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ASSESSING THE RHEOLOGICAL BEHAVIOR OF BIO-ASPHALT BINDER WITH INTEGRATING BIOWASTE-DERIVED ACTIVATED CARBON

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Abstract

Current endeavors are being made to develop substitute asphalt binders using different biomass sources for upcoming flexible pavement construction, propelled by sustainability and the escalating expenses of traditional petroleum-centered asphalt. The primary objective of this research is to explore the feasibility of employing activated carbon (ATC) produced from biowaste, specifically walnut shells and sawdust, as a modification for petroleum-based virgin asphalt binders through chemical, physical, and rheological assessments. A comprehensive array of evaluations was carried out, encompassing examinations of homogeneity, physical characteristics, Carbon, Hydrogen, Nitrogen, Sulphur, and Oxygen (CHNSO) analysis, proximate analysis, infrared spectroscopy, multiple stress creep and recovery (MSCR), rheological attributes, and temperature sweep. The CHNSO analysis provided the elemental composition and helped develop molecular formulas for ATC. The results show that binders modified with ATC exhibited a heightening carbon content proportionate to the AC ratio, analyzed at 5%, 10%, and 15%. Temperature sweep tests revealed that adding AC significantly increased binder stiffness in accordance with the complex modulus (G*) and phase angle (δ). This increased rigidity from the ATC modification declines the temperature susceptibility of the modified binders.

Keywords:
Biowaste;
Activated Carbon ;
Dynamic shear rheometer;
Multiple Stress Creep;
Recovery.

1 Introduction

Conventional asphalt binders utilized in Hot Mix Asphalt (HMA) production are predominantly sourced from petroleum refining processes [37]. However, the escalating costs associated with petroleum-based paving asphalt underscore the reliance on non-renewable resources. Consequently, there is a pressing need to explore alternative binder materials, either partially or entirely replacing petroleum-derived asphalt, to foster sustainable development within flexible pavement construction. Recently, biomass materials from various bioresources, such as waste nutshells, wood, corn stalks, animal waste, and waste cooking oil, have garnered considerable attention within the asphalt pavement industry [2,38,39]. An enduring effort is being made to create a bio-asphalt that integrates ATC from organic waste as an innovative asphalt modifier [36].

Numerous research investigations have been undertaken to assess the performance of different bio-asphalt materials. Yunus et al. state that ATC is a carbonaceous material characterized by its extensive surface area and notable adsorption capabilities, often sourced from carbon-rich materials. The manufacturing of ATC encompasses two primary techniques: physical activation and chemical activation [42]. Yilmaz et al. investigated incorporating ATC produced from vinasse and marc through distillation or fermentation processes aligned with objectives related to sustainability [30]. This demonstrated that adding ATC into the base binder changes its rheological characteristics and enhances its resistance to aging. Further, Powder AC (PAC) in asphalt modification has been explored for its ability to create a network skeleton within the binder molecules, increase shear modulus values, reduce phase angles, and improve resistance to rutting. This highlights the potential of PAC as a cost-effective and efficient modifier for asphalt pavements [6]. Liu et al. employed a similar study that incorporated ATC powder (ACP) into asphalt to replace a portion of the conventional filler, mineral powder (MP). ACP addition in asphalt mastic showed mixed effects on rheological performance, with the optimal blend being 40% ACP and 60% MP based on comprehensive rheological properties [35]. Chaala et al. also verified that Pyrolytic carbon black (PCB) can be used as a filler in a binder to reduce temperature effects and improve rheological properties, with concentrations tested at intervals of 5% ranging from 5 to 30% [8].

Kumar et al. experimented with using Biochar, a by-product of biofuel production from Mesua ferrea seed cover waste. Mesua ferrea, commonly known as Ceylon ironwood, is a tropical tree native to South Asia that is valued for its medicinal and industrial uses. The experiment concluded that biochar could improve asphalt binders' rutting and aging resistance, making it a promising asphalt modifier for warm tropical climates like India [20]. Zhao et al. evaluated the rheological performance of biochar-modified binders derived from switchgrass through pyrolysis. These binders effectively reduce temperature susceptibility and increase rutting resistance in asphalt binders, making them a sustainable alternative to commercial ATC within 10%wt addition [41]. Feng et al. investigated the rutting performance of incorporating pyrolysis carbon black (PCB) made from waste tires in a binder, significantly improving binder performance and resistance to permanent deformation at high temperatures, making it suitable for road construction and waste tire recycling [11,13]. Chebil et al. assessed adding 5-15% softwood bark charcoal to road binder to improve its viscoelastic properties, thermal resistance, and rust resistance while reducing crack propagation and settling during long hot storage periods [9]. Rasul et al. investigated the impact of ATC obtained from sawdust polymerization on conventional asphalt binders, observing increased rutting resistance but reduced fatigue cracking upon AC addition [28].

ATC, sourced from biowaste, demonstrates great promise as a biomass resource with extensive applications in the field of asphalt, acting as a viable replacement for conventional binders. The global production of agricultural and biowaste is approximately 1 billion tons annually [31]. The magnitude and effectiveness of activated carbon production are demonstrated in various research endeavors. For example, a manufacturing facility is engineered to generate 14.5 metric tons of activated carbon daily, utilizing sources like coconut shells and other lignocellulosic materials, including sawdust, nut shells, and leaves.

Biowaste sources exhibit significant economic potential, possibly yielding profits exceeding USD 69 per dry feedstock ton when considering CO2e (carbon dioxide equivalent) emission reductions valued at USD 80 per CO2e ton [30]. CO2e is a standard unit used to measure and compare the impact of different greenhouse gases on global warming. China stands out as a major producer of ATC, generating over 6 million tons annually, though the inefficient recycling of biowaste may lead to social and environmental challenges [12]. Residual ATC has garnered attention as a potential bio-modifier for producing AC-based bio-asphalt. All the above research indicates that bio-asphalt presents a promising alternative to conventional petroleum-based asphalt in the pavement industry. However, the issue of diversity in AC sources and processing methods requires further investigation to facilitate practical applications in asphalt pavement industries.

Due to its high population density, a country like India generates an estimated hundred thousand tons of biowaste annually, which remains underutilized for ATC production. Given this scenario and the potential to maximize ATC output, focusing on its effective utilization is essential. The production cost of approximately 100 kg of AC is about USD 25, making it a highly cost-effective option [31,43]. Different chemicals produce distinct molecular elements that influence binder properties during the modification process. While carbon and ATC have been utilized in prior binder modification procedures, this study is novel in its use of walnut shells and the incorporation of phosphoric acid, which is recognized for its high carbon content and beneficial chemical properties. This study has focused on evaluating the performance of bio-asphalt modified with ATC derived from sawdust and walnut shells through chemical activation processes. From a sustainability perspective, this study fills a gap. It employs comprehensive chemical, physical, and rheological performance evaluations to investigate the potential application of ATC as a bio-modifier for petroleum asphalt. Significantly, this research emphasizes characterizing the ATC's impact on the rutting resistance of virgin-modified binders, an aspect largely overlooked in existing literature.

2 Research Methodology

The research adhered to a structured methodology, as illustrated in Figure 1; ATC was utilized to modify the base binder of viscosity grade 30 (VG30). ATC was derived separately from sawdust and walnut shells, producing 40 grams of sawdust-activated carbon (SDAC) and 50 grams of walnut shell-activated carbon (WNAC) from 1 kilogram of raw material, respectively. Characterization encompassed Proximate analysis, SEM, CHNSO, and FTIR analyses. The proportions of SDAC and WNAC were 5%, 10%, and 15% by weight of the base binder. Homogeneity was assessed through a separation test. Subsequent evaluations included physical property assessments and rheological tests conducted on both the base and modified binder.

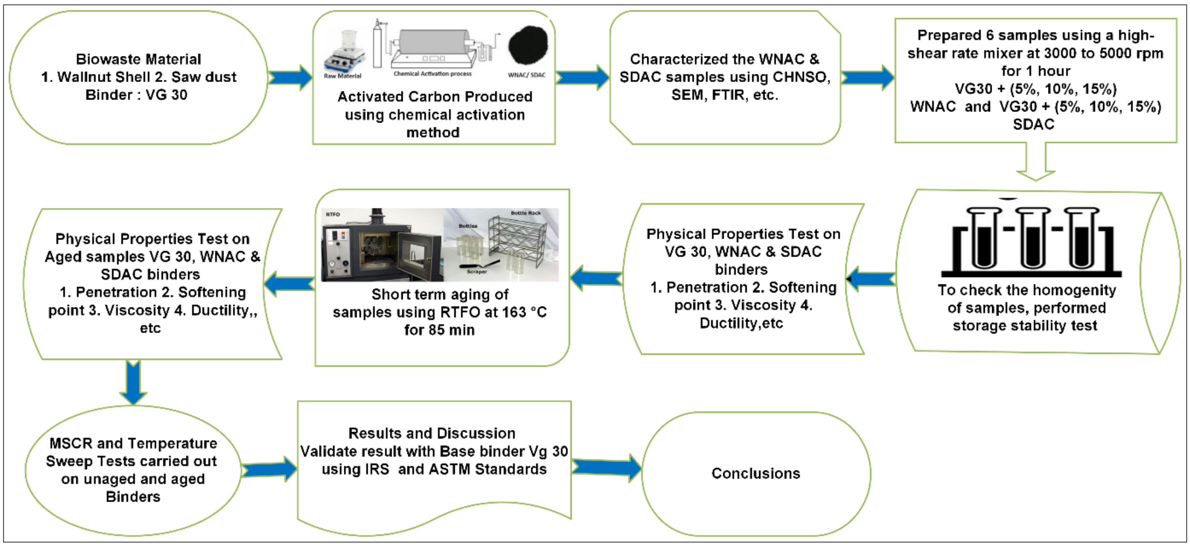


Figure 1: Flowchart of Research

2.1 Materials and Methods
2.1.1 Modifiers

The ATC utilized in this study is derived from sawdust and walnut shells through a chemical activation process, resulting in a black powder, as depicted in Fig 2. The primary constituent of this biowaste-derived ATC is carbon. These waste materials were selected for their cost-effectiveness, high carbon content, and abundance. They were sourced from a furniture manufacturing company and the dry fruit sector. In Pune, India, these materials are produced in significant quantities, ensuring a reliable supply for ATC production. Waste products like almond and walnut shells and other nutshells are readily available from various industries for local collection and utilization. Conversely, sawdust is an economical and plentiful source of lignocellulosic material, being a by-product of woodworking processes such as sanding and planning [31]. In India, where the production cost of activated carbon is approximately 2 to 3 USD per kilogram, it represents an economically viable and sustainable option for binder modification.

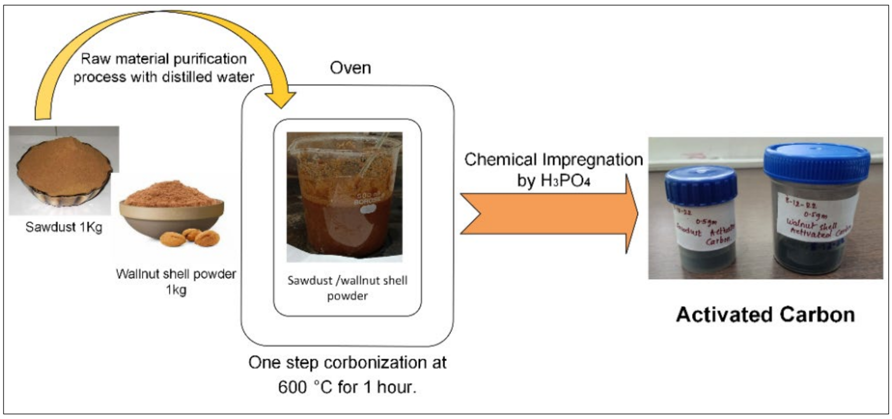


Figure 2: Chemical activation process of SDAC and WNAC

2.1.2 The procedure for making ATC

Before desiccation in an oven for five hours at 155–160°C to eliminate moisture content, the raw materials were purified using distilled water to remove impurities. The materials then underwent carbonization in an inert atmosphere within a muffle furnace for one hour at three different temperatures: 300°C, 600°C, and 700°C. These temperatures were selected to determine the optimal conditions for producing activated carbon with the best physical and chemical properties for binder modification. Examining the effects of these temperatures aims to identify the temperature that yields the highest quality activated carbon. Subsequently, one mole of phosphoric acid (H3PO4) was added daily to the materials to facilitate chemical activation. After the activation process, any residual acid was removed from the activated samples by filtration through filter paper and rinsing with distilled water to prevent any potential deteriorative reactions. Finally, the samples were desiccated in a kiln at 155°C [26], as shown in Fig 2.

2.1.3 Characterization of ATC

Characterization conducted on ATC derived from walnut shells and sawdust demonstrates that each test supports the inclusion of ATC in binder modification. The optimal activation temperature was determined through experimentation at varying temperatures (300°C, 600°C, and 700°C), underscoring the criticality of precise temperature control in ATC production. Higher iodine values indicate increased surface area and pore volume, peaking for SDAC and WNAC at 600°C with values of 1150.47 mg/g and 1200 mg/g, respectively, then decreasing at 700°C to 900 mg/g and 1000.5 mg/g respectively, thereby establishing 600°C as the optimal condition for ATC production. FTIR spectra of each binder sample reveal chemical functional groups identified between 1665 cm^{-1} and 1750 cm^{-1} in SDAC and WNAC, respectively, akin to those in the VG 30 binder. However, AC demonstrates significantly higher absorbance for functional groups, including C-O stretch, C=O stretch, and -OH stretch, indicative of the quantitative presence of carbon compounds from the ATC resource. [10]. CHNSO analysis was conducted to determine the percentage of each element and develop molecular formulas for SDAC ($C_{625}H_{454}N_{11}SO_{99}$) and WNAC ($C_{405}H_{75}NS_2O$). Compared to the raw materials, the carbon content increased by 18% for SDAC and 75.6% for WNAC. WNAC demonstrated a 36.5% higher carbon content than SDAC, as illustrated in Table 1. The proximate analysis evaluated the chemical attributes of ATC, with untreated carbon (UC) utilized for comparison, as depicted in Table 2.

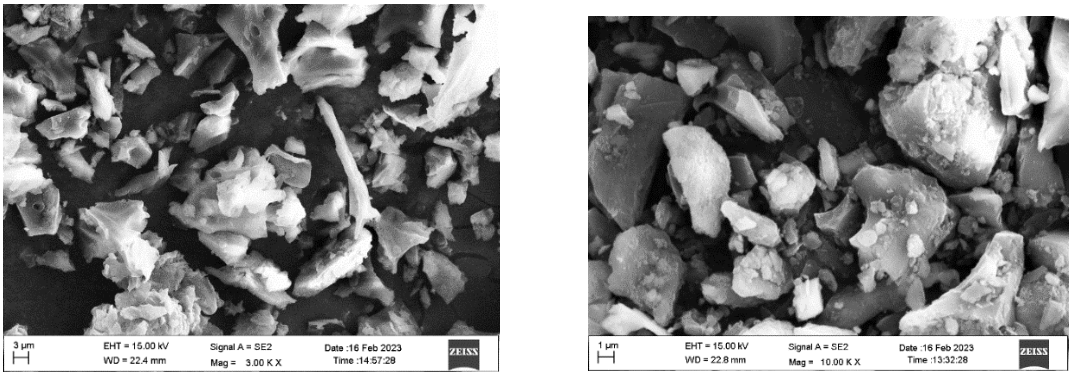
Table 1: CHNSO Test Values

Specimen	Carbon %		Hydrogen %	Nitrogen %	Sulphur %	Oxygen %
	Raw Material	AC Material	AC Material			
Walnut shell AC	37.7	66.21	1.03	0.19	0.39	22.68
Sawdust AC	41.65	49.07	2.99	0.29	0.21	10.35

Table 2: Proximate Analysis

Characteristics	WNAC	SDAC	UC
Ph value	9.3	8.5	6.8
Bulk (g/ml)	0.32	0.34	0.38
Moisture Content (%)	5.8	6.8	15.30
Ash Content (%)	3	4	25.50
Volatile Matter Content (%)	10.82	7.89	72.33
Iodine Value (mg/gm)	1200	1150.47	1500.60

The surface morphology of the ATC was examined using a Scanning Electron Microscope (SEM), as shown in Figure 3. This showed that the walnut ATC exhibited a more heterogeneous structure with smaller pores than the sawdust ATC. Consequently, the porosity of the raw material increased after activation, making the ATC more compatible with the binder. It is the analysis through which the material's internal structure is known [33]. SEM was done from the Metallurgy lab of COEP, Pune, India, to know the porosity of ATC after activation. Observing the microstructure of ATC, it is simple to see small pores present. Notably, compared to ATC made from sawdust, ATC made from walnut shells shows a greater abundance of these pores. Additionally, the ATC's exterior surface is filled with cavities. The particles in the samples are evenly distributed throughout the substance and appear to be arranged randomly. The particle size range for walnut shell ATC is 5.17μm to 20.62μm, whereas the range for sawdust ATC is 2.5μm to 11.48 μm. The SEM analysis of the SDAC and WNAC samples proved instrumental in determining the optimal dosage percentages for the modifiers.



(a) (b)

Figure 3: SEM image of (a) WNAC sample and (b) SDAC sample

2.1.4 Asphalt binder

This investigation utilized a VG 30-grade asphalt binder sourced from the Transportation Engineering Laboratory at the College of Engineering in Pune, India. Table 3 delineates the physical properties of this VG30, which meets all specified criteria within the Indian region. Subsequently, ATC was incorporated into the unmodified control asphalt to formulate the modified binder.

Table 3: Physical properties of VG30 binder

Property	Standard	Specification	Result
Penetration (1/10 mm) at 25℃	IS: 1203-2022	Min 45	47
Softening point(℃)	IS: 1205-2022	Min 47	48.6
Viscosity at 60℃ (Poise)	IS: 1206-2021 (Part 1-3)	2400-3600	3200
Ductility(cm)	IS: 1208-2023 (Part 1 & 2)	Min 40	74

2.1.5 Material preparation

The VG30 binder was initially heated in a furnace set at 160°C for around one hour. Subsequently, 5%, 10%, and 15% of SDAC and WNAC by weight were added to the VG30 asphalt binder once the temperature stabilized at 180°C. This was followed by continuous blending for 60 minutes at a 3000 to 4000 rpm speed using a high-shear mixer device (IKA T-25 ULTRA-TURRAX Digital High, as illustrated in Figure 4) to achieve a homogeneous mixture.

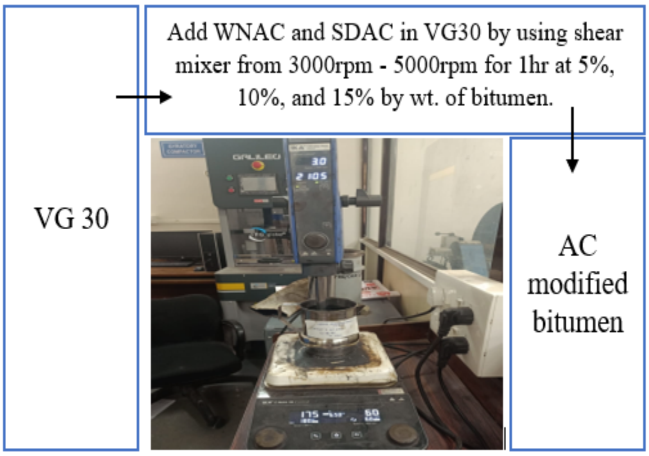


Figure 4: Material preparation with high share rate mixer

2.2 Testing Procedures

2.2.1 Separation test (Storage Stability Test)

The homogeneity of the modifier with the binder, illustrated in Figure 5, was evaluated through a separation test per IRC SP 53[17]. The WNAC and SDAC modified binder was placed in aluminum tubes (25 mm diameter, 160 mm height) and stored vertically in an oven at 163°C for 48 hours. After cooling, the tubes were segmented into three parts, and storage stability was assessed by measuring the softening point difference between the upper and lower sections. Table 4 indicates that the softening point difference remained below 2.5°C up to 10% WNAC and SDAC, meeting IRC SP 53-2010 requirements. Based on previous research, a 15% WNAC sample was included, with a slight temperature variation of up to 1°C considered acceptable [34].

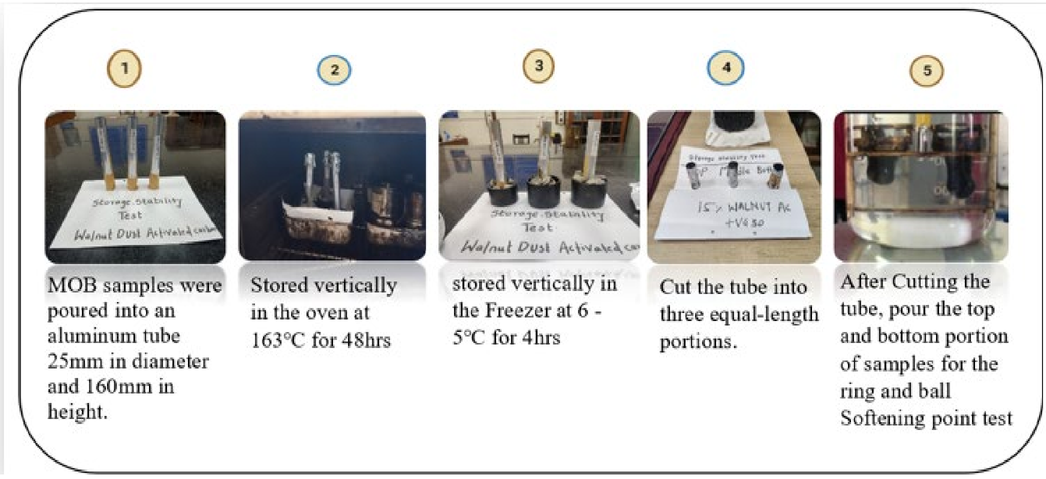


Fig 5: Separation test process

2.2.2 Physical and Rheological Properties

The adequacy of the SDAC and WNAC modified asphalt binder was assessed through physical and rheological properties tests, including penetration (IS:1203-2022) [15], ductility (IS:1208-2023)[16], softening point (IS:1205-2022)[17], and viscosity tests [24]. Unaged and aged samples of VG 30 and SDAC and WNAC modified binders ' high-temperature deformation (rutting) properties were evaluated using MSCR and temperature sweep tests with a Dynamic Shear Rheometer (DSR).

2.2.3 Temperature Susceptibility

The penetration index quantifies the binder's sensitivity to temperature changes, aiding in predicting its performance. Using formulas (1) and (2) from the Shell Binder Handbook [28], penetration indices were calculated for both unmodified and modified binders. The high-temperature susceptible binder has parameter A values between 0.0015 and 0.06, while the penetration index (PI) ranges from -3 to +7 for extremely low-temperature susceptible binder. A lower PI value indicates a higher temperature susceptibility [14].

$$A = \frac{log(P_{25}) - log\,800}{25 - Tsp} \tag{1}$$

$$PI = \frac{20 - 500A}{1 + 50A} \tag{2}$$

Where,
- A = Temperature susceptibility in °C
- P_{25} = Penetration at 25℃ in mm
- Tsp = Softening point temperature in °C
- PI = Penetration Index

2.2.4 Rotational viscosity test

The Brookfield Viscometer, as per ASTM D-4402 [4], was utilized to measure the apparent viscosity. Rotational viscosity tests were performed at 150°C for mixing (IRC SP 53-2010, MORTH 2013 [25], AASHTO M 156 [1]) and 165°C for transportation. These tests were conducted on modified and VG30 binders for unaged and short-term aged conditions with a constant spindle speed of 20 rpm using the SC4-27 cylindrical spindle (spindle diameter=11.76 mm, side length=33.02 mm, effective length=39.29 mm).

2.2.5 Short-Term Aging Process (RTFO)

Short-term aging of asphalt binders involves the initial oxidation that occurs from the mixing procedure to the laying of the asphalt at the construction site, typically taking about 4 to 5 hours. This process significantly impacts the performance and durability of the pavement. In a laboratory setting, this aging process is simulated using the Rolling Thin-Film Oven (RTFO) test, as described by ASTM standards ASTM D2872-21[3]. The RTFO test reproduces the effects of heat and air on the binder, simulating the conditions experienced during mixing and laying. Further tests on the aged binder provide insights into its properties and performance, enabling engineers to design more durable asphalt mixtures [42].

The short-term aging of WNAC and SDAC-modified binder was performed using RTFO equipment following standards. Samples were aged at 163°C for 85 minutes, and the mass loss before and after aging was determined [7]. Figure 7 illustrates the variations in mass percentages of the VG30 and modified binders, with mass loss adhering to predetermined standards of not exceeding 1%. The positive trend in mass loss percentage observed for VG30 and SDAC/WNAC samples can be attributed to reduced volatile elements [21].

2.2.6 Temperature Sweep test

This test assessed the high-temperature susceptibility of the modified binder by utilizing a Dynamic Shear Rheometer, as shown in Figure 6. As per Feng [13], rheological characteristics enable observing the binder's viscoelastic response to cyclic strain or stress changes. The failure temperature is identified by achieving a minimum G*/sin(δ) value of 1 kPa for the unmodified binder and 2.2 kPa for the modified binder. Dynamic complex modulus (G*) quantifies material stiffness and response to oscillatory deformation. At the same time, δ provides insight into elastic and viscous balance, offering clues to resistance against permanent deformation in hot climates, as indicated by the rutting factor G*/sin(δ), also known as performance grade (PG) of asphalt binder [27].

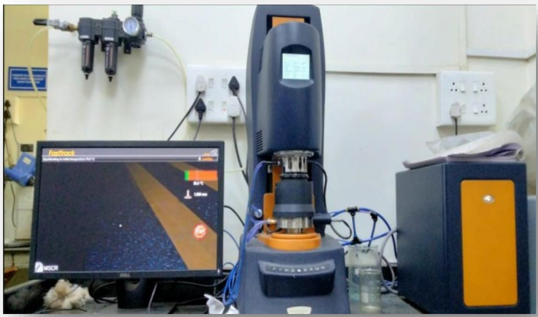


Figure 6: Dynamic shear rheometer (HR1 hybrid rheometer)

2.2.7 Multiple Stress Creep Recovery Test

The MSCR test, as per ASTM D7405-08 [5] standards, was utilized to evaluate the permanent deformation potential of the asphalt binder under elevated temperature conditions. The specimen was positioned between plates with a diameter of 25 mm and a gap of 1.0 mm. Employing the creep-recovery loading paradigm, the DSR subjected the sample to 1-second creep followed by 9-second recovery, constituting a cycle repeated ten times under lower stress of 0.1 kPa. Subsequently, the stress was escalated to 3.2 kPa, and the procedure was repeated for another ten cycles. Key performance parameters of the MSCR test include recovery percent (R) and non-recoverable compliance (Jnr). R and Jnr were computed using equations (3) and (4) for each creep-recovery cycle. Average values of R and Jnr were determined from the ten cycles for each stress level, resulting in four parameters: R0.1, Jnr0.1, R3.2, and Jnr3.2. In this investigation, all binder specimens underwent MSCR testing at a constant temperature of 60°C, disregarding their respective Performance Grade (PG) temperatures, to facilitate equitable comparison of rutting resistance [23,34].

$$R = \frac{\gamma_p - \gamma_n}{\gamma_p - \gamma_0} \quad (3)$$

$$Jnr = \frac{\gamma_n - \gamma_0}{\tau} \quad (4)$$

Where,

R = Recovery percent in percentage
Jnr = Non- recoverable compliance in kPa
γ_p = peak strain post-1-second creep
γ_n = non-recoverable strain following 9 seconds of recovery
τ = creep stress level in each cycle in kPa
γ_0 = initial shear strain

2.3 Results and Discussion

2.3.1 Physical Properties

Figures 8, 9, and 10 depict the fundamental characteristics of ATC-modified and VG30 binders. The rise in AC content by 5%, 10 %, and 15% of WNAC penetration value decreased by 10%, 19%, and 25%, respectively, and in the SDAC case, it decreased by 23%,29%, and 36%, respectively, as compared to VG 30 binder. The softening point value increases by 4%, 7%, and 8% for WNAC and 4%, 4.5%, and 5% for SDAC compared to VG 30. This suggests a strengthening of the binder and an enhancement in its high-temperature attributes as a result of the ATC alteration. In comparison to the VG30 binder, there is a notable average 23.4% decrease in penetration value in the condition and an average 10% elevation in softening point value, which positively influences the properties of the binder. As a result of the ductility test, an increase in ductility was seen in 5% of WNAC and SDAC binders by 20%, and 23% indicated the enhanced elasticity of the modified binder due to incorporating ATC.

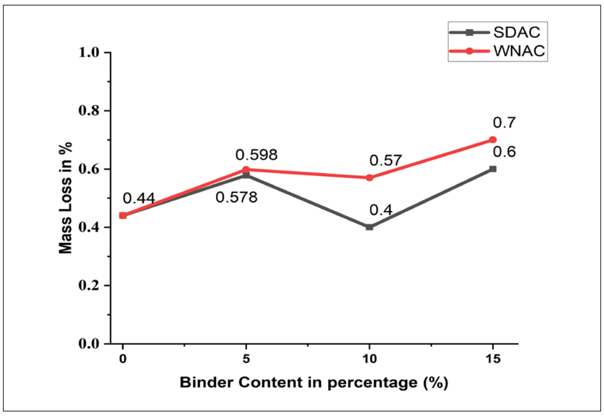


Figure 7. Mass loss after short-term aging

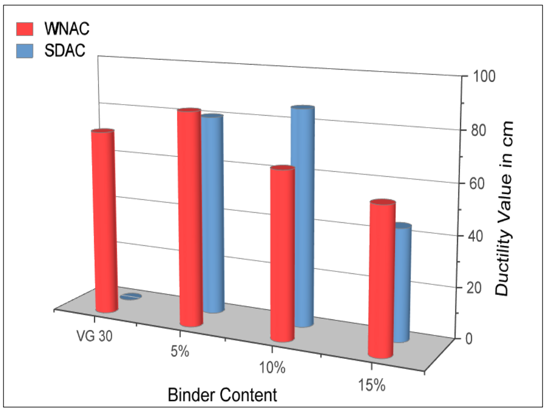


Figure 8. Ductility value after short-term aging

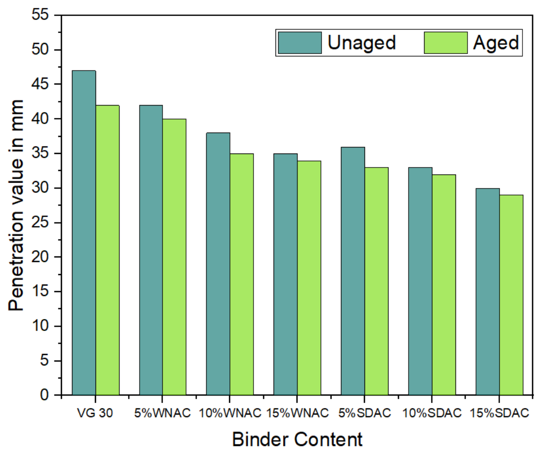


Figure 9. Penetration Value

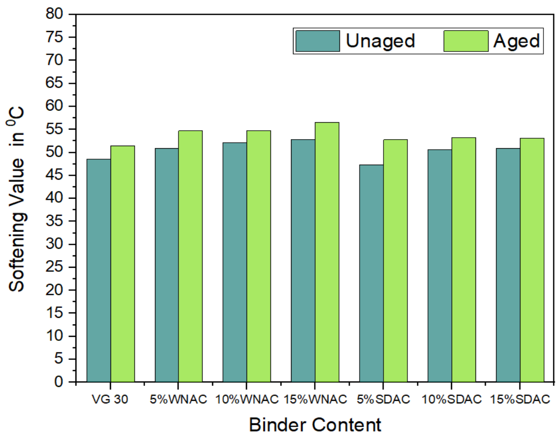


Figure 10. Softening Value

Table 4: Separation Test Values

Softening point (℃) / Content (%)	VG30	WNAC			SDAC		
		5%	10%	15%	5%	10%	15%
Top	48.6	52.4	51.5	49.0	47.9	50.2	48.5
Bottom	49.4	53.4	52.9	51.7	46.8	51.5	51.7
Difference	0.8	1	1.35	2.65	1	1.3	3.2

2.3.2 Penetration Index (PI)

Utilizing the PI index, the temperature susceptibility of the modified binder was assessed. Demonstrated in Figure 11 are the escalating PI values of both the VG30 binder and ATC-modified binders after the short-term aging process. Results show the PI values of all the modified binders more than -2 except for 5 and 15% SDAC. Such results suggest a decline in the temperature susceptibility of the binder that has been modified with ATC. Consequently, the binder's flowability at elevated temperatures is hindered, thereby enhancing its resistance to rutting. In regions with high temperatures, such a characteristic is favored for preserving the structural integrity and durability of the road pavement.

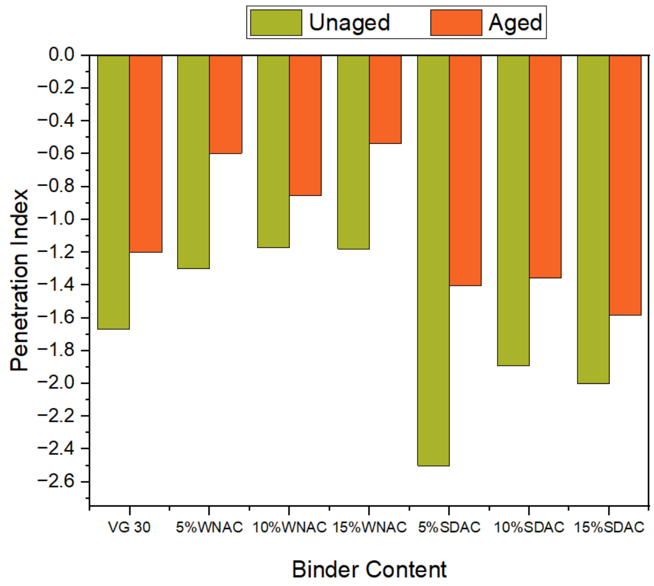


Figure 11. Penetration Index of Binder content

2.3.3 Rotational viscosity effects

The rotational viscosities (RV) for both the VG30 and Modified binders, analyzed at temperatures of 150°C and 165°C (as shown in Figures 12 and 13), demonstrated increased viscosity upon the incorporation of SDAC and WNAC into the VG30 binder. The results indicated that the WNAC15% modifier exhibited over a 90% increase in viscosity compared to VG30, both aged and unaged conditions, at both temperatures. Similarly, other modified binders, 5%, and 10% WNAC exhibited over a 75%and 80% and in 5%, 10%, and 15 % SDAC binders, 60%,78%, and 81%increses viscosity, respectively, compared to VG30. This increase in viscosity can be attributed to the higher carbon particle content resulting from incorporating SDAC and WNAC. The mixing process of the modified binder suggests the likelihood of chemical reactions and physical dispersion, potentially forming a new network structure due to the temperature-resistant properties of the ATC particles. Moreover, SDAC and WNAC can enhance the VG30 binder and improve its recovery ability under stress application.

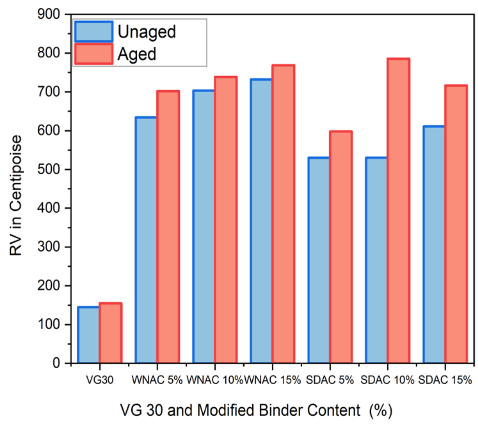


Figure 12. Rotational Viscosity (RV) at 150℃

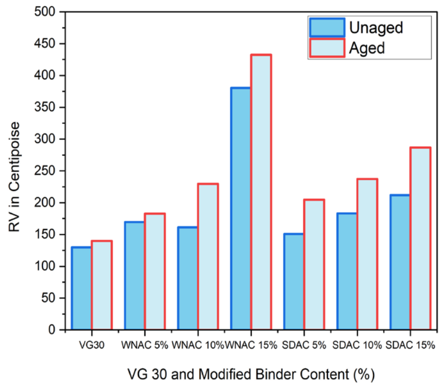


Figure 13. Rotational Viscosity (RV) at 165℃

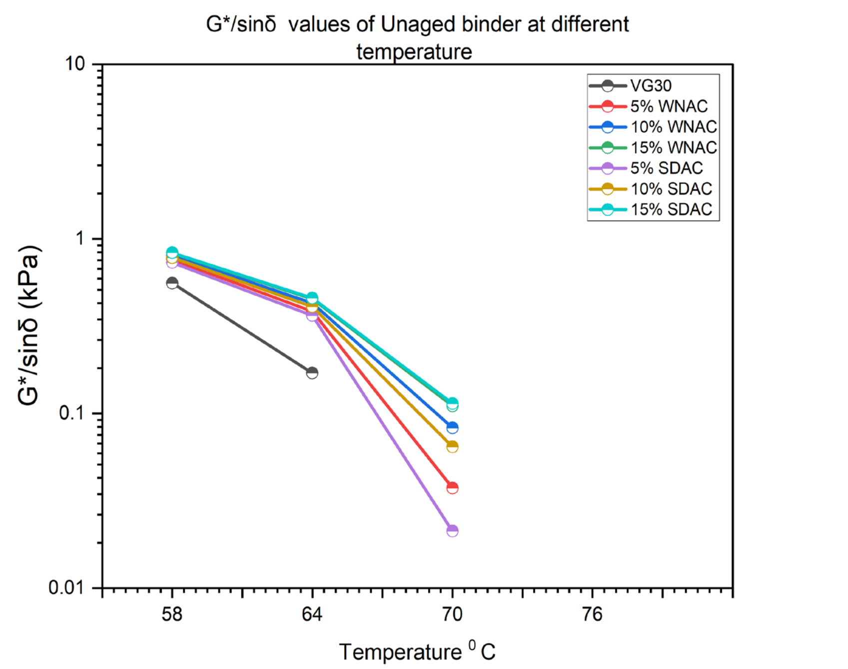
2.3.4 Performance Grade Estimation

The failure temperature from the temperature sweep test reveals the binder's Performance Grade (PG), which is critical for determining its resistance to deformation and thermal susceptibility. Table 5 displays the PG grade of the binder, showing that SDAC has slightly superior rutting stability when considering failure temperature compared to WNAC, enhancing rutting resistance. Adding AC improves the binder's strength and load-bearing capacity at elevated temperatures, as evidenced by increased stiffness. This enhancement is crucial for maintaining structural integrity in high-temperature, high-traffic areas. A higher G*/sinδ value indicates greater solidity and less deformation at elevated temperatures.

Table 5: PG grade of Binders

Binder Content	Failure temp. (℃) Unaged	Failure temp. (℃) aged	High temp. Performance grade
VG30	64	67	PG 64
5% WNAC	70.8	71.5	PG 70
10% WNAC	71.5	70.7	PG 70
15% WNAC	71.9	67.3	PG 70
5% SDAC	70.6	71.0	PG 70
10% SDAC	71.4	71.1	PG 70
15% SDAC	72.2	74.5	PG 70

Figure 14 (a & b) illustrates the complex shear modulus (G*/sin(δ)) before and after binder aging, showing the impact of temperature. Increased AC modifiers raise the complex shear modulus, indicating superior rutting resistance compared to the VG30 binder. In the unaged condition, Figure 14(a) shows maximum failure temperatures of 71.9°C for WNAC and 72.2°C for SDAC at 15% content, enhancing their PG grade from PG 64 to PG 70. Figure 14(b) demonstrates a significant increase in the complex modulus (G*) after aging, indicating increased stiffness and reduced phase angle (δ). Short-term aging causes oxidation and evaporation of volatile elements, increasing binder rigidity. Consequently, WNAC 15% did not advance to the next grade, PG 76, as the modified binder failed at a temperature of 74.5°C. The temperature sweep analysis shows a correlation between G*/sinδ and temperature, where the parameter decreases as temperature increases, indicating enhanced rutting resistance. Both walnut and sawdust-modified binders now exhibit a higher high-temperature grade.



(a)

Figure 14 (a). G*/sin δ value of binder content at different temperatures
For Unaged samples

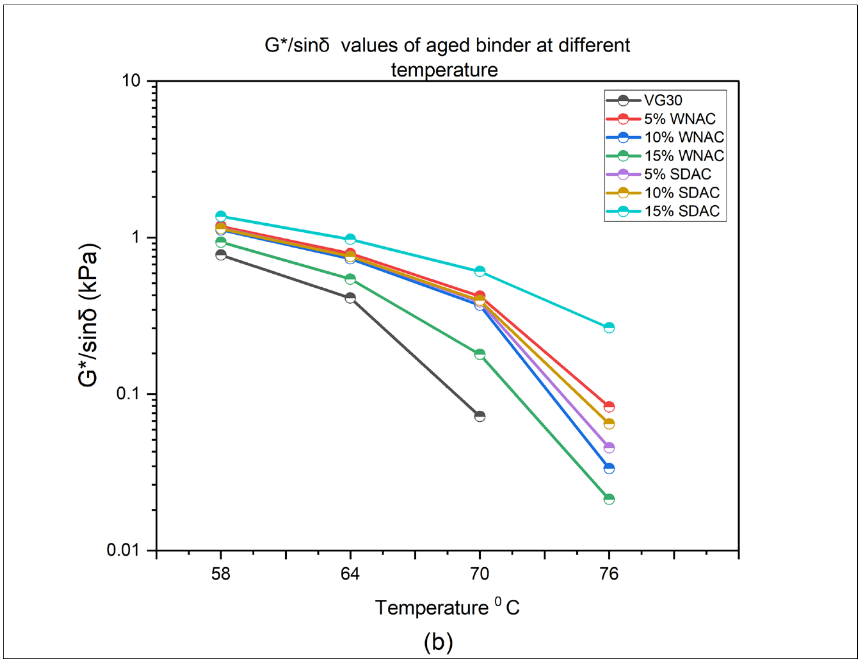


Figure 14 (b). G*/sin δ value of binder content at different temperatures For aged samples

2.3.5 Rutting resistance

The MSCR test, conducted using the DSR on VG 30 and 5%, 10%, and 15% AC-modified binders, demonstrates the positive impact of AC addition on permanent deformation resistance. The current specification parameter for assessing the rutting potential of asphalt binders is Jnr 3.2kpa. The results of Jnr values under two different levels of creep stress for all binders tested are illustrated in Figure 15, indicating a reduction in Jnr values due to incorporating SDAC and WNAC. Specifically, with a 15% increment in WNAC, Jnr values decreased by approximately 24.55% at a 0.1 kPa stress level and 7.44% at a 3.2 kPa stress level. Similarly, with 5% SDAC, Jnr values decreased by 11.37% at a 0.1 kPa stress level and 4.67% at a 3.2 kPa stress level compared to VG 30. Additionally, Fig.16 represents the percentage recovery exceeded as compared to VG 30 binder by 80%, indicating enhanced elastic recovery properties contributing to rutting resistance. These findings suggest that the modified binders exhibit reduced susceptibility to permanent deformation, with higher recovery values indicating favorable elastic characteristics, particularly at lower stress levels.

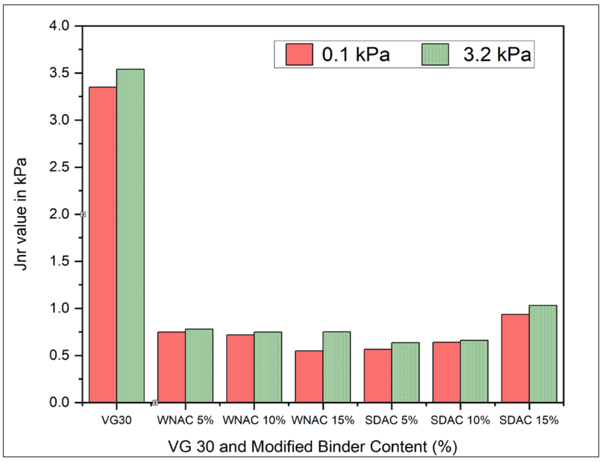


Figure 15. Non-recoverable compliance (Jnr) evaluation of all tested binders at 60 °C

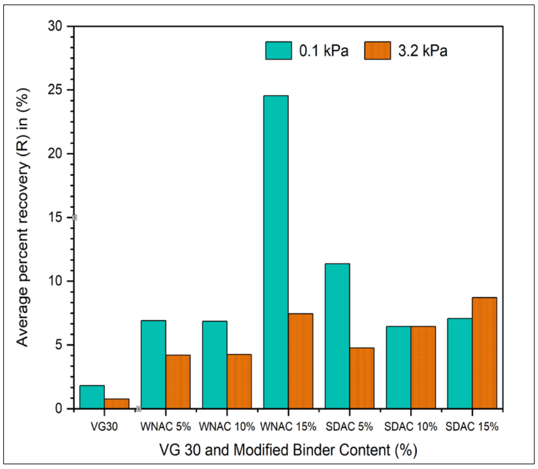


Figure 16. Average Percentage Recovery (R)

3.0 Conclusions

This study uses a chemical activation process to produce and analyze activated carbon derived from walnut shells and sawdust. Proximate analysis, SEM, CHNSO, and FTIR initially characterized the activated carbon samples. Subsequently, Walnut-activated and Saw duct activated carbon was incorporated into the binder at 5%, 10%, and 15% by weight. The effects of WNAC and SDAC-modified binder on physical properties and high-temperature deformation (rutting) behavior were examined. These results were compared against VG30 to evaluate the effectiveness of the activated carbon-modified binders. The key findings are as follows:

- The comprehensive characterization indicated that activated carbon exhibits beneficial properties for binder modification. Through CHNSO analysis, the unique molecular structure of AC, characterized by its high surface area, porosity, and functional groups, facilitates its role in modifying binders. This enhances the binder's physical and chemical properties, improving performance in terms of stability, durability, thermal resistance, and mechanical strength.
- Proximate analysis reveals that higher iodine values correspond to increased surface area and pore volume, with SDAC and WNAC reaching their maximum at an optimal temperature of 600°C.
- FTIR analysis shows that activated carbon exhibits significantly higher absorbance for functional groups such as C-O stretch, C=O stretch, and -OH stretch, reflecting the substantial presence of carbon compounds derived from the activated carbon source.
- SEM evaluation shows enhanced porosity in the raw material post-activation, enhancing the compatibility of the activated carbon with the binder. These findings demonstrate that activated carbon offers chemical compatibility and structural benefits as a binder modifier.
- The physical properties of the modified binder, produced using activated carbon from walnut shells and sawdust, showed a reduction in penetration and ductility values while softening point and viscosity values increased. The PI value also increased, indicating enhanced stiffness and reduced temperature susceptibility. It is suitable for high-temperature regions that typically experience standard air temperatures ranging from 40°C to 45°C, with pavement surface temperatures reaching up to 60°C.
- The RTFO test results showed an increased mass loss for binders, with 15% and 5% for WNAC and SDAC, attributed to reduced volatile content. Binders modified with 10% AC demonstrated the best results.
- Rheological results indicated that $G^*/\sin\delta$ (rutting parameter) values increased with activated carbon content and decreased with rising temperatures. With 5% SDAC and 15% WNAC, the binder achieved a higher grade than VG30, demonstrating increased hardness and resistance to permanent deformation. The high-temperature performance grade of VG 30 and activated carbon-modified binder is PG64 and PG70, respectively, indicating enhanced rutting resistance.
- MSCR results showed that both modified binders are well-suited for applications requiring high rutting resistance and good elastic recovery. The percentage recovery reached 24.50% for 15% WNAC and 11.37% for 5%SDAC, with these two modifications showing superior rutting resistance overall. Also, 10% of SDAC and WNAC show 10.22% and 9.34% recovery.

The study findings indicate that the modified activated carbon binder is more ductile than the VG30 grade. Activation of the raw material significantly increased porosity, and fundamental tests revealed that activated carbon-modified binders give better results than VG30, showing versatility in hot climates and enhanced performance and reliability. Sawdust AC at 5% and Walnut activated carbon at 15% were particularly suitable, enhancing binder hardness and rutting resistance to a PG70 grade. These findings suggest potential for future research to assess the attributes of the modified binder in long-term aging trials and evaluate modified asphalt mixtures for practical applications.

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