions, the solvents evaporate, and the asphalt returns to its original semi-solid state. Hydrated asphalt is commonly utilized in surface layers, bonding layers, and maintenance operations. [4]

Fig I.6. cutback bitumen [4]

We may identify three sections of cutback based on the quality of additives and the extent of their evaporation:

- **Rapid curing cutback:** So that the additive is a highly volatile diluent such as naphtha or gasoline oil. [4]
- **Medium curing cutback:** The additive is a diluent with medium evaporation, like kerosene. .[4]
- **Slow curing cutback:** The added oils are slow to volatilize. [4]

Medium Curing (MC)	MC-30		MC-70		MC-250		MC-800		MC-3000		Test Methods
Property	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
Kinematic viscosity at 60°C, mm2/s	30	60	70	140	250	500	800	1600	3000	6000	ASTM D-2170
Flash point (Cleveland open cup), °C	38	-	38	-	66	-	66	-	66	-	ASTM D-92
Distillation test: Distillate, volume percent of total distillate to 360°C:											ASTM D-402
to 225°C	-	35	-	25	-	20	-	-	-	-	
to 260°C	30	75	10	70	5	55	-	40	-	15	
to 316°C	75	95	65	93	60	90	45	85	15	75	
Residue from distillation to 360°C, percent volume by difference	50	-	55	-	67	-	75	-	80	-	
Tests on residue from distillation:											
Viscosity at 60°C, Pa	30	120	30	120	30	120	30	120	30	120	
Ductility at 25°C, cm	100	-	100	-	100	-	100	-	100	-	ASTM D-113
Solubility in trichloroethylene, %	99.0	-	99.0	-	99.0	-	99.0	-	99.0	-	ASTM D-4
Water, %	-	0.2	-	0.2	-	0.2	-	0.2	-	0.2	ASTM D-95

Fig I.7. Medium Curing Cutback Bitumen Specification[4]

Rapid Curing (RC)	RC-70		RC-250		RC-800		RC-3000		Test Methods
Property	Min	Max	Min	Max	Min	Max	Min	Max	
Kinematic viscosity at 60°C, mm2/s	70	140	250	500	800	1600	3000	6000	ASTM D-2170
Flash point (Cleveland open cup), °C	-	-	27	-	27	-	27	-	ASTM D-92
Distillation test: Distillate, volume percent of total distillate to 360°C:									ASTM D-402
to 190°C	10	-	-	-	-	-	-	-	
to 225°C	50	-	35	-	15	-	-	-	
to 260°C	70	-	60	-	45	-	25	-	
to 316°C	85	-	80	-	75	-	70	-	
Residue from distillation to 360°C, percent volume by difference	55	-	65	-	75	-	80	-	
Tests on residue from distillation:									
Viscosity at 60°C, Pa	60	240	60	240	60	240	60	240	
Ductility at 25°C, cm	100	-	100	-	100	-	100	-	ASTM D-113
Solubility in trichloroethylene, %	99.0	-	99.0	-	99.0	-	99.0	-	ASTM D-4
Water, %	-	0.2	-	0.2	-	0.2	-	0.2	ASTM D-95

Fig I.8. Rapid Curing Cutback Bitumen Specification. [4]

Slow Curing (SC)	SC-70		SC-250		SC-800		SC-3000		Test Methods
Property	Min	Max	Min	Max	Min	Max	Min	Max	
Kinematic viscosity at 60°C, mm2/s	70	140	250	500	800	1600	3000	6000	ASTM D-2170
Flash point (Cleveland open cup), °C	66	-	79	-	93	-	107	-	ASTM D-92
Distillation test:									ASTM D-402
Total distillate to 360°C, volume %	10	30	4	20	2	12	-	5	
Solubility in trichloroethylene, %	99.0	-	99.0	-	99.0	-	99.0	-	ASTM D-2042
Kinematic viscosity on distillation residue at 60°C, mm2/s	400	7000	800	10000	2000	16000	4000	35000	ASTM D-2170
Asphalt residue:									ASTM D-243
- Residue of 100 penetration, %	50	-	60	-	70	-	80	-	ASTM D-5
- Ductility of 100 penetration residue at 25°C, cm	100	-	100	-	100	-	100	-	ASTM D-113
Water, %	-	0.5	-	0.5	-	0.5	-	0.5	ASTM D-95

Fig I.9. Slow Curing Cutback Bitumen Specification. [4]

I.4.4. Polymer - Modified Bitumen :

Since it has been used for thousands of years, bitumen is becoming an increasingly valuable material in engineering. The use of polymers—virgin, waste, or blends of polymers—for bitumen modification is gaining traction. Over the past 20 years, both the number of academic groups studying polymer-modified bitumen and the body of peer-reviewed research on the subject have increased dramatically. Research on polymer-modified bitumen first focused on empirical and technical metrics including aging and softening points. Nonetheless, a broad range of methodologies have been employed recently to examine the impact of polymer addition on bitumen properties, polymer-bitumen morphology, and bitumen-polymer interaction. .[4]

Polymer-modified bitumen (PMB) is an engineered bitumen grade used in pavement, heavy-duty traffic roads, and home roofing solutions. It provides extra strength, high cohesiveness, and resistance to fatigue, stripping, and deformations. .[4]

Fig I.10.Polymer - Modified Bitumen [4]

- **Common types of polymer-modified bitumen:**

The following table lists some common asphalt cement and HMA modifiers and their general purpose/use.

Type	General Purpose or Use	Generic Examples
Filler	Fill voids and therefore reduce optimum asphalt content Meet aggregate gradation specifications Increase stability Improve the asphalt cement-aggregate bond	Mineral filler crusher fines lime Portland cement fly ash Carbon black
Extender	Substituted for a portion of asphalt cement (typically between 20–35 % by weight of total asphalt binder) to decrease the amount of asphalt cement required	Sulfur Lignin
Rubber	Increase HMA stiffness at high service temperatures Increase HMA elasticity at medium service temperatures to resist fatigue cracking	Natural Latex Synthetic latex (e.g., Polychloroprene latex) Reclaimed rubber (e.g., crumb rubber from old tires)

Table I.1. Common types of polymer-modified bitumen [4]

I.5. Definition of an emulsion:

Bitumen and water are distributed in globules to form two-phase bitumen emulsion systems [5]. They fall into four categories: clay-stabilized emulsions, cationic, anionic, and nonionic. Neutral nonionic emulsions are seldom used for road applications. Emulsions stabilized with clay are employed in the industry. Schade van Westrum applied for a patent in 1906 on bituminous dispersions in water for the construction of roads. Because cationic emulsifiers may adsorb onto solid surfaces, they are widely used. [6]

I.6. Types of emulsifiers:

Bitumen emulsions are divided into three sections:

I.6.1. Quick-freezing emulsion:

Quick-freezing emulsion: Paint and irrigation work are employed for surface treatment work because they don't require mixing procedures and may be applied at room temperature with a degree of use ranging from 50 °C. This quickly separates the emulsion after the road is cleaned, leaving bitumen as a cover with aggregate. [3]

I.6.2. Medium freezing emulsion:

This kind is separated into two categories:

- M-1: This liquid is a low-viscosity substance used on roads to remove coarse materials like broken stones, gravel, or debris that has been sieved.
- M-2: The material is commonly used in mixing stations with coarse gravel aggregate and broken stones, and it has an average viscosity. [3]

I.6.3. Slow-freezing emulsion:

This type works on projects that take a lot of time. This works well for fixing and improving the properties of fine aggregates, or aggregates that contain a lot of soft grains, such as fine sand or some special soils This kind works on labor-intensive tasks, restoring and enhancing the characteristics of fine aggregates, such as fine sand or soil with a high percentage of soft grains. [3]

I.7 Classification and specification of bitumen emulsion:

The emulsion typically contains water between 25% and 45% and asphalt between 55% and 75%. The extraction factor ranges from 0.5% to 3%, and the most common type is anionic soap. The speed of splitting or freezing depends on the type and amount of emulsifying agent, and depending on the type of emulsifying agent [7], bitumen emulsions are divided into two basic types:

I.7.1 Anionic Emulsion:

The use of fatty acids, alkyl sulfates, or sulfonates as anionic bitumen emulsifiers has been in use since the late 1920s. [6] They require deprotonation of a base such as sodium hydroxide to produce a negative charge on the main group, and anionic route emulsions are categorized in order of stability as follows:

a) Class A1: unstable. A cold-applied emulsion that breaks down quickly upon application and is often not appropriate for blending with aggregate. [7]

b) Class A2: semi-stable. An emulsion that can be used cold and is stable enough to blend with specific aggregate grades before breaking down. [7]

c) Class A3: Stable. An emulsion is employed that is sufficiently stable both mechanically and chemically for all applications involving mixing with aggregates, including those that include high percentages of particles or chemically active ingredients like hydrated lime or cement. [7]

d) Class A4: sealant slurry. an emulsion made specifically to be used cold during the slurry seal process. [7]

NOTE: If necessary, additives can be added at the time of laying to change the mix's viscosity or setting time. [7] The division of this class will be as follows:

d.1) Class A4: slow setting. Suitable for combining in mobile mixing machines, bulk transit concrete mixers, or basic mixers for hand laying. [7]

d.2) Class A4: rapid setting. Use only with specially designed mobile mixing equipment. [7]

Caractéristiques	Méthodes normalisées de référence	Rapide				Lente			Surstabilisée	
		Classes				Classes			Classes	
		EAR 50	EAR 55	EAR 60	EAR 65	EAL 55	EAL 60	EAL 65	EAS 55	EAS 60
Teneur en eau (%)	NF T 66-023	49 à 51	44 à 46	39 à 41	34 à 36	44 à 46	39 à 41	34 à 36	44 à 46	39 à 41
Pseudo viscosité Engler à 25 °C		< 6	< 15	> 2	> 6	< 15	> 2	> 6	< 15	< 2
Pseudo viscosité STV à 25 °C (diamètre de l'orifice d'écoulement 4 mm)	NF T 66-020	—	—	< 18	—	—	< 18	—	—	< 18
Homogénéité : - particules supérieures à 0,63 mm	NF T 66-016	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
- particules comprises entre 0,63 et 0,16 mm		< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25
Indice de rupture	T 66-019	> 0,5	> 0,5	> 0,5	> 0,5	0	0	0	—	—
Stabilité au ciment	NF T 66-024	—	—	—	—	> 2	> 2	> 2	≤ 2	≤ 2
Charge des particules	T 66-021	négative	négative	négative	négative	négative	négative	négative	négative	négative

Fig I.11. Specification of anionic emulsions[4]

I.7.2. Cationic Emulsion:

The cationic group of emulsifiers, including quaternary amine salts, amides, imidazolines, ethoxylated amines, and simple primary, secondary, or tertiary amines, is the preferred type for most road applications. Catalytic emulsions, developed in the 1950s, require an acid to protonate the head groups to activate them. [6] Cationic road emulsions are classified in order of stability:

a) Class K1: rapid-acting emulsion that exhibits early resistance to precipitation and quick link deposition when in contact with road surfaces, allowing for the use of both cold and hot grades. [7]

b) Class K2: medium acting. The binder in emulsion deposits slowly enough to enable mixing with some clean coarse aggregate before refracting to create a continuous sticky film that doesn't require stripping or utilizing cool. [7]

c) Class K3: slow acting. Class K3 cationic slurry seal emulsions are cold-applied emulsions with delayed binder deposition, allowing mixing with fine particles before breaking to generate a continuous sticky layer without peeling, suitable for specialized mobile mixing equipment. [7]

Caractéristiques	Méthodes normalisées de référence	Rapide			Semi-rapide			Lente		Surstabilisée		
		Classes			Classes			Classes		Classes		
		ECR 60	ECR 65	ECR 69	ECM 60	ECM 65	ECM 69	ECL 55	ECL 60	ECL 65	ECS 55	ECS 60
Teneur en eau (%)	NF T 66-023	39 à 41	34 à 36	30 à 32	39 à 41	34 à 36	30 à 32	44 à 46	39 à 41	34 à 36	44 à 46	39 à 41
Pseudo viscosité Engler à 25 °C	NF T 66-020	2 à 15	> 6	—	> 2	> 6	—	< 15	2 à 15	> 6	< 15	> 2
Pseudo viscosité STV à 25 °C (diamètre de l'orifice d'écoulement 4 mm)		—	—	> 9	< 18	—	> 9	—	—	—	—	< 18
Homogénéité :												
- particules supérieures à 0,63 mm	NF T 66-016	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
- particules comprises entre 0,63 mm et 0,16 mm		< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25	< 0,25
Stabilité au stockage par décantation (1)	T 66-022	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Adhésivité (2) :												
- émulsion à stockage limité (1)												
1ère partie de l'essai	NF T 66-018	≥ 90	≥ 90	≥ 90	≥ 90	≥ 90	≥ 90	—	—	—	—	—
2e partie de l'essai		≥ 75	≥ 75	≥ 75	≥ 75	≥ 75	≥ 75	—	—	—	—	—
- émulsion stockable (1)					≥ 75	≥ 75	≥ 75	≥ 75	≥ 75	≥ 75	—	—
Indice de rupture	NF T 66-017	< 100	< 100	< 100	80 à 140	80 à 140	80 à 140	> 120	> 120	> 120	—	—
Stabilité au ciment	NF T 66-024	—	—	—	—	—	—	—	—	—	≤ 2	≤ 2
Charge des particules	NF T 66-021	positive	positive	positive	positive	positive	positive	positive	positive	positive	positive	positive

Fig I.12. Specification of cationic emulsions[4]

I.8. Characterization of bitumen emulsions:

Creating bitumen emulsions involves a difficult stability problem. A stable dispersion is required for storage and transit without breaking, but once the emulsion is put on the road surface, it should break rapidly. From a technological point of view, bitumen emulsions' stability, adhesivity, and viscosity are said to be their three key characteristics. [2]

I.8. 1. Emulsion stability:

This includes the two contradictory requirements for bituminous emulsion stability: breaking rate and storage stability.

I.8. 1.1. Storage stability:

Insufficient storage stability causes emulsion settling, Gravity acts on denser bitumen droplets, which can be estimated using Stokes' law. Repulsion and attraction forces in lotions are also present. Repulsion arises from electrostatic double layers on droplets, while attraction is related to droplet mass. After colonization, bitumen droplets aggregate into clumps called flocculation and coalesce into a larger sphere, either spontaneously or mechanically. [2]

I.8. 1.2. Breaking rate:

Emulsifier molecules are present in emulsions both on droplet surfaces and in the aqueous phase. Ions from micelles and droplet surfaces revert to equilibrium when emulsifier ions are eliminated. When the emulsion comes into contact with mineral aggregate, the surface charge is weakened due to ion absorption. The disintegration process is started by the droplet, and as it gets closer to the aggregate, bitumen melts more quickly due to the droplet's surface charge depleting. [2]

I.8. 2. Emulsion adhesivity:

Cationic emulsifiers are particularly effective in reducing the free surface energy of polar aggregates and creating a thermodynamically stable state with minimal surface energy by attracting the emulsifier to the aggregate surface. Most cationic emulsifiers are anti-stripping agents; this ensures initial adhesion [2]. However, the quality of the bond between asphalt and aggregate depends on several factors, namely:

- Type and amount of emulsifier.
- Bitumen type and composition.
- pH value of emulsifier solution.
- Particle size distribution of emulsion.
- Aggregation type.

In all applications where bitumen is used as a binder between solid surfaces, a key requirement is that the bitumen "wet" the surface to create maximum contact area. However, when the aggregate surface is covered with water, the wetting of the aggregate becomes a three-phase phenomenon, which can only occur when the balance of interfacial energy favors asphalt wetting. [2]

I.8. 3. Viscosity:

Since bitumen emulsions are typically sprayed on, the system's viscosity is important for applying bitumen. The way an emulsion is dispensed from a spray bar depends on its viscosity which is defined as the time it takes for a given volume to flow out of a container, using flow cups to assess its viscosity or Rheometers for better study. A liquid's rheology, also referred to as its viscosity, is its behavior under force; it determines the material's physical characteristics for a certain use, such as bitumen emulsions. [2]

I.9. Advantages of using Bitumen Emulsion:

- ✓ The manufacturing and processing are handled by a team of highly skilled professionals from the industry who are dedicated to producing high-quality bitumen Emulsion**.**
- ✓ No need for the heating process when operating.
- ✓ No risk of fire during storage, transportation, and implementation
- ✓ Extensive application in road construction and maintenance. [4]

I.10. Nature of the constituents of a bitumen emulsion

1. **binder:** it may be pure or modified bitumen: Bitumen is a by-product of heavy hydrocarbons and is a black crude oil residue obtained through natural distillation or refinery distillation. [5]
2. **water:** Water from the public network is usually used as the water for the emulsion. On the other hand, the ion content needs to be controlled. At high concentrations, these can promote the coalescence of bitumen droplets. In addition, magnesium and calcium ions may react with some emulsifiers to form compounds that no longer have surfactant properties. To avoid these disadvantages, maximum concentration limits for these ions in water are set. Magnesium ions are 150 mg/L, and calcium ions are 200 mg/L. [5]
3. **Chemical agents: emulsifier and acid:** The fatty amine (diamine, polyamine), quaternary ammonium, amido-amine, and imidazoline types of emulsifiers are utilized in the road sector. Since they are more soluble in this phase, they are typically added to water.[5]Certain commercial emulsifiers, though, dissolve in bitumen. Since the majority of emulsifiers lack surfactant qualities by nature, protonating them in solution frequently requires the addition of an acid. The aqueous phase of the emulsion is thus formed by the water, emulsifier, and acid assembly. [5]

I.11.Manucfacture of bitumen emulsion:

Bitumen emulsions are formed by mixing bitumen and water, separating and dispersing it in the water phase. The aqueous phase typically contains emulsifiers, such as acidification or alkalization. Colloid mills are used for intense mixing, while SMEP (20) uses intense turbulence to distribute bitumen and water phases. To mix bitumen and water, an emulsifier is added, either by dissolving it in water with an acid or base or by adding it to the water shipped to the plant. The manufacturing process can be discontinuous or continuous. The bitumen must be heated to reduce its viscosity, and the emulsion is pushed in different directions toward the mill head at predetermined rates. The bitumen-water interface stabilizes the solution. After leaving the mill, the emulsion must be below -95°C to prevent boiling off and raising bitumen content. Industrially produced emulsions are stored in transportable containers, occasionally heated and agitated to prevent bitumen droplets from settling. [6]

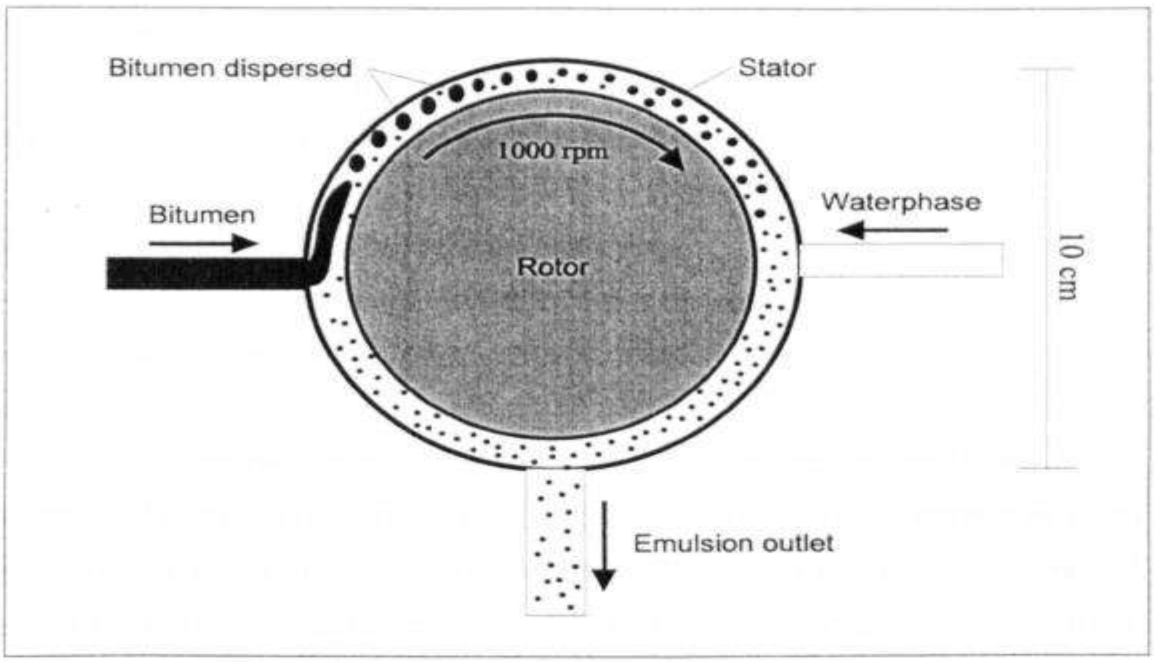

Fig I.13. Diagram of the emulsification process[6]

CONCLUSION:

In light of all spoken before, in conclusion. Depending on where it comes from and how it is made, there are numerous varieties of bitumen and bituminous emulsion, it is possible to describe them as a highly hydrocarbon complex mixture with viscoelastic properties.

II. Research on hydrocarbon binders.

INTRODUCTION:

There are always updates in road construction in particular or civil engineering in general in terms of the materials used therein. Engineers constantly improve the properties of these materials in various ways. and some of these researches are mentioned in this chapter.

II.1. Bitumen modified by industrial by-products:

II.1.1.PERFORMANCE OF POLYMER MODIFIED BITUMEN FOR FLEXIBLE PAVEMENTS:

- Polymer-modified bitumen (PMB) is a specially engineered type of bitumen where polymers are added to improve its properties. The addition of polymers to bitumen allows for the modification of physical properties such as softening point, brittleness, and ductility**.**

Fig. II . 1. Polymer

ABSTRACT: The study presents an experimental study on flexible pavements with bituminous surfacing in India. It reveals that conventional bitumen performance has limitations due to increased traffic, commercial vehicle overloading, and temperature variations. The study shows that bituminous concrete mix with polymer modified bitumen significantly improves rutting resistance, indirect tensile strength, and resilient modulus.[8]

Indirect Tensile Strength of Bituminous Concrete Mixes		
Test Sample	Indirect Tensile Strength (kPa)	
	Bituminous Concrete Mix with 60/70 Grade Bitumen	Bituminous Concrete Mix with PMB-70
1	444	592
2	553	621
3	480	561
4	492	591

Resilient Modulus of Bituminous Concrete Mixes		
Test Temperature (°C)	Resilient Modulus (MPa)	
	Bituminous Concrete Mix with 60/70 Grade Bitumen	Bituminous Concrete Mix with PMB-70
30	3,153	3,764
35	2,580	3,366
40	1,800	2,147

Table II.4: Results.[8]

CONCLUSION: The study reveals that Polymer Modified Bitumen outperforms conventional bitumen in terms of performance, with high elastic recovery (79%), better age resistance, and higher weight loss in a thin film oven, Marshall stability (27%), and significantly higher rutting resistance.The bituminous concrete mix with polymer modified bitumen exhibits a 20% higher indirect tensile strength at 30°C, and a significantly higher resilient modulus at 30-40°C test temperatures.[8]

II. 1.2.STUDY ON WASTE POLYVINYL CHLORIDE MODIFIED BITUMEN FOR PAVING APPLICATIONS

- PVC stands for polyvinyl chloride, which is a synthetic thermoplastic material made by polymerizing vinyl chloride. The properties of PVC depend on the added plasticizer. It is commonly used for various purposes such as making clothing, shoes, pipes for carrying water, electrical insulation, films, and more.

Fig. II. 2. PVC

ABSTRACT: The world is facing a waste crisis due to the problematic plastic polyvinylchloride (PVC). A study found that PVC pipe waste can be used as a modifier in making bituminous products for paving applications. The blend was treated with a chemical and compared to unmodified bitumen. The results showed increased strength, stability, and resistance to permanent deformation in rutting. [9]

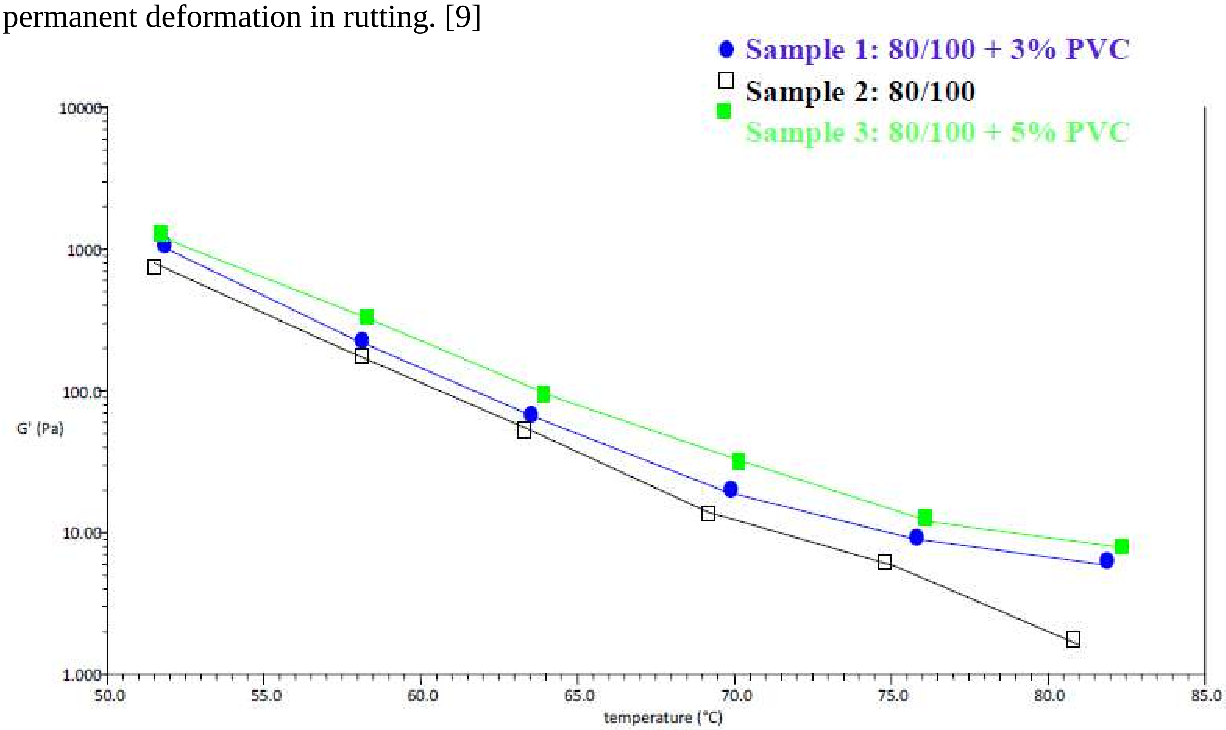

Fig. II.3: Effect of addition of PVC pipe waste on storage modulus.[9]

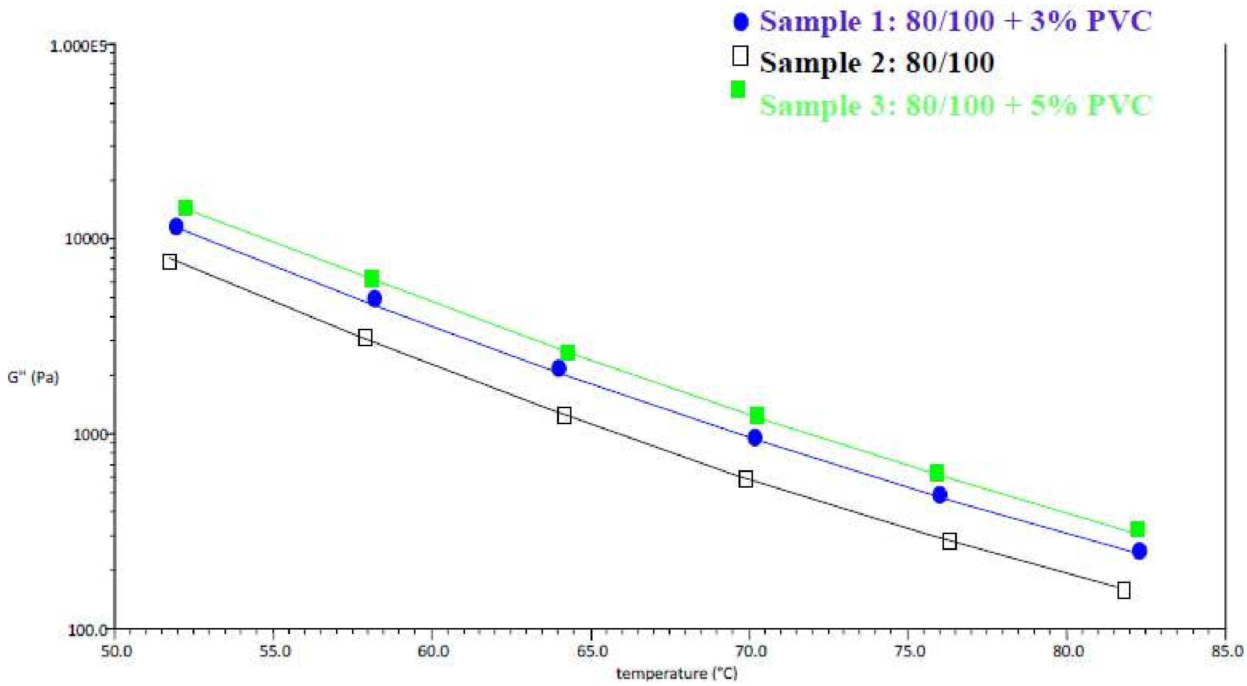

Fig. II.4: Effect of addition of PVC pipe waste on loss modulus[9]

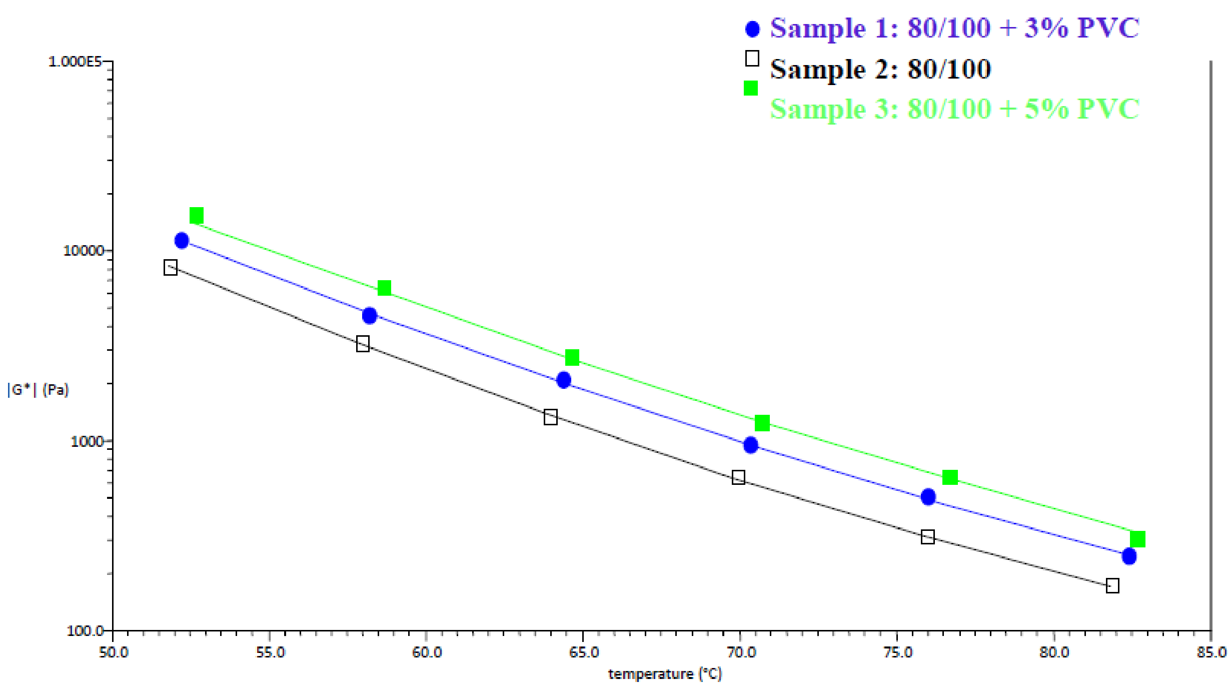

Fig.II.5: Complex modulus of neat and waste PVC modified binders at different Temperatures.[9]

CONCLUSIONS:

Based on the results of the laboratory study the following conclusion can be drawn:

1. PVC pipe waste can be successfully used in paving applications.
2. The addition of PVC pipe waste to the bitumen enhances both the binder's as well as the mix's properties.
3. Waste PVC modified binder showed better G' and G" values which concludes to the increased stiffness of the binder as well as better viscous response of the binder.
4. Improved phase angle and complex modulus values were achieved after addition of waste PVC to the binder. It shows better resistance to the permanent deformation of the mix as compared to the mix prepared by neat VG 10 binder.[9]

II. 1.3. Analysis of the Real Performance of Crumb-Rubber-Modified Asphalt Mixtures:

- Crumb rubber modified asphalt mixture is a type of asphalt where crumb rubber modifier (CRM) is added to improve the performance of the bitumen binder. This modification process involves blending crumb rubber with asphalt at elevated temperatures, resulting in enhanced properties such as improved durability and resistance to cracking. It is a sustainable solution that utilizes recycled rubber to enhance the overall quality of asphalt pavements.

Fig. II.6. Crumb-Rubber

ABSTRACT: The study evaluates the field performance of crumb-rubber-modified asphalt mixtures as a surface layer on high-volume traffic roads. It compares the performance of these mixtures to traditional SBS-modified bitumen under severe traffic and climate conditions. The results suggest that this application could be a potential solution to minimize environmental problems caused by end-of-life tires in landfills.[10]

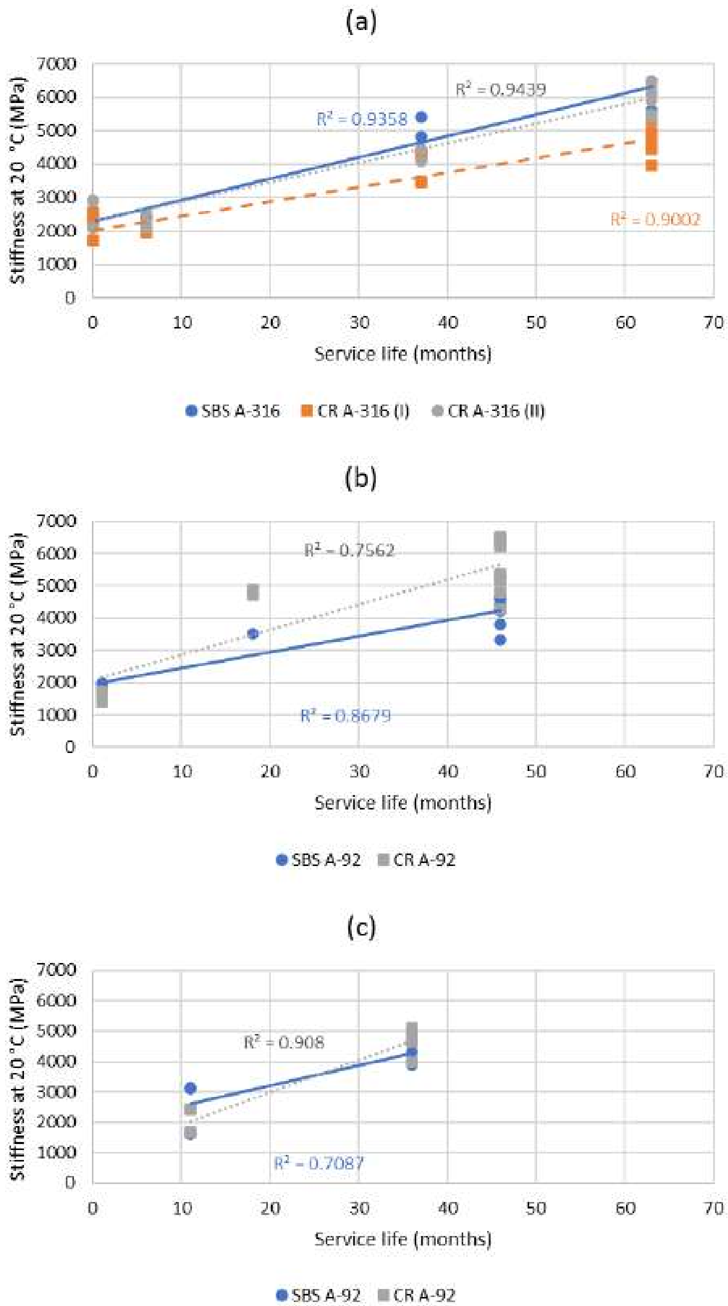

Fig. II.7 Evolution of the densities measured in the cores obtained along the service life of the highway sections studied: (**a**) A-316; (**b**) A-92-I; (**c**) A-92-II. [10]

CONCLUSIONS:modified bitumen under severe traffic and climate conditions in real road pavements.For this purpose, cores were extracted on different dates from the surface layers of three highway sections that were constructed using a crumb-rubber-modified bitumen (PMB 45/80-60 C), and they were compared with cores extracted on the same date and at the same location from surface layers constructed with SBS-modified bitumen (PMB 45/80-60). These cores were tested at the laboratory to determine their density (UNE-EN 12697-6), stiffness (UNE-EN 12697-26, annex C) and resistance to fatigue (UGR-FACT). From the results obtained in this study, the following conclusions can be drawn:

The study found that surface layers' density remains constant over time, regardless of the asphalt binder used (SBS or crumb-rubber-modified). However, stiffness is significantly affected by service life due to environmental agents. The mixture BBTM 11B showed a stiffness increment between 43 and 105 MPa per month, with no clear dependence on binder type or climate conditions. Long-term resistance to fatigue cracking was similar, with increased resistance during the first 20-40 months and fatigue damage after.[10]

II.2 Bitumen modified with bio-sourced by-products:

II.2 .1.A Comparative Analysis of Algae Influence on Characteristic Properties:

- Algae are a large and diverse group of aquatic organisms characterized by their ability to photosynthesize.

Fig. II.8. Algae chlorella

ABSTRACT: The study aimed to evaluate the properties of bitumen modified with algae, using two types of algae (chlorella and microchlorella) and three blends with varying algae contents. The blends were tested using Penetration, Softening Point, Elastic Recovery, Force Ductility, Dynamic Viscosity, and Storage Stability tests. The results showed that adding 5% algae changed the unaged bitumen classification from 70/100 to 50/70, hardening the reference bitumen.[11]

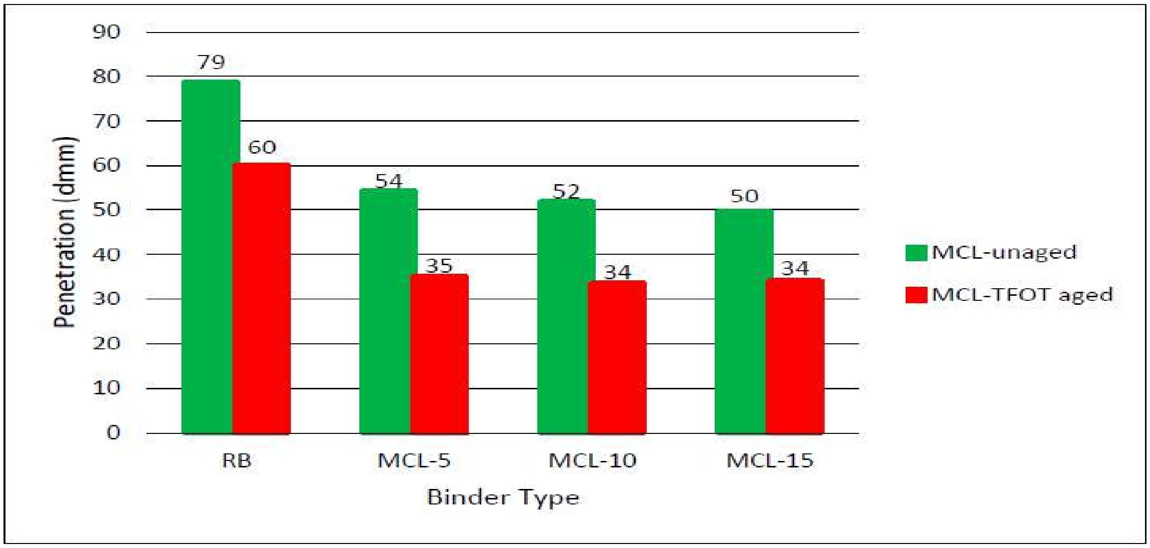

Fig. II. 9. Penetration of MCL-modified bitumen.[11]

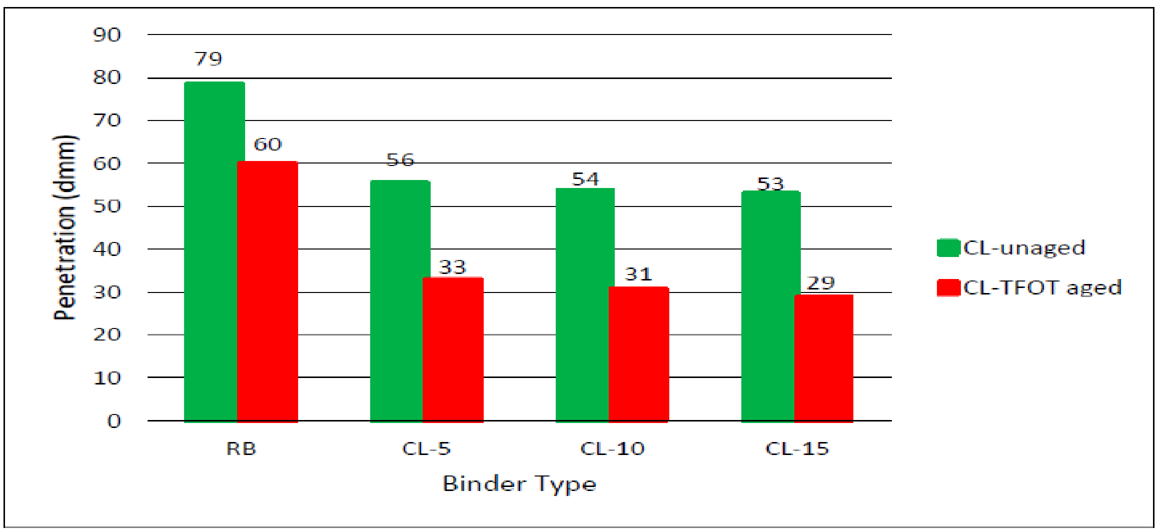

Fig. II.10. Penetration of CL-modified bitumen[11]

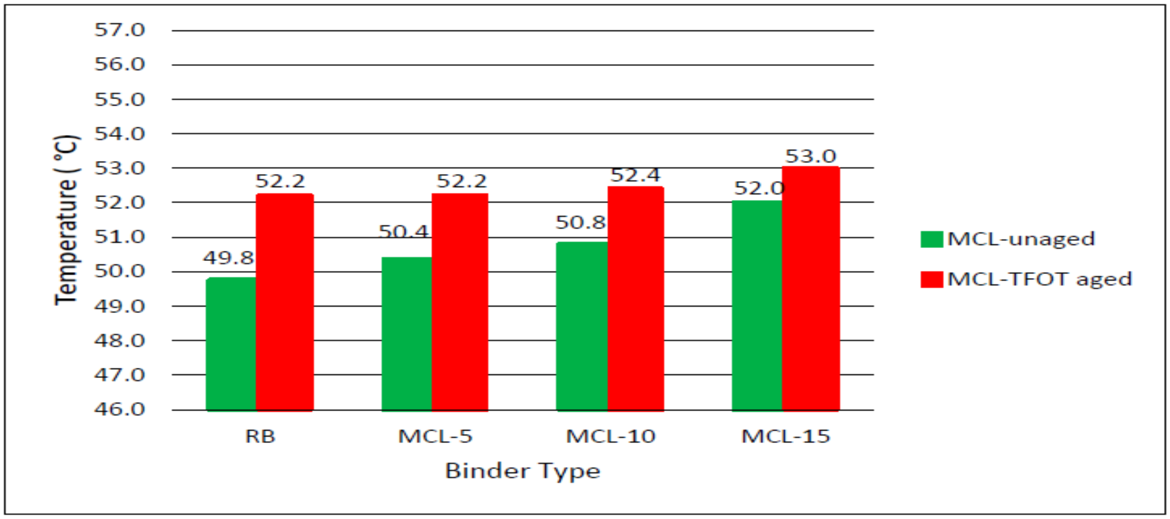

Fig. II.11. Softening point of MCL-modified bitumen.[11]

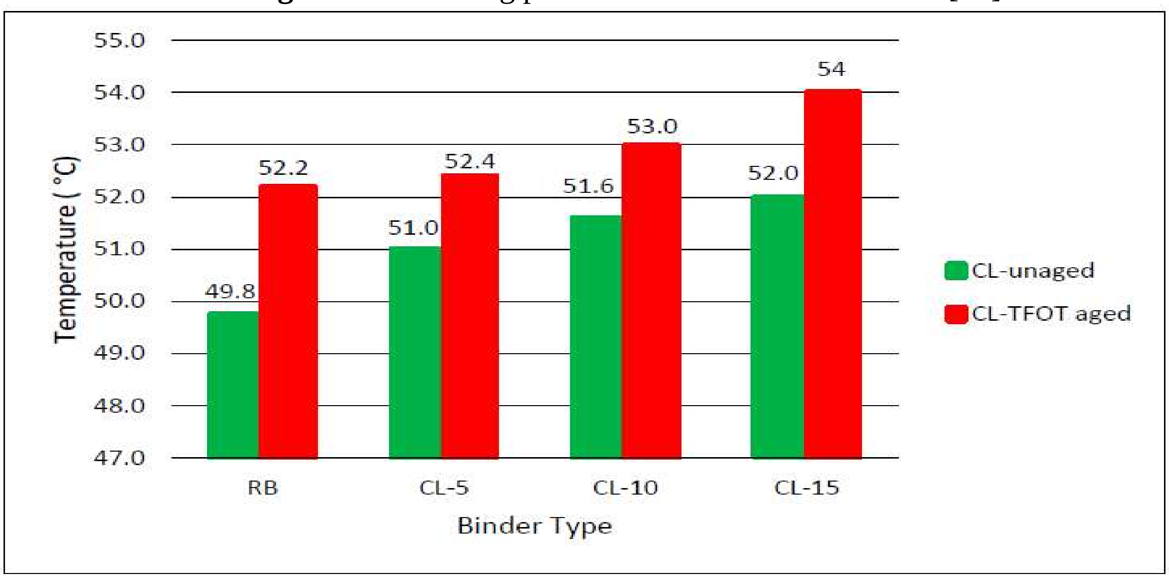

Fig. II.12. Softening point of CL-modified bitumen[11]

CONCLUSIONS: The study found that both types of algae stiffened the original 70/100 bitumen, with no significant impact on elasticity. The addition of algae reinforced the elastic phase, with increased dynamic viscosity and mixing temperatures. Ageing increased the temperature sensitivity of bitumen, but had a smaller impact on bio-modified blends. A strong correlation was found between activation energy and VTS Index, suggesting further investigation is needed.[11]

II.2 .2.Bio-Bitumen :

ABSTRACT: The depletion of renewable resources like petroleum products has led to increased focus on bio-based alternatives. Bio-fuel production involves converting organic waste materials into bio-fuels through pyrolysis. This process produces bio-char and bio-gases, which are carbonaceous substances. However, biochar has not been used in pavement applications, particularly as a bio-modifier for asphalt binders. This study evaluated the use of bio-char as a bitumen modifier, comparing it to bitumen in terms of consistency, temperature susceptibility, and ductility. The addition of bio-char enhanced temperature resistance, making it a potential option, especially in India's hot tropical climate.[12]

Test	0%	5%	10%	15%	20%
Penetration Value (mm)	64.445	37.222	25	19.222	15.778
Softening Point (°C)	32.5	47.5	49.135	54	63
Ductility Value (cm)	>75	36.667	15.667	11.2	7.6
Flash Point (°C)	276	318	325	360	>360
Fire Point (°C)	310	320	338	>360	>360

Table.II.5: Test Results [12]

CONCLUSIONS: Bio-char of materials like waste walnut shell powder, sawdust obtained from furniture and wood waste, crop straw from farm waste and packaging solid waste was produced by method of pyrolysis in muffle furnace at a very high temperature in the absence of oxygen. Various physical properties such as Penetration Test , of bio-char modified bitumen were studied and analyzed for different percentage of bio-char content. Tests such as penetration test with penetrometer, softening point test by ring and ball apparatus, ductility test by using ductility machine and flash and fire point tests were performed on given specimens to study parameters such as temperature susceptibility for warmer regions, rutting resistance, consistency and ductility. The results obtained showed decrease in penetration values and ductility as bio-char content increased. There was an increase in softening point and flash and fire points as the content of bio- char increased. This indicates that temperature susceptibility has increased as softening point increased along with increase in stiffness as penetration value decreased. Increase in stiffness reduced rutting action and formation of depressions. [12]

II.2 .3.The Influence of Coffee Husk Ash as a Filler on the Performance of Bituminous Concrete Mix):

- **Coffee husk** refers to the dried husk of the coffee cherry or coffee fruit that is derived from the processing of coffee beans. It is a by-product of coffee production and can be generated during both dry and wet processing methods.

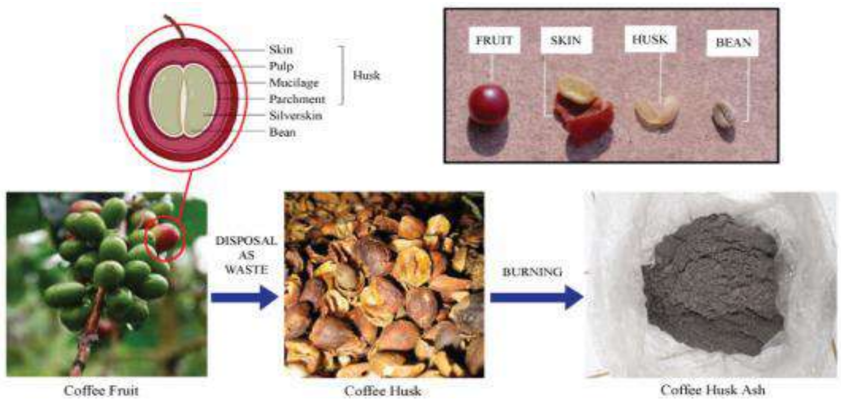

Fig. II.13. Coffee Husk Ash[13]

ABSTRACT: The study explores the impact of coffee husk ash and basaltic stone dust on the performance of bituminous concrete mixes in road construction. Thirty asphalt concrete specimens were prepared with these fillers, with bitumen content ranging from 4.0% to 6.0%. The results showed satisfactory Marshall properties, with CHA filler providing better resistance to moisture effects. The CHA filler increased the indirect tensile strength by 35.80% compared to basaltic stone dust. Both fillers met the minimum limiting value of 80%, making coffee husk ash an environmentally friendly alternative to basaltic stone dust.[13]

Bitumen (%)	ρ A (gm/cc)	VA (%)	VMA (%)	VFA (%)	Stability (kN)	Flow (mm)	Stability (kN) (after 24 h)
4.0	2.389	10.01	17.97	44.30	9.67	2.22	8.44
4.5	2.398	9.71	17.71	45.19	10.15	2.37	9.26
5.0	2.403	4.56	17.95	74.61	10.20	2.41	9.56
5.5	2.406	4.12	18.27	77.44	10.97	2.34	10.75
6.0	2.408	3.83	18.64	79.44	9.97	2.62	9.81
Standard values		3–5	Min 13	65–75	Min 8	2–4	Min 8

Table.II.6: Laboratory mix design result with BSD.[13]

Bitumen (%)	ρ A (gm/cc)	VA (%)	VMA (%)	VFA (%)	Stability (kN)	Flow (mm)	Stability (kN) (after 24 h)
4.0	2.13	12.39	18.97	34.70	10.91	2.77	9.67
4.5	2.23	7.79	15.76	50.59	11.95	3.08	11.06
5.0	2.25	6.31	15.46	59.17	13.98	3.17	13.54
5.5	2.27	4.44	14.83	70.04	14.54	3.37	15.32
6.0	2.28	3.43	14.97	77.11	13.87	3.60	13.84
Standard values		3–5	Min 13	65–75	Min 8	2–4	Min 8

Table.II.7: Laboratory mix design result with CHA.[13]

Bitumen (%)	Load (kN)		Area (mm^2) ($\pi^* t^* d$)	Indirect tensile strength (kPa)		TSR (%)
	Standard	Conditioned		Unconditioned	Conditioned	
4.0	9.67	8.44	29.393	209.44	182.80	87.28
4.5	10.15	9.26	31.265	206.67	188.55	91.23
5.0	10.2	9.56	31.401	206.79	193.82	93.73
5.5	10.97	10.75	33.716	207.13	202.98	97.99
6.0	9.97	9.81	31.279	202.92	199.66	98.40

Table.II.8: Indirect tensile strength results for basaltic stone dust as a filler.[13]

Bitumen (%)	Load (kN)		Area (mm^2)	Indirect tensile strength (kPa)		TSR (%)
	Standard	Conditioned		Unconditioned	Conditioned	
4.0	10.91	9.67	29.411	236.15	209.31	88.63
4.5	11.95	11.06	31.787	239.33	221.51	92.55
5.0	13.98	13.54	35.213	252.75	244.79	96.85
5.5	14.54	15.32	32.565	284.25	299.49	105.36
6.0	13.87	13.84	32.04	275.59	274.99	99.78

Table.II.9: Indirect tensile strength results for coffee husk ash as a filler.[13]

CONCLUSIONS: The study evaluates the impact of coffee husk ash (CHA) on the engineering properties of bituminous concrete mixtures compared to basaltic stone dust. The optimum bitumen content is 5.53%, providing a CHA filler. CHA increases stability by 35.8% compared to BSD, but both yield stability values above 8 kN. The Marshall quotient (MQ) values of 4.44 kN/mm and 4.20 kN/mm are within the AASHTO specification range.

II.3.<u>MODIFIED EMULSIONS:</u>

II.3.1.<u>Bitumen emulsion modified with two types of SBR latex:</u>

- Styrene Butadiene Latex Rubber is a type of modified synthetic rubber derived from styrene and butadiene.

Fig. II.14.SBR Latex

- **Materials:**

60/70 bitumen was prepared and turned into a cationic rapid setting (CRS) bitumen emulsion by a colloid mill, and SBR latex. [14]

- **PMBE preparation:**

Because bitumen emulsion from the CRS-2 type and SBR latex from the anionic type could not be mixed to create PMBE, X-SBR latex and SBR latex-1502 were converted to the cationic type. Additionally, PMBE was prepared using the post-blending procedure at a temperature of 50°C.Under a light microscope. [14]

- **Physical properties experiments:**

Normal experiments of bitumen including needle penetration test at 25°C (ASTM D5), and softening point test (ASTM D36) were done on the residue of PMBE types. Then, to examine the temperature sensitivity of modified bitumen, the needle penetration index (PI) was utilized, which is typically calculated based on

Eq. (1):

$$\mathbf{PI} = \frac{\mathbf{1952 - 500 \times log(}\boldsymbol{pen}\mathbf{25) - 20 \times}\boldsymbol{SP}}{\mathbf{50 \times log5pen25) - SP - 120}} \qquad (1)$$

In which pen25 is needle penetration at 25°C in terms of tenths of millimeters and SP is softening point in terms of degrees centigrade. [14]

- **DSR test:**

Rheological properties of bitumen emulsion residue were measured based on AASHTO T 315 via a DSR machine. According to this method, all samples were under a fixed frequency of 10 rad/sec from 30 to 90°C.

- **Results and Discussion:**

1. Physical properties:

Investigating the common bitumen experiments results showed that adding the two polymers to base bitumen leads to a continual decrease of needle penetration, a continual increase of softening point, and PI. These, in turn, reduce the sensitivity of PME to temperature changes. Furthermore, the effect of SBR polymer on temperature sensitivity reduction with equal consumption percentage is more than that of X-SBR. [14]

- **DSR rheological properties:**

The performance of bitumen emulsion modification was measured using phase angle and complex modulus results from DSR. $G*/\sin\delta$ was calculated using standard AASHTO T 315, comparing the results of nonmodified and modified bitumen emulsion residues with different percentages of SBR latex. The molecular structure of polymers related to two SBRs also influenced $G*/\sin\delta$. $G*/\sin\delta$ is a rutting factor in surface performance grade (SPG) for loading thick asphalts, with a minimum of 1kPa. However, the application of bitumen emulsion in asphalt pavements like chip seals and thin pavements does not affect rutting. The last suggested amount for controlling bleeding is 0.65kPa. [14]

Conclusion:

This chapter concludes that the new vision of the world is to exploit the remains of bio-sourced by-products and industrial by-products in different fields of industry

Experimental part

III. Tests on products and materials used

INTRODUCTION:

This chapter includes various experiments to determine the properties of the materials used and the method of preparation, namely: Bitumen 40/50, Bitumen Emulsion (ECM65%) and spent coffee grounds.

III.1.PREPARATION OF THE USED MATERIALS:

III.1.1.sample preparation of SCG:

About 2.8 kilograms of SCG have been dried on 100C° to make sure there was no moisture left. Then it was burned in equal batches at 400C° for 4 hours, and that's called pyrolysis breaking down some of its organic components and converting it into activated carbon.

- Pyrolysis: The chemical decomposition of organic materials at elevated temperatures in the absence of oxygen or any halogen, and involves a change in chemical composition accompanied by a change in the physical state of the material by Breaking down some of its organic components and converting them into active carbon. This change in the material is irreversible and can be used to develop new materials and improve the properties of existing materials.

After that, it was sifted (sieve 0.08mm) to have a granular powder with precision diameters before it was added to bitumen and bitumen emulsion.

Photo.III.1. SCG after Pyrolysis

➢ Physics Tests:

Chemical Structure of spent Coffee grounds after pyrolysis:

DRX Analysis:

It is an analytical technique used to determine the structure of crystalline materials.

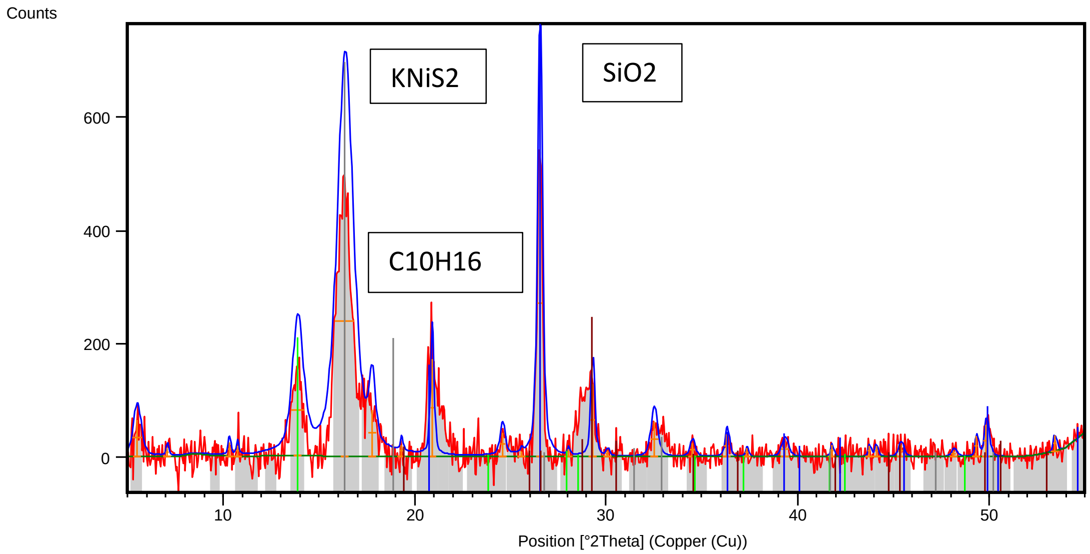

Fig. III.1. The most important minerals

Chemical formula:

SiO_2: silicon dioxide
KNiS2: Potassium Nickel Sulfide
C10H16: Adamantane

III .1.2. <u>Preparation of bitumen:</u>

3 different ratios of the sample prepared of SCG (3%,6%,10%) were added to 40/50 bitumen and these ratios were mixed into the device **HIGH SHEAR LABORATORY MIXER** while using **UNIVERSAL TEMPERATURE CONTROLER** to maintain its liquid condition.

The conditions that were maintained during preparation are 3000 cycles for one hour.

III.1.3. <u>Preparation of bitumen emulsion:</u>

2 different ratios of the sample prepared of SCG (3%,6%) were added to cationic emulsion medium acting ECM65 and these ratios were mixed into the device **LABORATORY BITUMINOUS MIXERS** while it was cold .The conditions that were maintained during preparation are max speed (according to the used device) for 45 minutes.

Photo.III.2.HIGH SHEAR LABORATORY MIXER

Photo.III.3. LABORATORY BITUMINOUS MIXERS

III.2.HYDROCARBONIC BINDER TESTS:

To determine bitumen and bituminous emulsion under standards there are six tests.

III.2.1. Mechanical tests:

- **Bitumen tests:**
- **penetrability test (NF-EN1426):**

The standard penetration of bitumen is defined as the penetration at 25°C of a needle standardized, loaded with 100 g, and left for 5s. A penetrometer is used to make the measurements. The standard penetration is used to test the hardness of road bitumen, which is then classified. Bitumen is identified by two values that indicate its lower and upper limits of penetrability at 25°C.

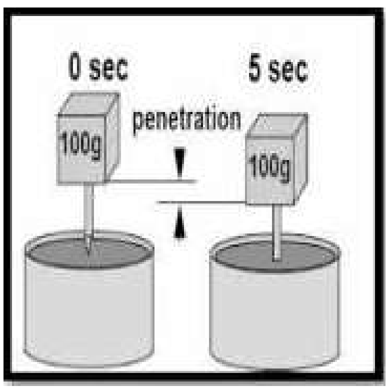

Fig.III.1. Principle of the Penetration test

Photo.III. 4. Penetration test**.**

- **Softening point test (NF EN 14 27):**

The softening point of bitumen is the temperature at which the substance attains a particular degree of softening. As per NF EN 14 27, it is the temperature in C° at which a standard ball passes through a sample of bitumen in a mold and falls through a height of 2.5 cm when heated under water or glycerin at specified conditions of the test. The binder should have sufficient fluidity before its application in road use. The determination of the softening point helps to know the temperature up to which a bituminous binder should be heated for various road use applications.

Photo.III.5. Softening point test.

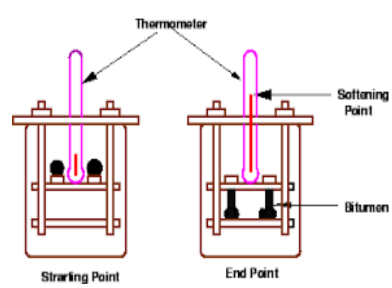

Fig.III.2. Principle of the softening point test

- **Ductility (NF T66-006):**

The ductility of a bituminous material is measured by the distance to which it will elongate before breaking when two ends of a briquet specimen of the material, of the form described in the figure, are pulled apart at a specified speed and a specified temperature. Unless otherwise specified, the test shall be made at a temperature of 25 C° and with a speed of 5 cm\min.

Photo.III.6. Mold for Ductility test specimen**.**

Photo.III.7. Ductility test**.**

- **Relative density (NF EN 12697-6):**

This test method covers the determination of the specific gravity (relative density) and density of semi-solid asphalt binder by use of a pycnometer. The definition of bitumen density is the ratio of the mass of a definite volume of bitumen to the water of the same volume at a known temperature.

Photo.III.8. pycnometer**.**

Photo.III.9. Relative density test apparatus**.**

- **<u>Bituminous emulsion tests:</u>**
- **The rupture index NF T66_017:**

When the emulsion is entirely broken up, as indicated by the mixture's mass setting, the amount of fines added is calculated by weighing to within 0.1 g. The rupture index of the cationic emulsion can be calculated by multiplying the acquired mass by 100 and dividing it by the emulsion mass.

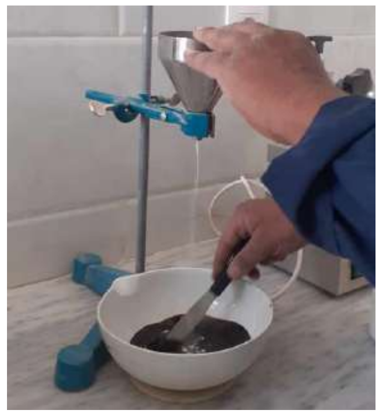

Photo.III.10. The rupture index test**.**

- **pseudo-viscosity NF T66-020:**

The viscosity of the bitumen emulsions is measured using flow viscometers. The test consists of measuring the time taken by a specified amount of emulsion to flow through an orifice of a given size at a temperature of 25 C°.

Fig.III.3. viscometers**.**

<u>Conclusion:</u>

thus, the different steps and processes are outlined and the results of the hydrocarbon binder tests are discussed in the next chapter.

IV. Discussion and interpretation of results.

INTRODUCTION:

This chapter is an explanation and comparison of test results obtained on bitumen and bitumen emulsion

- The results obtained from the aforementioned experiments are in the following table:

	BITUMEN			
	0٪	3٪	6٪	10٪
penetrability **(EN1426)**	48.5	25.83	29.5	22.7
Ductility(cm) **(NF T66-006)**	98	34\35\36.5	32\33\40	32\35\41
softening point **(EN 14 27)**	55.7C°	57.7C°	57.8C°	58.7C°
Density **(EN 12697-6)**	1.041	1.051	1.056	1.067

Table IV. 1. Hydrocarbon binder tests on bitumen.

IV.1.Analysis of bitumen results:

IV.1.1.Influence of SCG on penetrability test:

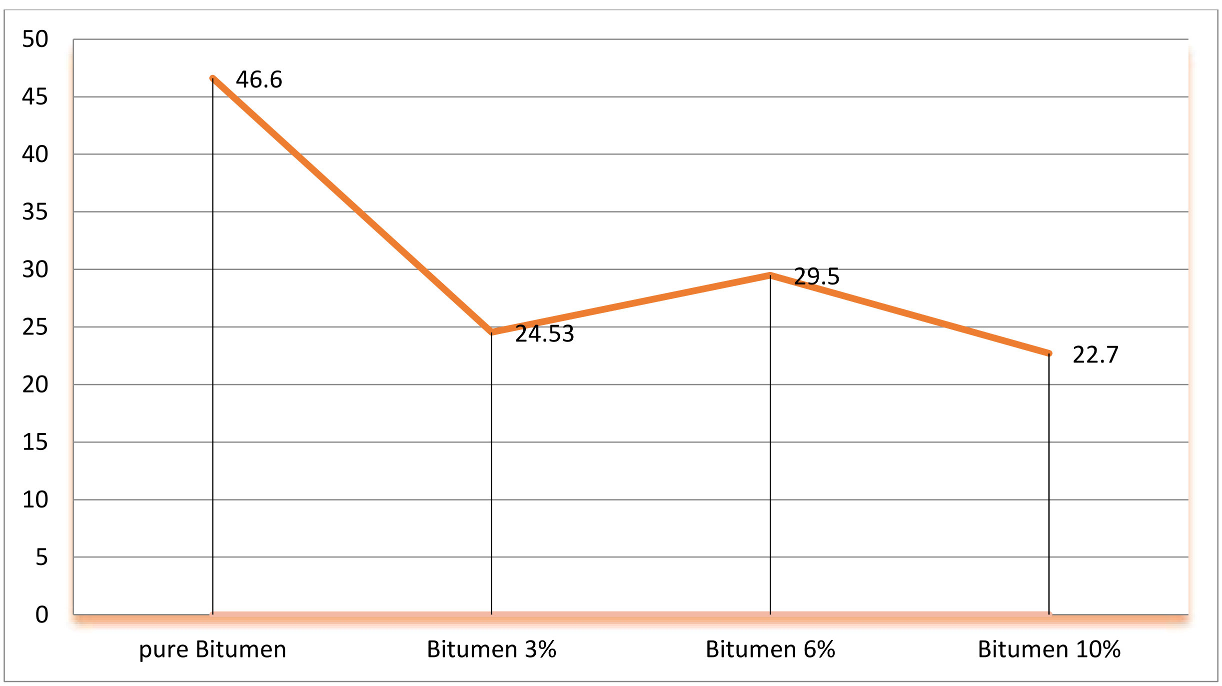

Fig.IV.1. The curve of penetration values in terms of the quantity of SCG.

The above curve shows a change in Penetration values while increasing the content of SCG in bitumen. The Penetration value of pure bitumen changed dramatically with the first addition of coffee at 3% from 46.6mm to 24.53mm, a clear change in bitumen grade from 40\50 to 20\30. At 6% the penetrability value Increased from 24.53mm to 29.5mm yet it stayed within the grade of 20\30 then it decreased until the value of 22.7mm at 10%. this decrease in penetrability values is due to the interaction of SCG with bitumen, which contributed to an increase in the hardness of the bitumen.

IV.1.2.<u>Influence of SCG on the softening point test:</u>

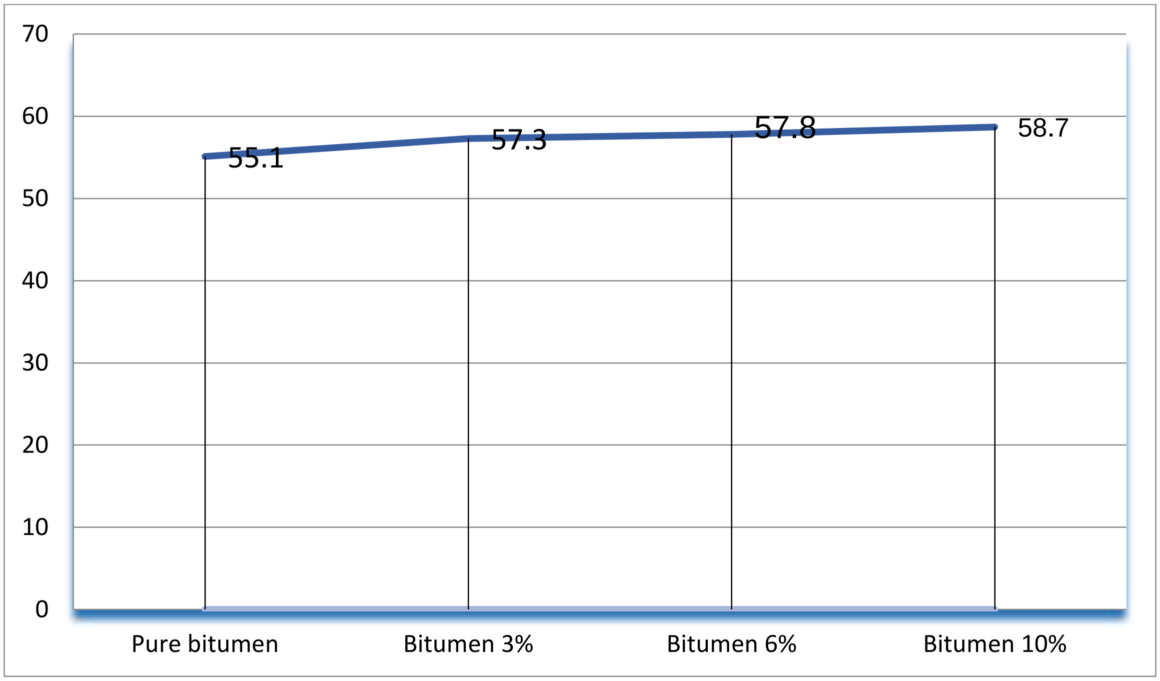

Fig.IV.2. The curve of softening point values in terms of the quantity of SCG.

The curve showing the evolution of the temperature in terms of the percentage of SCG shows an increase in the range of the studied percentages [0%, 10%] since it reached 55.1 °C before modification and an increase at the value of 57.3 °C at 3% while reaching 57.8° In the proportion of 6% and 58.7°C at 10%, the modified bitumen fulfill the standard values of grade 40\50 and 20\30 (NF T66-008). The interaction of SCG with bitumen made it withstand higher temperatures than it did in its pure state.

IV.1.3.<u>Influence of SCG on the Relative Density Test:</u>

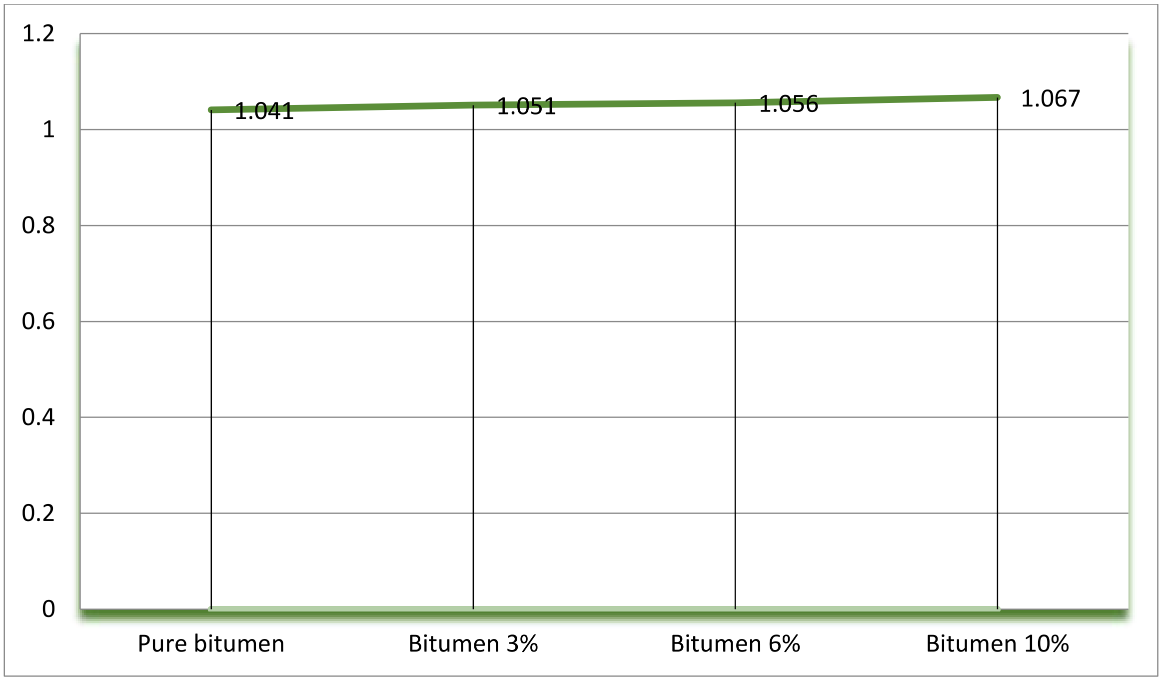

Fig.IV.3. The curve of Relative density values in terms of the quantity of SCG.

The curve showing the evolution of density values in terms of the percentage of SCG shows an increase in the range of the studied percentages [0%, 10%] since it reached 1.041 before modification and an increase at the value of 1.051 at 3% while reaching 1.056 and 1.067 In the proportion of 6% and 10%, the modified bitumen fulfill the standard values of grade 40\50 and 20\30 according to the French Association for Standardization. And this value typically indicates a denser and potentially higher quality bitumen.

IV.1.4.Influence of SCG on the Ductility Test:

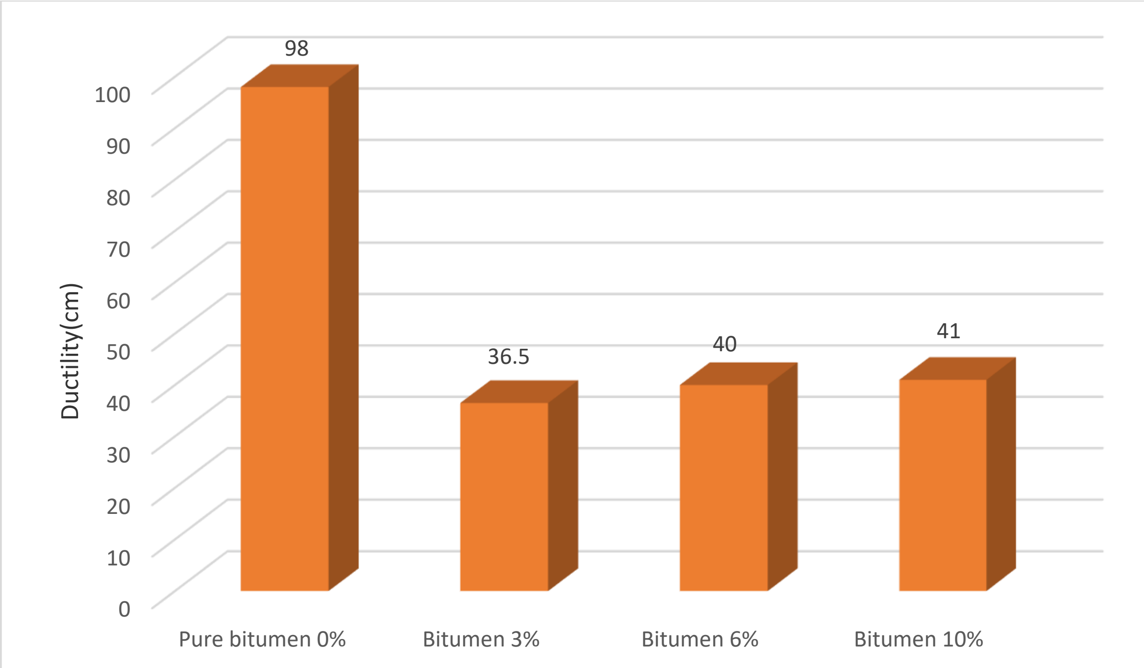

Fig.IV.4. The curve of Ductility values in terms of the quantity of SCG.

The graph above shows a noticeable change in the ductility values with increasing SCG content in the bitumen. So the first percentage of 3% SCG gave a low result compared to pure bitumen. At 6%-10%, the extension value increased slightly to 41cm. This lower ductility has the added benefit of improving the deformation resistance and stability of the asphalt mixture.

- The results obtained from the aforementioned experiments are in the following table:

	Bitumen Emulsion		
	0%	3%	6%
The rupture index (EN 13075-1)	80	76	/
pseudo-viscosity (NF T66-020)	6s	6s	/

Table IV. 2. Hydrocarbon binder tests on bitumen emulsion

IV.2.Analysis of bitumen emulsion results:

IV.2.1.Influence of 3% of SCG on the rupture index:

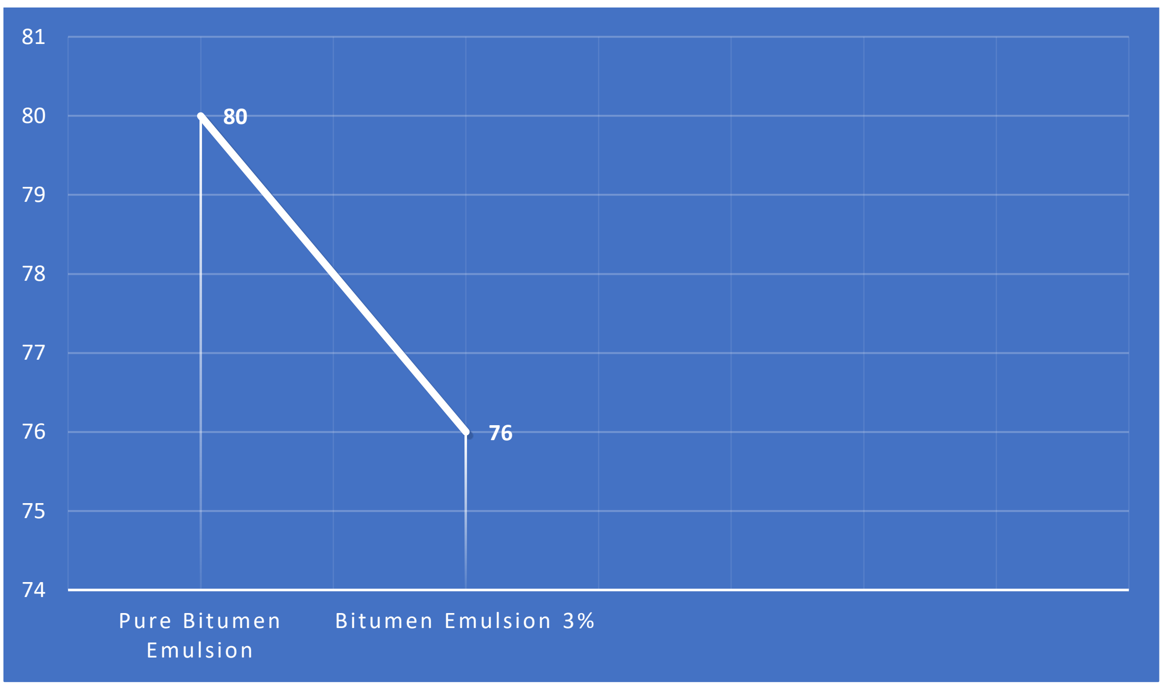

Fig.IV.5. The curve of rupture index values in terms of the quantity of SCG.

The above curve shows a change in The rupture index values while increasing the content of SCG in bitumen emulsion. The rupture index value of pure bitumen emulsion changed slightly from 80 to 76 with the first addition of SCG at 3% but that made a change in the bitumen emulsion class which went from ECM65 to ECR65 by classification NFT 66-017.

IV.2.2.Influence of 3% of SCG on pseudo-viscosity:

Table IV.2, shows the governorate of pure bitumen emulsion on its pseudo-viscosity value even after adding 3% of SCG and its flow indicates a low viscosity at 6s.

IV.2.3.Influence of 6% of SCG on bitumen emulsion:

The bitumen emulsion can disperse and accommodate spent coffee grounds at 3%, but at higher concentrations (6%), it may reach a saturation point, disrupt emulsion stability, and cause separation.

To address this issue, we can consider the following:

- ✓ **Optimized concentration**: Using a concentration below 6% but above 3% may help maintain stability while achieving the desired properties in the final mixture.
- ✓ **Testing**: Perform more tests with different concentrations to find the optimal balance between the amount of coffee consumed and the bitumen emulsion.

Photo.IV.1. Influence of 6% SCG on bitumen emulsion

Conclusion:

Considering the results obtained, we find that SCG positively affected the bitumen and bitumen emulsion despite the Ductility results and the unsuccessful success of the modified bitumen emulsion mixture at 6%

General Conclusion

General Conclusion

The study conducted on the use of coffee waste crumbs as a bitumen modifier revealed promising results for the dosing percentages of 3%, 6%, and 10%. The analyses carried out on the modified mixtures demonstrated significant improvements in terms of rheological, mechanical, and durability properties.

We summarize the results obtained by the tests carried out as follows

For pure bitumen:

- Increased softening point, which indicates better thermal stability in the face of high temperatures. (advantageous property in the hot zone)

- Reduced penetration, suggesting increased resistance to cracking and driving nails.

- Low ductility, which does not favor coating, but on the other hand, this weakness favors the action of water to reduce water penetration and thus minimize desinking.

for Emulsion:

- The results of the emulsion rupture index tested varied abruptly for coffee crumb

dosing greater than 3%

Finally, we can conclude that the use of coffee waste powder as a bitumen modifier is proving to be a promising solution to improve pavement performance while reducing environmental impact.

The encouraging results obtained at doses of 3%, 6%, and 10% confirm the potential of this technology. However, more research is needed to optimize formulations and implementation techniques to ensure widespread adoption.

REFERENCES

[1] د.قبائلي نبيل ,محاضرة مواد البناء سنة ثالثة ليسونس اشغال عمومية,جامعة قاصدي مرباح ورقلة.

[2] Professor Stephen Brown. The shell bitumen handbook. Chertsey, Surrey [England] :Shell Bitumen U.K in 1990.

[3] خليل أحمد أبو أحمد,المواد الإسفلتية و طرق ضبط الجودة و إنشاء الطرق,دار الرتب الجامعية ,01يناير2002

[4] https://rahabitumen.com/bitumen-emulsion

[5] Layella .Ziyani. Etude des phénomènes physico-chimiques à l'interface émulsion de bitume/substrat minéral - Application à la formulation de Bétons Bitumineux à l'Emulsion (BBE). Matériaux. Université Nantes Angers Le Mans, 2013. Français

[6] . Needham B. Sc, Developments in bitumen emulsion mixtures for roads, Thesis submitted to the University of Nottingham for the degree of Doctor of Philosophy.May1996.

[7] British Standard434:part1:1984:Bitumen road emulsion (anionic and cationic).

[8] Ashok Pareek, Trilok Gupta, and Ravi K Sharma, PERFORMANCE OF POLYMER MODIFIED BITUMEN FOR FLEXIBLE PAVEMENTS, Int. J. Struct. & Civil Engg. Res. 2012.

[9]Ambika Behl, P.K Jain, Girish Sharma, STUDY ON WASTE POLYVINYL CHLORIDE MODIFIED BITUMEN FOR PAVING APPLICATIONS, research, and outcomes, Perth, Australia 2012.

[10] Francisco Javier Sierra-Carrillo de Albornoz, Fernando Moreno-Navarro, and María del Carmen Rubio-Gámez, Analysis of the Real Performance of Crumb-Rubber-Modified Asphalt Mixtures, Granada, Spain,2022.

[11] Stavros Kalampokis, Evangelos Manthos, Avraam Konstantinidis, Christos Kakafikas and Artemis Kalapouti, Bio-Modified Bitumen: A Comparative Analysis of Algae Influence on Characteristic Properties, Thessaloniki, Greece, 4 March 2024.

[12] Pandit. S.U, Aditya Marathe, Riddhi Patil, Anusha Karanje, Bio-Bitumen, International Research Journal of Engineering and Technology (IRJET), Jun 2022

[13] The Influence of Coffee Husk Ash as a Filler on the Performance of Bituminous Concrete Mix)

[14] The rheological properties of a bitumen emulsion modified with two types of SBR latex

Annexe

مخـــبر الاشغـــال العموميـــة في جنـــوب البـــلاد

LABORATOIRE DES TRAVAUX PUBLICS DU SUD

FEUILLE DE PAILLASSE

Mesure de la masse volumique et de la densité de bitume et des Liant bitumineux

- Méthode du pycnomètre à bouchon capillaire -

NF EN 15326 + A1 : 2009

Structure	Unité Ghardaia	**N° Dossier**	OURGLA
Lieu de travail	S^{ce} Hydrocarboné	**Echantillon**	03% / 06%

	Équipement	N° Inventaire ou N° série	Constat*	Valeur de correction**
Vérification des équipements (étalonnage, vérification et état)	Étalonnage de pycnomètre 01	02	C	
	Étalonnage de pycnomètre 02	03	C	
	Étalonnage balance	L.022.03.S.008	C	
	Étalonnage étuve	L.039.15.S.008	C	
	Étalonnage bain marie	L.020.15.S.001	C	✓
	Étalonnage de thermomètre	172379 RMC	C	✓
	Date D'étalonnages des Pycnomètres (GM-N-07-02)	05/01/2024	C	+1

Description de l'échantillon :

(*) : C= conforme, NC=non conforme.

(**) **Important :** Toutes les valeurs mentionnées doivent être corrigées par les valeurs de correction

N°	ETAPE	EXIGENCE	VALEUR	
1	Date et Heure Début D'essai	1505/2024	9:00	
2	Prendre une quantité suffisante à l'aide d'une lame chauffée	• 1 L max	Masse Echantillon= 600 g	
3	Mettre la quantité prélevée dans un récipient fermer avec un couvercle desserré dans l'étuve	• Température ≥ TBA attendu + 100°C • Durée : 2 h maximum	Température = 150 °C Durée d'étuvage = 100 min	
4	Mettre le bain d'eau à température d'essai	• T ± 0.2 °C	Température d'essai = 25.0 °C	
5	Remplir le bécher avec l'eau	• L'eau distillée fraichement bouillie et refroidie.	✓	
6	Immerger partiellement le bécher dans le bain d'eau pendant 30 minutes	• À une hauteur telle que le fond du bécher soit immergé à une profondeur minimale approximative de 100 mm	Durée de conservation = 30 min	
7	• Vérifier la masse des pycnomètres en (mg)	• $A_{ét}$: mase pycnomètre étalonné (voir GM-N-07-02) • A_1 : mase pycnomètre vide • $A_v = A_{ét} - A_1$ • Si $\|A_v\|$ >5mg: refaire l'étalonnage	**Pycnomètre 02** $A_{1ét}$ = 36,659 A_1 = 36,659 A_{V1} = 0,000	**Pycnomètre 03** $A_{2ét}$ = 34,970 A_2 = 34,970 A_{V2} = 0,000

	• noter la masse B de chaque pycnomètres en (mg)	B:la masse de pycnomètre avec le liquide d'essai (voir GM-N-07-02)	B_1 = 60,239		B_2 = 62,631	
8	Chauffer à une température entre 50 et 80°C avant verser l'échantillon	• Entre 50 et 80 °C	Température 60,0 °C			
9	Verser suffisamment de liant dans les pycnomètres	• Remplir environ aux trois quarts (3/4) de sa capacité • Éviter l'inclusion de bulles d'air.	✓			
10	Laisser les pycnomètres et son contenu (bitume) refroidir à la température ambiante	• Température ambiante entre 18 et 28 °C. •Pendant 40 min,en le protégeant de la poussière	Heur Début	9:00	T°	20,4 °C
			Heur Fin	9:40	T°	20,5 °C
11	Peser le pycnomètre avec le bouchon, et l'échantillon	• Au mg près	Pycnomètre	04	Pycnomètre	/
			C_1=	49,070	C_2=	50,952
12	Ajouter le liquide d'essai dans le pycnomètre qui contient au préalable l'échantillon, mettre en place le bouchon sans l'enfoncer	• Liquide d'essai : - Eau distillée fraichement bouillie et refroidie pour les bitumes purs, - Isopropanol pour les bitumes fluidifiés	Liquide d'essai = Eau Distillée			
13	Placer le pycnomètre dans le bécher à 25 ± 0,2 °C et presser le bouchon fermement pour le mettre en place.	• À 25 ± 0.2 °C • Laisser pendant 30 min	Heur Début	9:45	T°	25,0 °C
			Après 15 min	10:00	T°	25,0 °C
			Heur Fin	10:15	T°	25,0 °C
14	Retirer le pycnomètre du bécher. Sécher et peser. Puis peser le.	–	Pycnomètre	04	Pycnomètre	/
			D_1=	61,264	D_2=	63,477
15	Calculer la densité de liant,(**d**) avec 03 décimales et masse volumique (ρ)	$d_{25/25} = \frac{C-A}{(B-A)-(D-C)}$ $\rho = \frac{C-A}{(B-A)-(D-C)} \times \rho t$ • Eau : ρt = 0,997 g/cm³ à 25 °C • Isopropanol ρt= 0,7827 g/cm³ à 25°C • différence de |ρ| ≤ 0,002 g/cm³	$d_{25/25}$ = 1,067		$d_{25/25}$ = 1,056	
			$\rho 1$ = 1,064		$\rho 2$ = 1,053	
			$\rho 1 - \rho 2$ =		0,011	
16	Déterminer la densité et la masse volumique de liant comme étant la moyenne	–	$d_{25/25}$ =		1,061	
			ρ =		1,058	
17	Date et heure de fin d'essai	1505/2024	10:25			

Observation: **R.A.S**	Nom et Prénom du Technicien : Visa :

Nom et Prénom du Contrôleur : Date : Visa :	Contrôle et vérification	oui	non
	Qualification du technicien		
	Renseignement correcte		
	Vérification du matériel		
	Calcul correcte		

مخـــبر الاشغـــال العموميـــة في جنـــوب البـــلاد

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Description de l'échantillon :

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5	Remplir le bécher avec l'eau	• L'eau distillée fraichement bouillie et refroidie.	✓	
6	Immerger partiellement le bécher dans le bain d'eau pendant 30 minutes	• À une hauteur telle que le fond du bécher soit immergé à une profondeur minimale approximative de 100 mm	Durée de conservation = 30 min	
7	• Vérifier la masse des pycnométres en (mg)	• A_{et} : mase pycnomètre étalonné (voir GM-N-07-02) • A_i : mase pycnomètre vide • $A_v = A_{et} - A_i$ • Si $\lvert A_v \rvert$ >5mg: refaire l'étalonnage	**Pycnomètre 02** A_{1et} = 36,659 A_1 = 36,659 A_{V1} = 0,000	**Pycnomètre 03** A_{2et} = 34,970 A_2 = 34,970 A_{V2} = 0,000