



## Evaluation of Dynamic Shear Rheometer Test Parameters and Effect of Carbon Black Particles Obtained from Agricultural Waste Recycling (Walnut Skin) in the Rehabilitation of Asphalt Binder Performance Grade

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### ABSTRACT

The use of recyclable materials in road construction, protect the environment, is an influential factor in the decision-making process for road projects. As one of the most important elements in nature and an original basis for the formation of life on earth, Carbon has been used in many different industries for its high surface area and porosity. Because of asphalt binder rheology characteristics, asphalt layers tend to return to their initial conditions after traffic flow but some of these deformations return in elastic form and some not return in plastic form. In this research, the Dynamic Shear Rheometer (DSR) test was used to analyze asphalt Binder performance Grade. Carbon Black particles processed from agricultural waste recycling (walnut skin) with specific weight percentages of 3, 5, 7 and 10, were used for asphalt binder rehabilitation. According to the results, the use of Carbon Black particles derived from the recycling of agricultural waste improved asphalt binder performance Grade from PG64 to PG74 for modified asphalt binder with 7% carbon black and rheological parameters like complex modulus increased 1.7 times and phase angle decreased approximately 0.85 times.

## 1. Introduction

Due to the activity of factories, service providers, and industrial workshops as well as industrial and household sewage, a huge

volume of waste was produced every day. In recent years, the industry that produces hot mix asphalt has undergone many changes due to the numerous changes caused by the use of waste materials in these mixtures [1-3].

Although this increases the cost of asphalt pavements structure, it will reduce the final cost of road networks construction in the long run due to reduced maintenance costs and reduced thickness of asphalt pavements. Meanwhile, it is possible to reduce the initial cost and increase efficiency by using waste materials that have the potential to improve the physical and mechanical properties of asphalt pavements [4].

Asphalt mixture is composed of aggregates, asphalt binder, and filler. Asphalt binder modification, as the most important issue in creating visco-elastic behavior in the asphalt mixture via various additives, has always been a focus of attention among pavement engineers[5].

Sulfur[6], lime[7], pozzolanic materials[8], various polymers with different structures[9], rubber[10], glass[11], carbon[12] and so on are the best among the additives used in asphalt binder modification.

Carbon is one of the most important elements in nature and an original basis for the formation of life on earth. This material exists in all living things and also can be found in a wide range of materials from fibers and carbon composites to electrode graphites. Carbon black referred to a group of materials.

with a high surface area and porosity. This type of graphite structure was important because it provided pores or gaps to accommodate molecules. These pores increased the level of internal activation and thus increased absorption from the surface area. Varieties of carbon black were unique and complex in terms of size, shape, cavities, and porosity[13].

The most important features of carbon black included:

- As regards the surface area, it was characterized by a high level of activity and absorption.
- It was characterized high porosity and a high contact area with the adsorbent phase.
- Like graphite, carbon black was a structure consisting of horizontal hexagonal plates irregularly interlocked into one another. Such atoms could be form bonds with other atoms and create multiple agent groups in activated carbon[14].

To evaluate the parameters that affect asphalt binder rheology, a Dynamic Shear Rheometer (DSR) was used and the following parameters were investigated: Complex Shear Modulus ( $G^*$ ), Storage Complex Shear Modulus ( $G'$ ) and Loss Complex Shear Modulus ( $G''$ ), Phase angle ( $\delta$ ), time, frequency, Complex Shear Viscosity ( $\eta^*$ ) and Storage Complex Shear Viscosity ( $\eta'$ ) and Loss Complex Shear Viscosity ( $\eta''$ )[15].

Significant actions in this research included the following:

- Review of the main parameters of Dynamic Shear Rheometer test
- carbon black derived from agricultural waste (walnut skin) used in asphalt binder
- Analyze the basic tests of modified asphalt binder with recycled carbon black
- Analyze the rheology and performance grade of modified asphalt binders with recycled carbon black

## 2. Literature Review

The use of carbon black in asphalt binder and the production of modified asphalt mixtures investigated. In order to evaluate the effect of carbon black on reduced the permanent deformation of asphalt concrete in a wide temperature range, Yao et al. (1986), conducted uniaxial creep tests. Fatigue, tensile strength, and stiffness tests were performed on carbon black modified samples. Carbon black with a diameter of 8 mm and weight percentages of 15 to 20 reduced the effect of temperature on the physical characteristics of the mixture. According to this study, asphalt binders stiffened by carbon black were suitable for reducing the potential of rutting in asphalt pavement under heavy traffic in hot climates [14].

A research project was conducted to study the effect of carbon black used in rubber production on reducing the temperature sensitivity of asphalt pavement. In order to achieve a specific percentage density, carbon black added to the asphalt binder by 0.2%. Viscosity results showed a real difference in the temperature sensitivity of the pavement sections [13].

Dedeer Leswer et al. (1995) examined the effect of carbon black recycled from rubber over other fillers as the asphalt binder rheology modifier. Carbon black was compared to stone fillers and spheroidal clay. It was mixed in the asphalt binder with a weight percentage of 20 to 40. The results showed that carbon black, as a suitable rheology modifier like polymer modified asphalt binders, had an appropriate reaction at a low temperature [16].

Si Hai Wen et al. (2004) investigated the effects of carbon black on thermal, mechanical and electrical properties of the asphalt mixture samples. By adding 7% carbon black to the asphalt binder, the softening point temperature increased from 44 to 81°C, the storage complex shear modulus increased and the electrical resistance decreased. By increasing the amount of carbon black, these effects continued [17].

Xiaoming Liu et al. (2014) evaluated the effect of carbon fillers on the electrical properties and conductivity of asphalt. Two conductive materials, graphite, and carbon fiber were used. Changes in the properties of materials were tested by dynamic analysis, rutting, Marshall Stability, Polymer Stability and electrical resistance tests [18].

Chong et al. (2014) evaluated the effects of carbon black on the anti-aging, rheology and conductivity properties of the black carbon/SBS polymer/asphalt composition. According to laboratory results, the three types of carbon black used in the study improved high-temperature properties, anti-aging and thermal conductivity of the SBS polymer modified asphalt binder but decreased the electrical resistance and storage stability of the mixtures [19].

## 3. Materials and Test Method

In this Paper, aggregate gradation is medium grading of continuous hot mix asphalt according to Topeka and Binder course. Aggregate and filler grading range Presented in Table 1.

Asphalt Binder with the abbreviation of PG64-22 used in this paper. It is a performance graded (PG) asphalt derived from specially selected crude oils via

carefully controlled refining processes. It is applicable to road construction and the standard specification of this asphalt binder was given in Table 2.

**Table 1.** Continuous hot mix asphalt grading according to Topeka and Binder course.

	Aggregate	Filler
Size	Passing Percent	-
25	-	-
19	100	-
12.5	95	-
9.5	-	-
4.75	60	-
2.36	44	-
0.3	13	100
0.075	16	80

**Table 2.** Standard Specification of PG64-22.

Test	Unit	Value	Standard Code
Penetration grad	mm (1/10)	67	ASTM D5
Softening point	<sup>0</sup> c	47	ASTM D36
Flash Point	<sup>0</sup> c	262	ASTM D92
Ductility	cm	102	ASTM D113
Density	gr/cm <sup>3</sup>	1.02	ASTM D70

Carbon Black has a very irregular network of carbon atoms that was commercially obtained from the thermal or oxidative decomposition of hydrocarbons. The use of carbon black in the industry as a filler material widely used to improve the electrical and optical properties of materials that were dispersed in them.

X-ray studies on carbon black showed that synthesized carbon black was composed of quaternary graphite layers in which carbon atoms have relatively similar positions to those observed in graphite.

the specifications of carbon black obtained from the recycling of agricultural waste(Walnut skin) were presented in table 3.

The appearance of Carbon black was shown in Fig. 1.



**Fig. 1.** Carbon Black obtained from the recycling of agricultural waste(Walnut skin).

**Table 3.** Standard Specification of PG64-22.

Test	unit	Value
Iodine number	(mg/g)	75-115
Dibutyl phthalate absorption	(ml/100 g)	85-95
Tinting Strength	%	120-135
Toluene Discoloration	%	>80
Ash content	%	<8
Heating Loss	%	<3
PH	-	>7
Sulfur Content	%	<1
Pour density	(g/l)	280-330
Size	mm	0.3-2.4
Specific surface	(m <sup>2</sup> /g)	750-1150

In this paper, firstly, the Carbon Black obtained from the recycling of agricultural waste(Walnut skin) added with 3, 5,7 and 10% by weight of Asphalt Binder.

Mixing continued until a homogeneous mixture was achieved. Then the basic experiments such as penetration degree according to ASTM D5, softening point according to ASTM D36, Ductility according to ASTM D113, Flashpoint according to ASTM D92 performed.

The Dynamic Shear Rheometer (DSR) according to ASTM D7175 used to evaluate of carbon black particles on the performance grade(PG) of PG64-22 in the high temperature. The name of test device was Anton Par and is made in the United State.

#### 4. Dynamic Shear Rheometer test

This test was used to determine the important values of behavioral parameters of asphalt binder such as complex modulus ( $G^*$ ) and phase angle ( $\delta$ ) using parallel plates under dynamic shear loading (oscillation loading).

it was applicable for asphalt binder with complex modulus in the range of 100 Pa to 10 Mpa. This range obtained at 5 to 85 degrees centigrade. The important purpose of this experiment was to determine the linear viscoelastic properties of the asphalt binder.

The main parameters and Specialized phrases in this experiment presented below:

$G^*$  : The ratio of dividing the absolute shear stress to the absolute value of the shear strain according to equation 1.

$$G^* = \frac{|\tau_{max}|}{|\gamma_{max}|} \quad (1)$$

$\delta$  : The phase angle is in the range of 0-90 °C and obtain,

-under the controlled strain: Between the injected sinus strain and the resulting sinus stress

-under the controlled stress: Between the injected stress and the resulting strain Fig. 2.

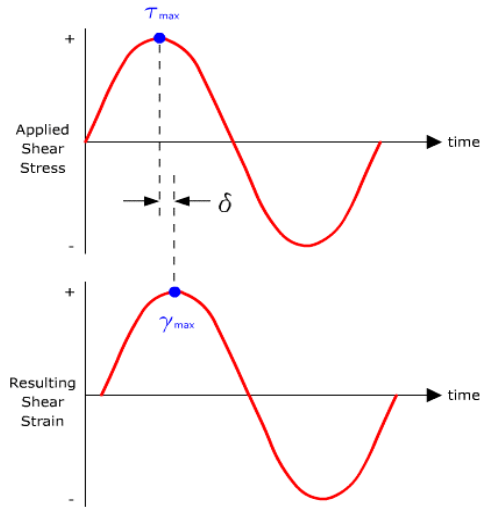


Fig. 2. Schematic Figure of phase angle in the Controlled shear stress, CSS.

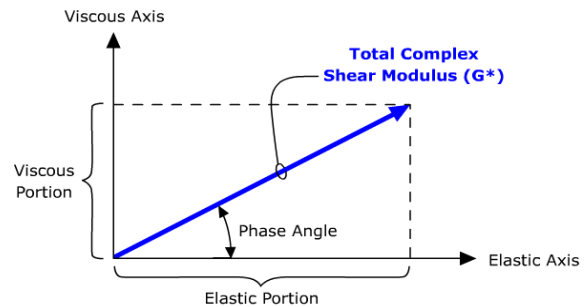
$G''$ : The Loss complex modulus (viscose part) represents a part of a complex modulus that indicates the amount of energy dissipation in a loading cycle. It calculated according to equation 2.

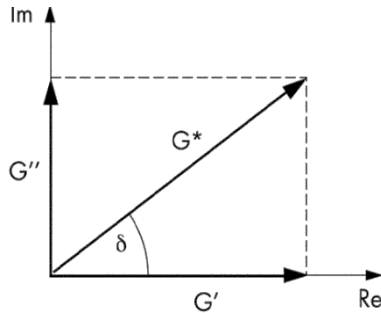
$$G'' = G^* \times \sin(\delta) \quad (2)$$

$G'$ : The storage complex modulus (elastic part) represents a part of a complex module that indicates the amount of energy stored in a loading cycle. It calculated according to equation 3.

$$G' = G^* \times \cos(\delta) \quad (3)$$

The better representation of these quantities is expressed in the Fig. 3





**Fig. 3.** Schematic Figure of phase angle and complex modulus with DSR test (Determine elastic and viscose parts).

Oscillation Loading: It is a type of loading in which the shear stress or shear strain was introduced into the test sample in an oscillatory manner, such that the shear stress or shear strain changes to the range of zero in the sinusoidal state.

Linear Viscoelastic(LVE) range: The region referred to the behavior of sample which complex modulus is independent of shear stress or strain.

$\eta$ : The shear-rate independent capillary viscosity or Complex shear viscosity or complex shear viscosity or dynamic viscosity or absolute shear viscosity was more convenient than loss and storage modulus for an engineer to evaluate the properties of a material and calculate according to equation 4.

(Equation 4:  $\eta = \frac{G^*}{f}$  )

Steric hardening: It was the association of asphalt binder molecules in the reservoir at ambient temperature. This molecular bond could increase the asphalt binder's shear complex modulus.

The amount of this molecular association of asphalt binder properties may be revealed a few hours after storage.

Also, the maximum shear stress and shear strain were calculated from equation 5.

( Equation 5:  $\tau_{max} = \frac{2T}{\pi r^3}$   $\gamma_{max} = \frac{\theta r}{h}$  )

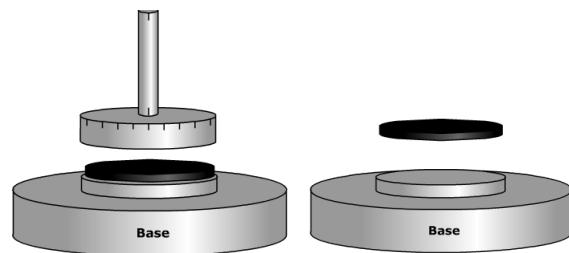
T: Torque (mN.m)  $r$ =radius(mm)

$\theta$ : rotation angle  $h$ : sample hight(mm)

In the DSR test process, a small sample of asphalt binder was placed between two plates(Fig. 4).

The lower plate fixed while the top plate with a frequency of 1.59 Hz (or 10 rad/s) moved in the direction of the sample, back and forth to make the shear stress.

This test is carried out on origin, short aged (RTFO) and long aged (PAV) asphalt binder. The test temperature, sample size, and plate diameter depend on the type of asphalt binder. For origin and aged asphalt binder with RTFO used specimens of thickness 1 mm and a diameter of 25 mm. Aged asphalt binder with PAV used specimens of thickness 2 mm and a diameter of 8 mm.



**Fig. 4.** Schematic Figure of sample placement with DSR test [20].

Asphalt binders as a viscoelastic material, behave such as elastic solids (the deformation caused by the loading could be retrieved - it is able to return to its initial form after removal of load) and, like the viscous liquid (the deformation caused by the loading could not be recovered - it is not able

to return to their original form after removal of load).

DSR test used in the plastic industry for a long time and now it used to measure two characteristics of the elastic and viscous in the asphalt industry.

## 5. Experiment Results

### 5.1. Asphalt Binder Basic Tests

The basic experiment test results of asphalt binder are presented in table 4. According to the results, modified asphalt binder changes are as follows. By adding carbon black to asphalt binder, the flashpoint has increased, which Increased ascending. This increase was due to the distribution of carbon black in the asphalt binder network.

The penetration grad of modified asphalt binder with carbon black particles has decreased. Because these particles make it stiffer and increase its strength.

The softening point of asphalt binder improved by adding carbon black. These changes are compatible with flash point changes. In the low amounts of 7% carbon black, asphalt binder has been stiffer and it's ductility increased but the excessive accumulation of these particles has reduced the tensile strength of asphalt binder.

**Table 4.** Basic experiments of Asphalt Binder.

Description	Additive percentage	Flash Point	Penetration grade	Softening point	Ductility
		°C	1/10 mm	°C	cm
OB	0%	313	67	47	102
Modified asphalt binder with carbon black	3%	325	63	56	111
	5%	328	62	59	113
	7%	330	60	61	114
	10%	331	58	62	111

### 5.2. Asphalt binder Rhology tests

In table 5, The performance grade of the asphalt binder is specified. With the ratio of complex modulus to the sinus of phase angle at the temperature range from 20 to 82 °C can evaluate the performance grade changes of asphalt binder at the high temperature.

To increasing of the asphalt binder performance grade, the ratio of  $G^*/\sin\delta$  for origin bitumen is equal or greater than 1 KPa and for the aged bitumen with RTFO test equal or greater than 2.2 KPa.

By adding 3% of carbon black to asphalt binder, the performance grade has not increased.

While the addition of 5% carbon black particles to asphalt binder, caused an increase in the temperature of bitumen to 70 °.

Adding 7% of carbon black has caused a two-step jump in asphalt binder performance results, which stopped at 10% carbon black.

**Table 5.** Performance grade of Asphalt Binder with Carbon Black.

Title	Temperature [°]			
	64	70	76	82
OB	1.49	0.59	0.23	0.09
OB-RTFO	4.06	1.70	0.71	0.30
BCG3%	2.66	1.12	0.47	0.20
BCG3%- RTFO	4.67	1.98	0.84	0.36
BCG5%	4.56	2.01	0.88	0.39
BCG5%- RTFO	7.96	3.54	1.58	0.70
BCG7%	7.17	3.31	1.52	0.70
BCG7%- RTFO	12.37	5.73	2.65	1.22
BCG10%	4.72	2.09	0.92	0.40
BCG10%- RTFO	9.27	4.17	1.88	0.85

OB is origin asphalt binder, OB-RTFO is origin asphalt binder after RTFO test, BCG3% is the modified asphalt binder with 3% carbon black particles, BCG3%-RTFO is the modified asphalt binder with 3% carbon

black after RTFO test and other abbreviations are base on this.

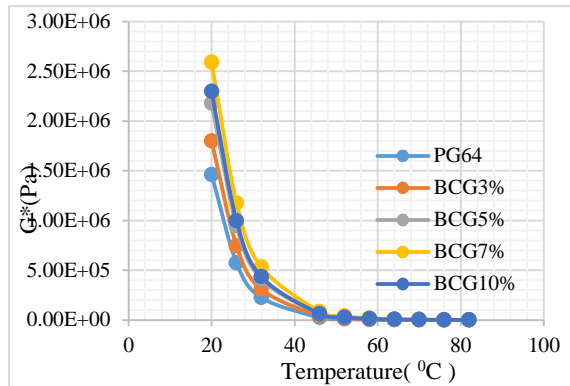


Fig. 5. Complex modulus-Temperature changes in modified asphalt binder with carbon black.

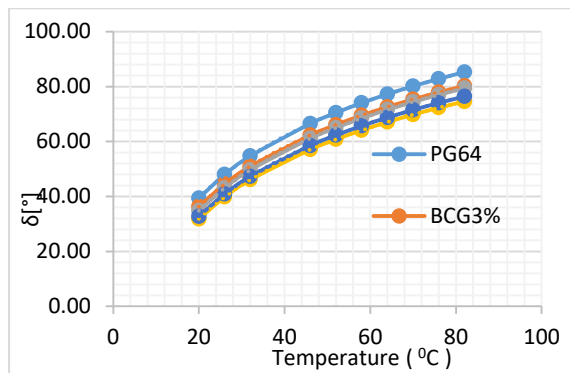


Fig. 6. Phase angle-Temperature changes in modified asphalt binder with carbon black.

An important branch of science corresponded to the deformation and flow of a material is Rheology. The rheological behavior of the asphalt mix corresponds to the molecular structure, linking bond, types and amount of additive in the asphalt binder.

Both  $G^*$  and  $\delta$  values changed with temperature and loading rate of the asphalt binder.  $G^*$  represented the deformation resistance to loading and it results from harmonic-periodic processes and should be written in the complex form according to equation 6.

(Equation 6:  $G^* = G' + i.G''$  )

$G'$  was the elastic part of a material which characterized the stored energy during a shear cycle.  $G''$  was the viscous part of a material which characterized the dissipated energy during a shear cycle. Therefore  $G^*$  show the viscoelastic behavior and its increase corresponded to a decrease in temperature and increase in load frequency.

Figure 6 shows complex modulus changes of modified asphalt binder with carbon black compared to temperature variations. According to the Fig.5, with the addition of carbon black particles obtained from agricultural waste (walnut skin), the asphalt binder became stiffer and thus increased its complex modulus. According to results, modified asphalt binder with 7% carbon black particles has the largest complex modulus and with the temperature rises, the asphalt binder complex modulus is reduced.

$\delta$  represented the relationship between the elastic and viscous responses during loading. It showed the delay between the applied stress and resultant deformation at each point. Lower  $\delta$  means lower delay and the elastic response of material increased. Phase angle increased as the temperature rises or frequency decrease. Small  $\delta$  founded at low temperature and high frequency.

Figure 6 shows phase angle changes of modified asphalt binder with carbon black compared to temperature variations. The phase angle increased with increasing temperature. Adding carbon black particles reduces the phase angle. The amount of these reductions is higher in 7% carbon black modified asphalt binder.

### 6. Conclusion

In this paper, the importance of recycling and application of carbon black from agricultural



waste as an additive in asphalt binder has been investigated. The optimum percentage of carbon black achieved between 5 to 7 percent according to the asphalt binder Basic tests. Modified asphalt binder with carbon black be stiffer and penetration degree reduced. Softening point and flash point improved, therefore thermal sensitivity decreased and resistance to erosion increased. In fact, carbon black increased the thermal resistance and with improving tensile strength, increased the ductility of modified asphalt binder.

The stress-strain behavior that defines with modulus can characterize the response of materials to a load. With applying stress or strain to a material, the movement is created inside the material as the response to the loading. Materials which were able to return to their first shape after the removal of stress named elastic materials. The behavior of this material is time- independent and for shear loading, can be characterized by a storage modulus ( $G'$ ). In another hand, the input energy in some materials dissipates which leads to permanent deformation. The behavior of this material is time-dependent and for shear loading, can be characterized by a dissipated modulus ( $G''$ ).

According to rheology test, the Complex modulus increased and phase angle decreased by adding carbon black. That showed the modified binders with carbon black have more elasticity and stiffness than unmodified binders. Performance grade of modified asphalt binder increased at high temperature and modified bitumen with 7 % carbon black has caused a two-step jump in asphalt binder performance results. According to the basic and rheology test, the optimum percent of carbon black achieved 7%. Adding more quantities of obtained carbon black from

agricultural waste recycling (Walnut Skin) because of the accumulation of these particles in asphalt binder, uncertain changes and mixing difficulty in the industry, not recommended. Also, many tests are required in asphalt binder and asphalt mixture to define exactly optimum percentage. It is noteworthy that adding carbon particles in the asphalt binder is economical and its price is lower than half the cost of the lime powder.

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