Screening, Testing and the Development of a Quality Standard for Bitumen

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***Abstract*—**Bitumen is by far the most widely used as paving material. The characteristics and properties of bitumen should meet international standard and specification. The testing and grading of bitumen has progressively been improved to meet the demanding needs for quality standard of bitumen. This study investigates the rheological and morphological properties of 80/100 penetration grade bitumen obtained from various sources which were from PETRONAS and SHELL refinery process. One of PETRONAS bitumen is manually blended in refinery that gives much different of properties compared to normal refinery process. The fundamental characteristics of bitumen has been determined using conventional tests such as Penetration, Softening Point, Ductility, Solubility in Trichloroethylene, Specific Gravity, Spot Test, Water in Bitumen and Flash Point. Rheological properties of the sample bitumen are analyzed by use of bitumen tests such as Brookfield Viscosity, Rotational Viscosity (RV), Loss on Heating and Dynamic Shear Rheometer (DSR). Morphology properties are analyzed by use of bitumen tests such as Atomic Force Microscopy (AFM), Field Emission Scanning Electron Microscopy (FESEM) and X-Ray Diffraction (XRD). In addition, the short and long term ageing properties of bitumen are analyzed, with the ageing process simulated by the Pressure Ageing Vessel (PAV). The result indicated the fundamental properties and morphology of the bitumen is dependent on the type of bitumen content. The results reveal that bitumen with manually blended are the hardest compared to bitumen from normal refinery process. PETRONAS bitumen show that they exhibited higher vapor content compared to SHELL bitumen. In addition, SHELL bitumen exhibited better ageing properties as compared to PETRONAS bitumen.

***Keywords*—**bitumen, manually blended, rheological, morphological, bitumen content, vapor content, ageing properties

1. Introduction

Billions are spend to build new roads and maintain thousands of kilometers of existing roads each year in the world. The bitumen industry is gradually involved in improving the product and its performance due to the dominant importance of the road network in the economic development and social structure of each country. These industries had influence the public bitumen research and establish cooperation with public institutions on research projects of common interest vary from country to country.

Bitumen is a construction material and fundamental element in road construction and maintenance. It is most common used in asphalt pavement with requirement of standard quality and consistency. Bitumen experiences a variety of thermo mechanical demand as a binder for road paving. The characteristics and properties of bitumen should meet the requirement of international standard in order to market bitumen.

Currently, bitumen is graded according to a number of traditional and often empirical tests in most countries in the world. For example, penetration and softening point have been the basis of the grading system in the UK. This test has been widely used around the world to set the quality standard of bitumen. By the way, fundamental properties such as viscosity have also been specified. For the past year, these specifications have provided a dependable means of classifying binders and are familiar to authorities, specifiers, binder suppliers and road contractors. To comply with these specifications, binder suppliers must have built up experience of how different binders based on these properties. This has included developing the expertise to manufacture good quality bitumen from a diversity of crude oils.

The demands for stronger and more durable road pavements have steadily increased by the increasing in traffic flow, higher axle loads and tyre pressure on road. Sengoz and Isikyakar (2007) stated the conventional bituminous materials have been used satisfactorily in most highway pavement and airfield runaway applications. However during the last decade increase in axle roads, heavy traffic, severe climatic conditions and construction failure lead to a need to enhance the properties of the base bitumen.

For many years, researchers and development chemist actively participate to produce and enhance the modified and unmodified bitumen mainly for the industrial usage. In 1997, a very different binder grading system was introduced in the USA. This was one of the principal outputs from the Strategic Highway Research Program (SHRP) and is based on a number of fundamental, rheological properties of binders. Within this system, rather than a binder being classified by for example penetration at 25oC (e.g 70 or 100 pen), it is classified by two number (e.g. "64-28", "58-22" etc). The first of these numbers is an indication of the binder's high temperature performance and the second relates to its low temperature performance. This performance grade (PG) may be thought of as a type of 'plasticity' range for the binder. Such a fundamental grading system should have the benefit of being applicable to both unmodified bitumen and speciality products such as Polymer Modified Bitumens (PMBs) (Claxton and Green, 1996).

Many studies have been conducted on bitumen in which grade have been determined for a number of bitumen that produced from a variety of crude oils by different refinery source and covering from many grades to see how they fit into this grading system. The comparison for unmodified bitumen is made for grading system by three different methods which are (1) grading by penetration at 25oC, (2) grading by absolute viscosity at 60oC, and (3) grading by absolute viscosity of aged asphalt residue after the rolling thin oven test (RTFOT) procedure.

Bitumen is a non-crystalline viscous material, black or dark brown, derived from petroleum either by natural or refinery processes which is substantially soluble in carbon disulphide (CS2), possessing adhesive and water-proofing qualities. It consists essentially of hydrocarbons and would typically comprise at least 80 % carbon and 15 % hydrogen, the remainder being oxygen, sulphur, nitrogen and traces of various metals (Whiteoak, 2003). Basically, bitumen is a "viscous-elastic' material depending on temperature and rate of loading in existence of purely viscous, purely elastic or a combination between both (Mouillet, 2008).

Bitumen is manufactured from crude oil. According to Whiteoak (2003), the crude oil originates from the remains of marine organism and vegetable matter deposited with mud and fragments of rock on the ocean bed. Conversion of the organisms and vegetable material into the complex of hydrocarbon is result from the application of heat within the Earth's crust and pressure from upper layer of sediment.

Research revealed that the first process in the manufacture of bitumen is atmospheric distillation (Nicholls, 1998). The first process take place is separating the light components from the crude oil by atmospheric distillation at typically 350oC as shown in Figure 2.1. Then, at higher temperature (350-425oC), the residue from atmospheric distillation is further refined. The vacuum distillation residue, also called 'vacuum residue', is the basic produced in the refining process. It is known as 'residual' or 'straight-run bitumen'.

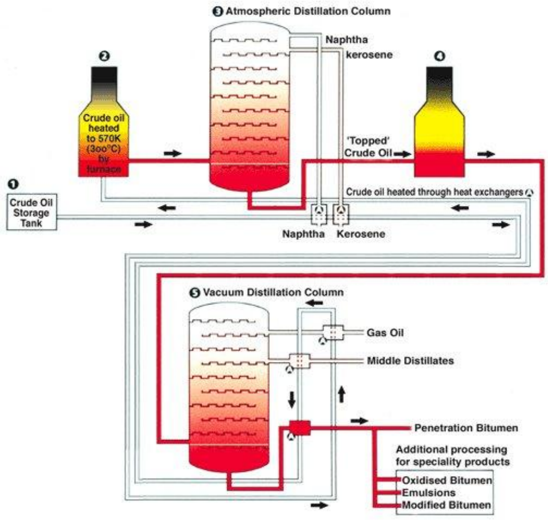

Figure 1 Distillation of Bitumen (courtesy from Nynas,2012)

Air blowing develop in the late 19th century was the first process that led to the manufacture of bitumen from otherwise too fluid crude source (Lesueur, 2008). The bitumen is heating in high temperature (200-275oC) for a few hours, sometimes in the present of catalyst, such as cooper sulphate or zinc ferric. It will produce the air blown bitumen or called as oxidize bitumen.

There are some 250 uses of bitumen (Asphalt Institute, 1989). It has been categorized in many field including agriculture, buildings, hydraulics and erosion control, industrial, paving, railways and recreation. With this multipurpose used of bitumen, it is clear that the bitumen is an important material in road design, construction and maintenance. The properties of bitumen are (Asphalt Institute, 1991):

i. Durability – Ability of bitumen to resist the effects of water, ageing and temperature variations

ii. Adhesion and cohesion – Adhesion is the ability to bind aggregate in bituminous pavement mixture together while cohesion is the ability to hold the aggregate particles firmly in place in the finished pavement.

iii. Temperature Susceptibility – All bitumen are thermoplastic that is they become harder as their temperature decrease and softer as their temperature increase. This property is important for determining the temperature of a mixture of bitumen and aggregate and to determine the appropriate compaction temperature.

iv. Hardening and Aging – The rate of bitumen hardening when mixed with hot aggregate and the aging that occurred during the life of the pavement due to environmental conditions.

So the objective of the project was to conduct product testing for 80/100 penetration grade bitumen obtained from various sources. The properties of bitumen then had been determined by using conventional and advanced tests.

2. **Experimental and methods**

2.1 Materials

The bitumen with a 80/100 penetration grade has been obtained from PETRONAS and SHELL refinery plant. In order to characterize the properties of bitumen, conventional and advanced test methods were performed. Two different 80/100 penetration grade bitumen from PETRONAS were tested. One was obtained from normal refinery process (designated as P1), the other was blended in refinery (designated as P2). These were compared with a 80/100 penetration grade bitumen obtained from SHELL (designated as S)

2.2 Test Methods

Conventional and advanced test methods are performed on each of the bitumen samples to following the determination of the properties of the materials. The imaged are analyzed after they had been captured by Atomic Force Microscopy and Field Emission Scanning Electron Microscopy. X-Ray Diffraction is also conducted to analyze the dispersion structure in the bitumen.

2.2.1 Conventional bitumen tests

The bitumen samples are subjected to the following conventional bitumen tests; penetration (ASTM D5), softening point (ASTM D36), ductility (ASTM D113), solubility in trichloroethylene (ASTM D2042), specific gravity (ASTM D70), spot test (AASHTO T102), water in bitumen (ASTM D95) and flash point (ASTM D92). Viscosity test has been conducted in two methods which were Brookfield viscometer (ASTM D2171) and rotational viscometer (ASTM D4402).

Besides that, the temperature susceptibility of the bitumen samples has been calculated in term of penetration index (PI) using the result obtained from penetration and softening point tests. Temperature susceptibility is defined as changes in hardness of the bitumen with changes in temperature.

2.2.2 Advanced bitumen tests

The bitumen samples are subjected to the following advanced bitumen tests; loss on heating (AASHTO T240-09), dynamic shear rheometer (AASHTO TP5-98) and pressure ageing vessel (AASHTO PP1-98).

The term morphology is often used in describing the microstructure of bitumen (Chen J. et al, 2002). To investigate the morphology of bitumen, atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM) and x-ray diffraction (XRD) has been used to characterize the nature of bitumen.

AFM test is an analysis of the microstructure of bitumen. The phase detection and topographic AFM images, displayed three different types of microstructure. Differences in three dimensional images are indicative that the concentration of asphaltene may vary with different bitumen from different crude sources.

FESEM is used to study the internal morphology of the bitumen by visual assessment. Morphology of bitumen is included the shape, size, texture and phase distribution of bituminous element in bitumen

XRD is used to analyze the dispersion structure in the bitumen. The radiation interacts with the electrons in atoms when X-ray radiation passes through matter resulting in scattering of the radiation. If the atoms are organized in planes and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur.

3. **Results and discussion**

3.1 Conventional bitumen tests

The standard properties based on Malaysian Standard MS124 1973 is tabulated in Table 1.

Test	Specification	Specification limits
Penetration (at 25 °C; 1/10 mm)	ASTM D 5EN 1426	50–70
Softening point (°C)	ASTM D 36EN 1427	46–54
Viscosity at (135 °C)-Pa s	ASTM D 4402	–
Thin film oven test (TFOT);(163 °C, 5 h)	ASTM D 1754 EN 12607-1	
Change of mass (%)		0.5 (max)
Retained penetration (%)	ASTM D 5 EN 1426	50 (min)
Softening point after TFOT (°C)	ASTM D 36.EN 1427	48 (min)
Ductility (25 °C), cm	ASTM D 113	–
Specific gravity	ASTM D 70	–
Flash point (°C)	ASTM D 92EN 22592	230 (min)

Table 1 Properties based on Malaysian Standard MS124 1973

No.	Tests [Unit]	Results		
		P1	P2	S
1.	Penetration [dmm]	91.4	69.2	73.1
2.	Softening Point [°C]	44.3	47.2	46.6
	(i) Penetration Index (+)	-1.17	-1.00	-1.88
3.	Ductility [mm] (+)	130.0	153.3	123.5
4.	Solubility in TCE [%]	99.83	99.95	99.93
5.	Specific Gravity	1.028	1.026	1.035
6	Spot Test	-ve	-ve	-ve
7	Viscosity (Brookfield)[Pa.s]	0.53	0.78	0.56
8	Rotational Viscometer [Pa.s]	0.36	0.47	0.38
9	Water in Bitumen [%]	0.20	0.15	0.10
10	Flash Point [°C]	324	326	336

Table 2 Conventional tests properties of P1, P2 and S

The result conventional bitumen tests can be seen in Table 2 as the values indicate important significant to properties of bitumen tests.

The penetration value for sample P1 is 91.4 mm which is within limit of specification for 80/100 penetration grade. The values lie in upper range of specified grade which is softest bitumen compared to others. The penetration value for sample P2 is 69.2 mm which is harder than designated grade. It is because sample P2 is manually blended in refinery that may affect the hardness of bitumen. Whilst sample S contend that bitumen grade was 80/100 penetration, test reveal that sample S is harder than designated grade.

The softening point for sample P2 and S are within the limit of standard properties of bitumen. Sample P1 has the lowest softening point which is in line with penetration test, as result becomes softest bitumen. The higher value in softening point temperature is favorable since bitumen with higher softening may be less susceptible to permanent deformation (rutting). The PI for all sample are within range of typical conventional paving bitumen which is between -2 and +2 (Whiteoak, D., 2003). The values above indicate that the Shell bitumen was most susceptible and P2 was least susceptible to temperature changes.

For ductility test, in advanced adding the sodium chloride, every samples meet the ASTM requirement for ductility which was more than 100 mm. Sample P2 exhibited the best ductility properties while sample S exhibited the worst ductility properties. Coating of aggregate is better with high ductility material so the binder will be better

Then, the bitumen sample has passed the ASTM requirement for solubility test. Sample S and P2 are nearly to zero contamination. The relative density of each bitumen sample has within the range of expected value which are from 1.02 to 1.05. Specific gravity tests are useful in making volume correction based on temperature. The result obtained from the test was negative for all bitumen samples. The samples turned to produce brownish color after it was dropped onto the filter paper. It showed that all bitumen samples had not been damaged during processing due to overheating. The undamaged bitumen tended to be more ductile and less susceptible to ageing effects.

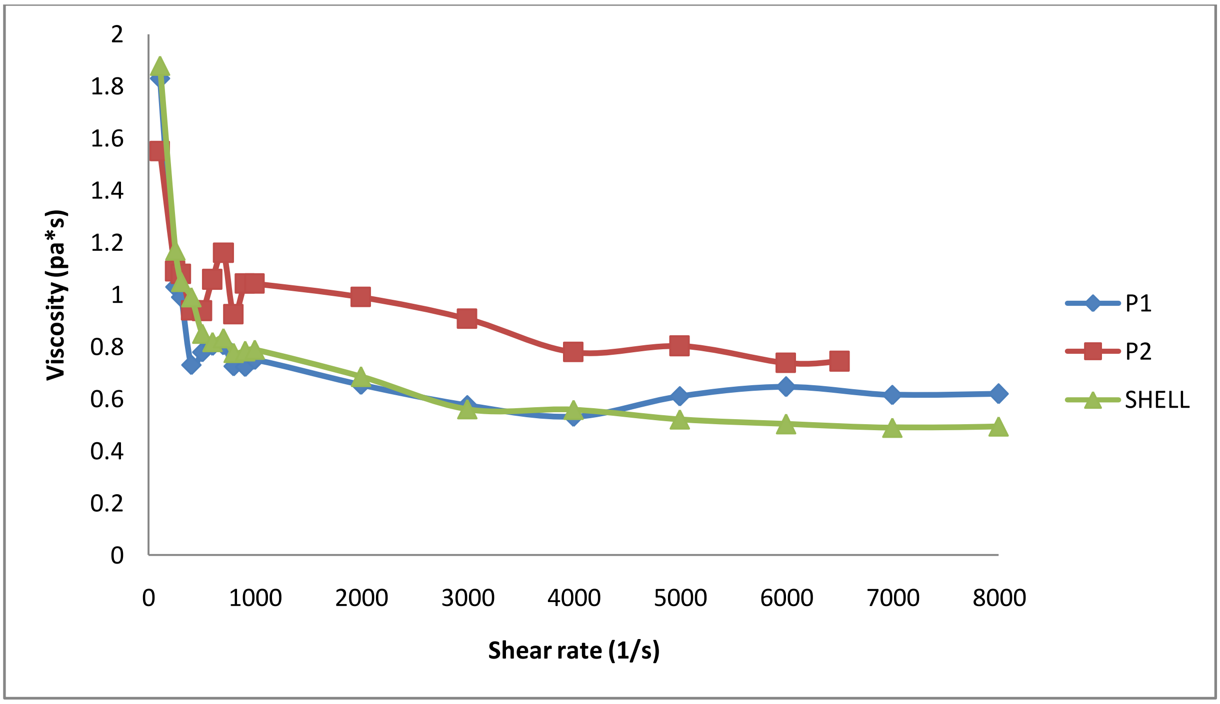

Figure 2 Combination of Viscosity vs Shear Rate for all samples

The viscosities for sample P1, P2 and Shell together with the shear rate are presented in Figure 2. The results show a consistent with the penetration and softening point results. Sample P2 exhibited highest viscosity while sample P1 exhibited lowest viscosity at shear rate 4000/s. The high value of viscosity indicates that the low fluidity of bitumen. Thus, harder bitumen will obtain higher value of viscosity. Bitumen binder easily lubricates the aggregate particle at low viscosity while high viscosity does not able the bitumen to coat the entire surface of aggregate in the mixing. This show that sample P2 and Shell have high viscosity and it required higher mixing, compaction and laying temperature than sample P1. The rotational viscometer for sample P1, P2 and Shell were also within range of viscosity requirement during mixing. As with the penetration and softening point results, the viscosities give an indication of stiffening effect of bitumen sample.

From the water in bitumen test result, it showed that all the sample of bitumen has been achieved below 0.2 % of water content which was in agreement with the specified requirement. Sample S has lowest water content while sample P1 shows highest water content. In term of safety, bitumen should have low water content to prevent foaming of bitumen when it is heated above the boiling point of water.

ASTM specification for 80/100 penetration bitumen for flash point is more than 225oC. From the test, all sample of bitumen had met the minimum requirement for flash point. Sample S bitumen had the highest value of flash point, followed by sample P2 and P1. This result related to the hardening potential of bitumen. With the high flash point, the bitumen was likely to experience a lower hardening potential in the field. The minimum flash point requirement is must for bitumen because of safety reason. The sample of P1 and P2 were likely to have high vapor content compared to Shell bitumen.

The loss on heating test result showed that all sample tested is less than 1% in terms of its mass loss or gain due to heating as AASHTO requirement which indicated that this loss or gain was not significant. Sample S bitumen exhibited mass gain while sample P exhibited mass loss. The result is expected as the sample that had low volatile content will experience mass gain. This is in line with the result obtained from flash point test.

3.2 Morphology

Atomic Force Microscopy (AFM) images of bitumen sample captured are presented in Figure 3.

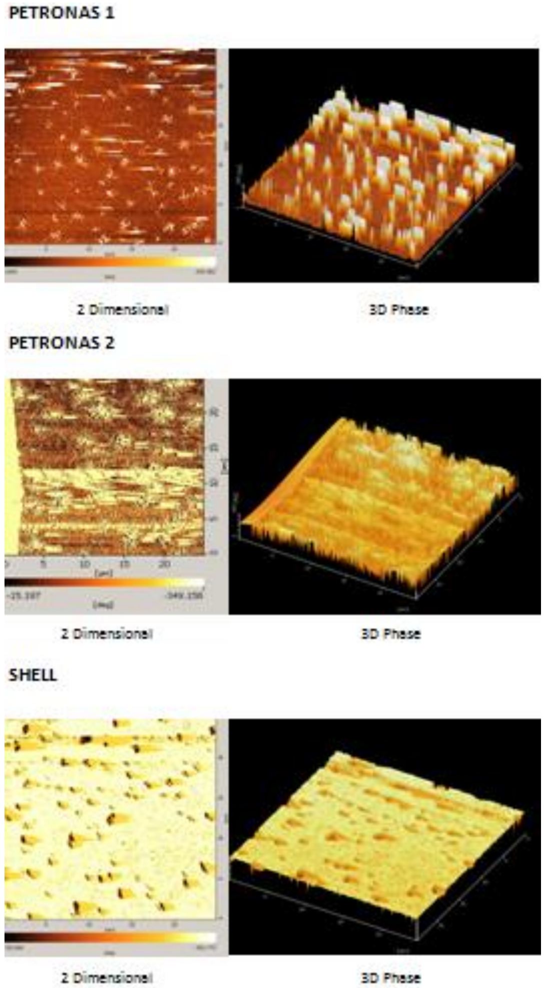

Figure 3 AFM images of bitumen sample

The AFM image arises from changes in composition and stiffness across a sample surface. The greater the contrast between the domains in friction image, the greater is the difference in stiffness and composition (Baumgardner et al, 2006). The contrast between the dispersed phase and the matrix was increased as indicated through Figure 17, 15 and 13. It is reasonable to assume that the stiffness of the matrix in bitumen is increased according to the contrast changes, as a result, the whole stiffness of the bitumen is clearly increased, which leads to the hardening of bitumen.

The appearance of ‘bee-like’ structure may be attributed to the crystallization of the wax or waxy molecules in asphaltene. Sample S indicated of higher asphaltene content while sample P1 indicated of lowest asphaltene content from the dense packing of the imaged obtained. High asphaltene content indicated that sample S may be difficult to ignite and burn.

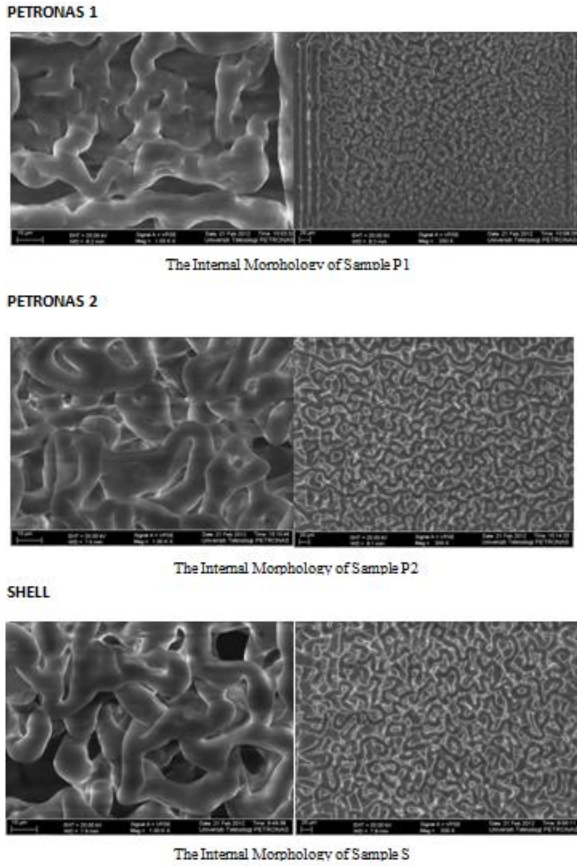

Figure 4 FESEM test on sample bitumen

The structured of bitumen for all sample are shown in Figure 4 for magnification at 1.00kx and 200x. Based on the morphology structure result, sample S showed greatest compactness morphology phase of the bitumen. This could be related that sample S had a higher viscosity. While for sample P1 and P2, there show quite similar phase for both sample which were less compact compared to sample S. Sample P1 showed least compactness as a result it had less viscous than others. This result may indicate greater amount of energy required to break down the Shell bitumen particle compared to PETRONAS bitumen.

Any disturbance from the diffractogram obtained in Figure 5 is indicated level of impurities in the bitumen. SHELL bitumen exhibited most stable condition during test. Sample P2 also exhibited a stable condition. Sample P1 exhibited least stable with 3 peaks indicative of possible impurities. The SHELL and P2 samples do not exhibit any intense peaks which portray them to be more amorphous and homogeneous.

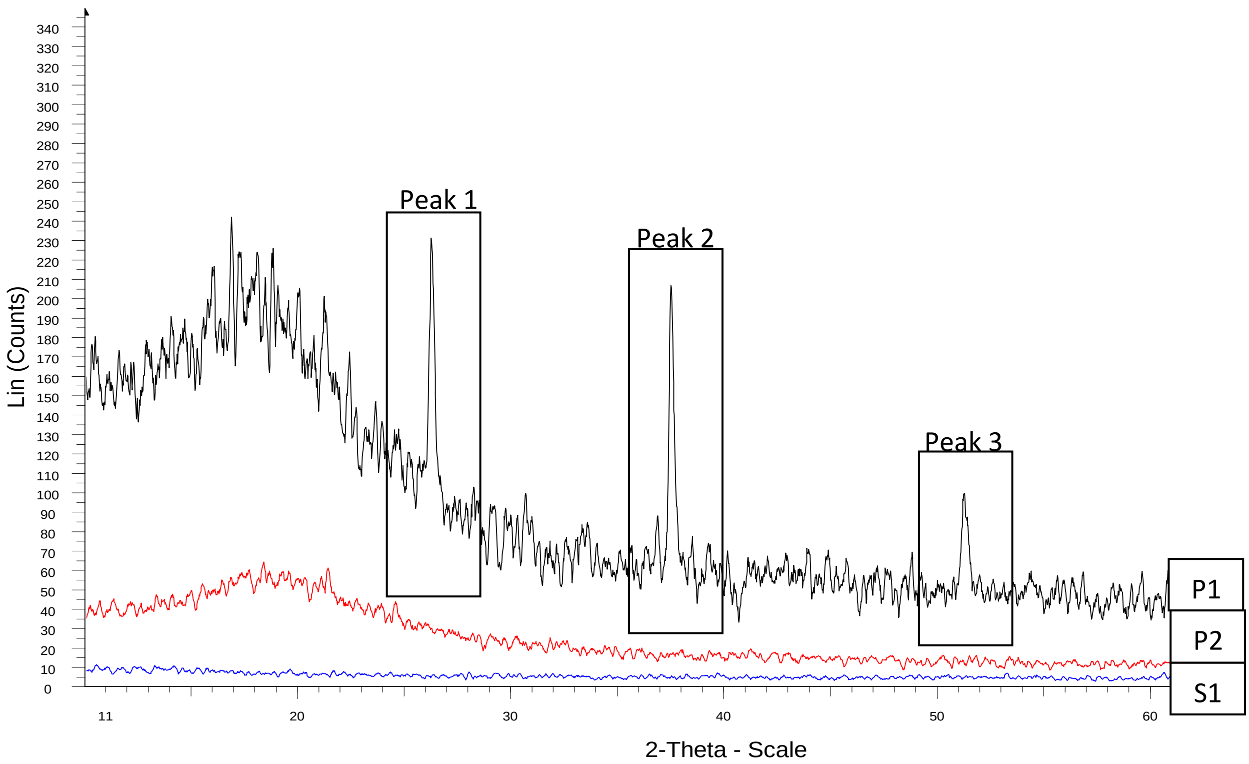

Figure 5 Results for diffractogram

3.3 Ageing effects and resistance to deformation

For all samples, the loss modulus G" is higher than the storage modulus G'. This means than the material behavior are visco-elastic liquid. Tangent of phase angle (δ) is the measure of viscous over elasticity of a material, in other word, the loss modulus over storage modulus. $G^*/\sin\delta > 1.0$ kPa is AASHTO requirement for virgin bitumen. G* reflects resistance to deformation of bitumen in service.

From the DSR test conducted to the three samples, P2 bitumen is found to have largest complex modulus, followed by SHELL and P1. The phase angle was highest in SHELL bitumen followed by P1 and P2. The larger the phase angle (δ), the greater is the viscous of material. Therefore, P2 bitumen is stiffer and more elastic than other samples. The sample exhibited best property against deformation.

After PAV test had been conducted to the three samples, the penetration values decrease indicating the bitumen becomes harder by ageing. The hardest bitumen is PETRONAS 2 bitumen followed by PETRONAS 1 bitumen and SHELL bitumen. In RTFOT minimum retained penetration must be greater than 47% (ASTM). This test shows that the ageing rate in PETRONAS bitumen is fastest as compared to SHELL bitumen which makes it more susceptible to deformation on a long term basis.

The softening point value is the temperature in which bitumen change from solid to liquid. The lower the softening point of bitumen is the lower the temperature in which bitumen can be used in. After PAV test, the softening point of all samples increase, and the highest softening point after PAV is PETRONAS 2 bitumen with 60.2 °C followed by PETRONAS 1 bitumen which is 54.7 °C and SHELL bitumen is 52.0^{o}C.

Viscosity shows how bitumen behaves at given temperature or over a temperature range. After PAV test, the viscosities for all samples increase. The highest viscosity is PETRONAS 2 bitumen with 1349.7 cP followed by PETRONAS 1 bitumen with 837.5 cP and SHELL bitumen with 700 cP.

From the retest of Penetration, Softening Point, and Rotational Viscometer test, it is concluded that ageing rate in PETRONAS bitumen is fastest as compared to SHELL bitumen which makes it susceptible to fatigue and cracking.

4. **Conclusion**

Based on the tests results of the sample bitumen, the following conclusion can be drawn.

SHELL and PETRONAS 2 bitumen are harder than designated 80/100 penetration grade. PETRONAS 1 is within specified grade. PETRONAS 2 bitumen is the hardest while PETRONAS 1 bitumen is the softest. These results indicate from the penetration, softening point and viscosity results. PETRONAS 1 and 2 exhibited better susceptibility to temperature changes compared to SHELL bitumen. This result indicated from penetration index obtained. PETRONAS 1 and 2 show better ductility properties compared to SHELL bitumen. PETRONAS 1 exhibited highest impurity. This result is determined from solubility in trichloroethylene and XRD test. PETRONAS 1 and 2 exhibited higher vapor content compared to SHELL bitumen. PETRONAS 1 and 2 exhibited mass loss while SHELL bitumen exhibited mass gain due to heating process. This is in agreement with higher vapor content in PETRONAS 1 and 2.PETRONAS 2 exhibited best resistance to deformation characteristics while PETRONAS 1 exhibited worst resistance to deformation. Ageing characteristics showed SHELL bitumen exhibited better ageing properties as compared to PETRONAS bitumen.

In summary, the properties and characteristics of every sample of bitumen can be obtained by conducting the conventional and advanced tests. Then, the quality standard for the bitumen can be developed as well.

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