Jurnal
Teknologi

Full Paper

THE PHYSICAL AND RHEOLOGICAL CHARACTERISTICS OF MODIFIED ASPHALT BINDER WITH TITANIUM DIOXIDE R15

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Article history
Received
2nd December 2015
Received in revised form
13th March 2016
Accepted
31st March 2016

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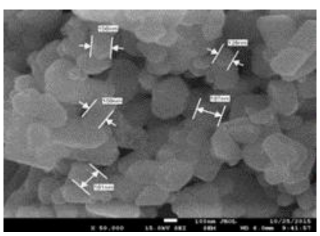
Graphical abstract



Abstract

The objectives of this study include determine the physical and rheological properties of the modified asphalt and also to examine the effectiveness of TiO_2 in lowering the viscosity of the asphalt compared to control asphalt. Nano-titanium dioxide R15 of 2%, 4%, 6%, 8% and 10% by weight of asphalt has been incorporated into unaged 80/100 asphalt mix in order to improvise its performance. The asphalt modified and control were examine using penetration test, softening point test, storage stability test, dynamic shear rheometer test (DSR), rotational viscosity (RV) and rolling thin film oven test (RTFO). As a conclusion, the decrease in compaction and mixing temperature of modified asphalt compared to original asphalt shows an improvement in the viscosity of the asphalt. Through DSR, the nano-TiO_2 modified asphalt does not degrade the performance grade when compared to control asphalt, where the values of complex modulus, G* does not differ much from each other for each of the concentration. This indicates that the modified asphalt is as competent as the original binder in resisting rutting at high temperature.

Keywords: Titanium dioxide; physical properties; rheological properties; modifies asphalt; asphalt viscosity

1.0 INTRODUCTION

Pavement distress is a process in which several different deterioration process act and interact, influenced by a variety of factors includes, environmental, material used and traffic loads [1-2]. The top layer is normally an asphalt layer. Asphalt is a mixture of organic liquids that are highly viscous, black, entirely soluble in carbon disulfide and composed primarily of highly condensed polycyclic aromatic carbons (PAHs). Several nanomaterials that are currently a topic of interest used in the pavement includes nanoclay, nano hydrated lime, titanium dioxide nanoparticle, carbon nanoparticlesetc. to improve the asphalt performance. In general, nanotechnology will produce benefits in two ways – by making existing products and processes more cost effective, durable and efficient and by creating entirely new products [3-5]. Other benefits are; improve the storage stability in polymer modified asphalt, increase the resistance to UV aging, reduce the moisture susceptibility under water, snow and deicers, improve the properties of asphalt mixtures at low temperature, improve the durability of asphalt pavements, save energy and cost, decrease maintenance requirements [6].

Titanium dioxide (TiO_2) has been known to be one of the popular nanomaterials in asphalt construction asides from nanosilica, nanoclay, and carbon nanotubes. TiO_2 is naturally occurred oxide that easy-to- find material in the earth's crust that is 0.6%. Its chemical formula is TiO_2 and it belongs to the family of transition metal oxides. TiO_2 presents in three crystalline form, namely rutile, anatase and brookite. Anatase TiO_2 shows greater photocatalytic activity in compared with rutile due to its activeness in reacting to chemical [7].

There are two papers had revealed the performance of TiO_2 in WMA [8-9]. Both paper revealed the potential of TiO_2 as asphalt modifier for WMA by integrating it into the binder and also for surface coating. In Grant et al., they hypothesized that TiO_2 can function as photocatalytic compound when used in the preparation of WMA. This material would combine the benefits of WMA such as reduced energy consumption and emission during production with the photocatalytic properties of TiO_2 to trap and degrade organic and inorganic particles in the air. Both application as asphalt modifier for WMA and surface coating are performed. A crystallized anatase TiO_2 powder was blended with asphalt PG64-22 at 3, 5, and 7% TiO_2 of binder weight. The Dynamix Shear Rheometer, Rotational Viscometer and Bending Beam Rheometer were used to characterise the asphalt modifier. For quantifying the photocatalytic efficiency of asphalt, a laboratory test setup was developed that consists of a pollutant source, zero air sources, calibrator, humidifier, photoreactor, and a chemiluminescent NO_x analyzer. The test setup was adapted from the Japanese standard JIS TR Z 0018 "Photocatalytic materials – air purification test procedure". As a result, the use of TiO_2 as a modifier to asphalt binder was not effective in removing NO_x pollutants from the air stream; however, the application of TiO_2 as part of a water-based spray coating achieved a NO_x reduction efficiency ranging from 39 to 52%.

Other than that, due to its high viscosity, asphalt can rarely be used in its raw form at ambient temperatures [8]. It is crucial to assure that the viscosity of the asphalt is maintained low when heated at a lower temperature without affecting the quality of the pavement. This will in turn decrease the emissions of greenhouse gases during production. Reduction in energy consumed and greenhouse gases emission is significant in conserving the environment we live in today.

2.0 EXPERIMENTAL DESIGN

The testing procedure for this study takes into account the physical and rheological properties of the modified and unmodified asphalt binder. The testing for physical properties included softening point test, penetration test and rotational viscometer test. The DSR test was used to determine the rheological properties, whereas rolling thin film oven test acts as a simulator for the short-term aging process of the asphalt. Storage stability is also conducted to determine the homogeneity of the TiO_2modified binder.

2.1 Materials

The material used in this study is asphalt penetration grade 80/100 from Chevron. The properties of the virgin binder are shown in Table 1.Titanium dioxide or its chemical formula, TiO_2 is commonly found in form of rutile, and to a lesser degree, anatase, and brookite, where the latter is less used. Nano-titanium dioxide R15 is used in this study.

Table 1 Specification requirement for asphalt80/100 (ASTM)

Property	Method	Specification
Penetration at 25°C(mm)	80-100	ASTM D 5
Softening Point (°C)	45-52	ASTM D 36

2.2 Preparation of Asphalt Binder and Nano-TiO_2

The mixing of the sample is made with 500g asphalt and the mixing speed is 5200rpm, for duration of 30 minutes at 155°C [11]. To conduct the mixing, 500g of oven heated asphaltis transferred to a hot plate and after the temperature of the sample stabilized at 155°C, specified amount of nano-TiO_2 (2%, 4%, 6%, 8% and 10%) is added gradually into the asphalt as the high shear asphalt mixer is rotating at specified speed for 30 minutes until it reaches homogenous blend to produce BT2, BT4, BT6, BT8 and BT10.

2.3 Softening Point test

Softening point of the modified asphalt binder and unmodified asphalt binder were tested by means of Ring-and Ball apparatus according to ASTM D36-95. The softening point is the mean temperatures at which the asphalt disks soften and allow the two ring balls to touch the bottom plate at a distance of 25 mm. It is a measure of the temperatures at which phase change occurred in asphalt materials [12]. Higher softening point indicates stiffer asphalt and lower temperature susceptibility at high temperature, which is more likely to resist rutting [13].

2.4 Penetration Test

Penetration test was carried out according to ASTM D5-97. The penetration is measured with a penetrometer by which a standard needle of 0.1mm is applied to the sample at 25°C for 5 seconds. Penetration test is a measure of the hardness of the asphalt material, the lower the value of penetration indicates that the stiffness of the binder is improved while higher value of penetration indicates softer consistency [14].

2.5 Rotational Viscometer test

In this study, rotational viscometer test is done according to ASTM D-4402. It is done to determine the viscosity of asphalt binders in the high temperature ranging from 60 to over 200°C using a rotational viscometer apparatus. The RV test for Superpave PG asphalt binder specification is always conducted at 135°C in order to measure the flowing resistance of asphalt materials. In general, a higher viscosity results in higher mixing and compaction temperatures [13].

2.6 Dynamic Shear Rheometer test

According to ASTM D7175, the DSR tests were performed to characterize the viscous and elastic behavior of asphalt binders by measuring the complex shear modulus (G*) and phase angle (δ) of asphalt binders without considering the effect of aging. Based on SUPERPAVE specifications, the rheometer software is set to apply a constant oscillating speed of 10 rad/s, which is approximately 1.592 Hz to create shearing action and the resulting strain and time lag is recorded. 25mm diameter spindle and 1mm gap were used in this study for test temperature ranging from 46 to 70°C. Intuitively, the higher the G* value, the stiffer the asphalt binder is. Whereas, the lower the phase angle is, the less viscous the material is, which means the asphalt binder is able to recover to its original shape after being deformed by a load [9].

2.7 Rolling Thin Film Oven test

Rolling thin film oven test was conducted according to ASTM D2872. This test exposes films of binder to heat and air and approximates the exposure of asphalt to oxidation and volatilization during hot mixing and handling to simulate the process of short term aging [15]. RTFO aging was conducted at 163 °C for 85 min to determine the mass quantity of volatiles lost from the asphalt during the test. The air flow was set at a rate of 4000 ± 200 ml/min and the carriage rotated at a rate of 15 ± 0.2 rev/min.

2.8 Storage Stability

Storage stability of the modified binder was tested using ASTM D5976. Hot storage stability test was conducted by filling an aluminium tube of 25 mm diameter and 140 mm in height with 50g of modified asphalt. The binder was then sealed and kept vertically in a vertical vessel at 163 ±5°C for 48 hours without disturbance. Next, it was allowed to cool in the fridge at a temperature of - 6.7 ± 5°C for a minimum period of 4 hours to solidify the binder. The samples were later cut horizontally into three equal pieces and the top and bottom parts were tested for their corresponding softening point using softening point test, to evaluate possible differences in characteristic.

2.9 Field Emission Scanning Electron Microscope (FE-SEM)

Field emission is the emission of electrons from the surface of a conductor caused by a strong electric field. An extremely thin and sharp tungsten needle (tip diameter 10 to 100 nm) works as a cathode. FE-SEM is used to project the surface imaging and morphological characteristic for any type of material. FE-SEM applications include [16];

- Thickness measurement of thin coatings and films
- Correlation of surface appearance and surface morphology
- Characterization of size, size distribution, shape and dispersion of additives, particulates and fibers in composites and blends
- Measurement of height and lateral dimensions of nanometer-sized objects

3.0 RESULTS AND DISCUSSION

3.1 Softening Point Temperature

The influence of various concentration of nano-TiO_2 on the softening point can be seen in Figure 1 Addition of additive into the asphalt penetration grade 80/100 slightly increases the softening point when compared to the control asphalt. The overall softening points for the various concentration of nano-TiO_2 modified asphalt are in a small range which indicates that TiO_2 has little impact in rising the softening point. In general, the decreasing value of penetration and increasing value of softening of nano-TiO_2 modified binder demonstrate the increased hardness and stiffness of the binder which is desirable in asphalt industry.

3.2 Penetration Value

In Table 2, it is shown that the average penetration value from 6 samples reading. It shows that the penetration was decreases as higher percentage of additive is added to the binder. But as it reaches concentration of 6%, the penetration value starts to increase and it drops back at 10% addition of nano-TiO_2. The addition of nano-TiO_2 into base binder has shown satisfying result in decreasing the penetration value compared to original binder. The decrease in penetration indicates improvement of the binder stiffness which is an important factor in modified binder property.

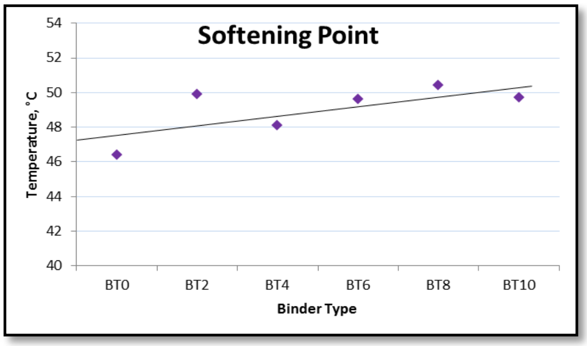


Figure 1 Softening point for unaged binder of various TiO_2 percentages

Table 2 Results of penetration test

Reading (mm)	Binder Type					
	BT0	BT2	BT4	BT6	BT8	BT10
Average	92.4	71.5	67.5	74.2	74.9	72.5

3.3 Viscosity

As can be seen in Figure 2, the viscosity of 4% TiO_2 modified asphalt is lower compared to original asphalt at 135°C. Addition of nano-TiO_2 has decreased the viscosity of asphalt binder because of dilution effect, and thus reduced construction temperatures of modified binder.

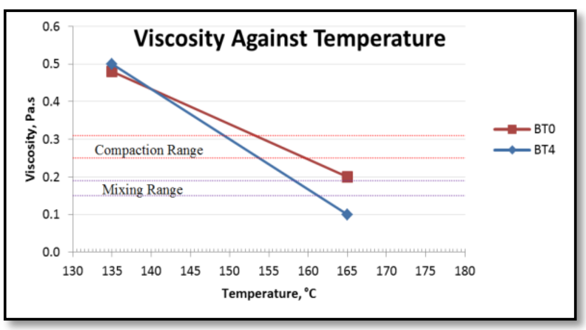


Figure 2 Viscosity value of original asphalt and 4% TiO_2 modified asphalt

Therefore, it could be said that nano-TiO_2 modified asphalt is friendlier to the environment because of less energy consumption and asphalt smoke emission [12]. But as the temperature increases to 160°C, the viscosity of BT4 becomes thicker than BT0. This deduces that TiO_2 modified asphalt has the best workability at lower temperature and therefore is suitable to be used in warm mix asphalt.

3.4 Complex Modulus and Phase Angle at Medium and High Temperature

The temperature dependency of the complex modulus as well as phase angle for both nano modified asphalt and conventional asphalt in temperatures is ranging between 46 °C and 70 °C. In Figure 3 and Figure 4, it can be seen that for the same binder, the G* values increase with RTFO aging, while the δ values decrease with aging. According to the Strategic Highway Research Program (SHRP), base asphalt 80/100 satisfies the standard of performance grade 64 °C, while the TiO_2 modified asphalt also possesses the same result which allows these materials to be used in hot climates, except for BT6 which carry a value slightly lower than 1kPa [17].

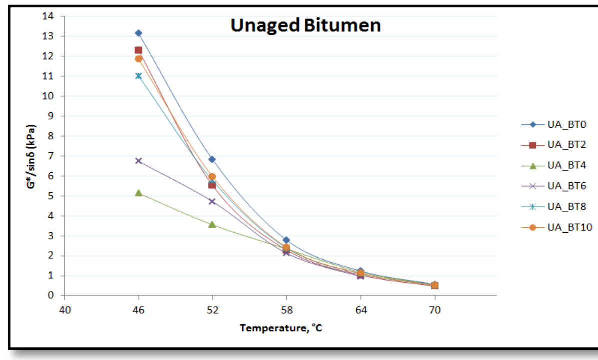


Figure 3 Graph of G*/sinδ against temperature of unaged original asphalt and modified asphalt

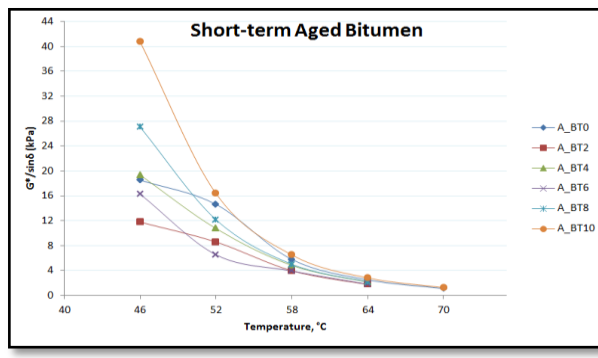


Figure 4 Graph of G*/sinδ against temperature of short-term aged original asphalt and modified asphalt

Referring to Figure 4, it is shown that all the modified asphalt are having less G*/sinδ in compared to control asphalt in unaged condition. This demonstrates that nano-TiO_2 modified asphalt does not enhance the high temperature deformation resistance. However, the curve for BT0, BT2, BT8 and BT10 shows that there is a sudden change of complex modulus value from 46°C to 52°C which is a factor that should be avoided in confronting rutting parameter.

On the whole, nano-TiO_2 modified binder does not degrade the performance grade of 64°C for unaged binder which deduces that it has the same rutting resistance potential as the control binder. In short-term aged condition, the G*/sinδ for modified asphalt also displayed lesser value than the aged virgin binder as shown in Figure 5 except for BT10.

3.5 Mass Loss

According to SUPERPAVE standard, the percentage of mass loss shall not be more than 1% for all binder grades. Based on the results obtained in Figure 5, none of the samples experience mass loss of more than 1%. The values ranging 0.06% to 0.11% which is satisfied the standard specification. Besides that, it is found that the mass loss value is increasing as more additive is added into the binder. This indicates that small amount of aging may occur in the asphalt during mixing and construction operations.

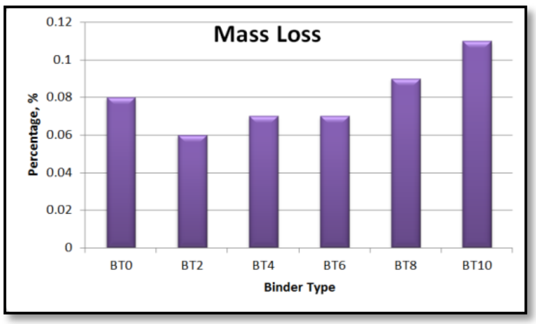


Figure 5 Mass loss of modified binder of various percentages

3.6 Compatibility

To achieve the expected properties in the pavement, a good consistency in the mixture of nano-TiO_2 modified asphalt is vital to avoid separation during storage and applying the asphalt [18]. Phase separation might take place in the modified binder during storage at higher temperatures, due to the dissimilarity in solubility and density between TiO_2 and asphalt. Softening point test is a medium to find out whether the interaction between the asphalt and TiO_2 are strong enough to resist separation during the high-temperature storage stability test. The difference between the softening points should not be more than 2.5°C or else it is considered not stable in storage [16]. The result for this test is presented in Figure 6. Apparently, the softening point differences of all the modified binders are less than 2.5°C. Therefore, it is clarified that the mixture is homogeneously mixed and it has good storage stability at high temperature.

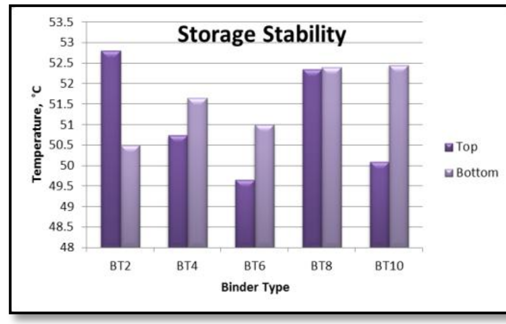


Figure 6 The difference in the temperature of top and bottom part of storage stability test

3.7 FESEM Result

FESEM is a test conducted to visualize very small topographic details on the surface or entire or fractioned objects. In this test, the object is scanned at a magnification of 10000x and 50000x.

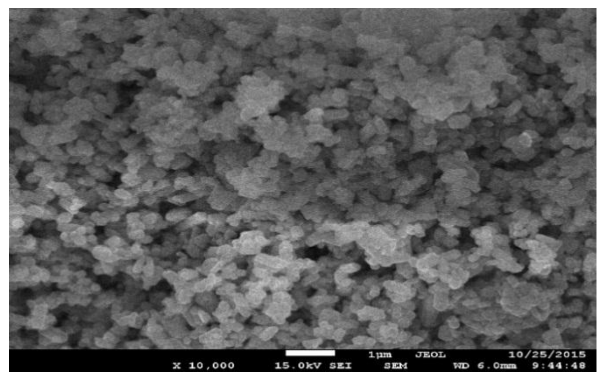


Figure 7 SEM image of nano-TiO_2at 10000x magnification

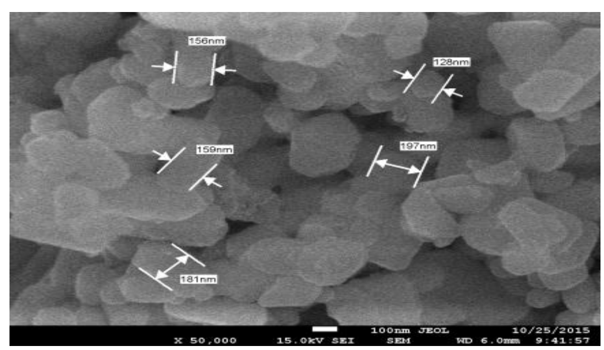


Figure 8 SEM image of nano-TiO_2 at 50000x magnification with surface diameter

The shape and diameter of the surface could be determined using this test which is an important aspect in the morphological analysis. Figure 7 and Figure 8 below show the form of nano-TiO_2 R15 that is used in this experimental study. As can be seen in the figure, the TiO2 is spherical shaped with diameters about 150 and 197micrometer.

4.0 CONCLUSIONS

In conclusion, nano-TiO_2 R15 is a good substance to be used as additive in warm mix asphalt as it improved the physical and rheological characteristics of the binder. Also based on the test results presented, the following findings and conclusions can be deduced with respect to the applications:

- The addition of nano-TiO_2 has significantly improved the penetration and softening point of the asphalt. This demonstrated the improvement of stiffness of the binder and also better temperature susceptibility.
- The nano-TiO_2 additive is homogeneously dispersed in the mixture of asphalt where it is vital in avoiding separation during high temperature storage and applying the asphalt.
- For modified binder, it is evaluated that the $G^*/\sin\delta$ of the unaged binder is not as positive as the unmodified binder, but it is still in the same performance grade as the control binder which is 64°C, therefore, the resistance of the binder towards rutting is still acceptable.
- Modified binder with addition of 4% TiO_2 is found to have a compaction and mixing temperature at 152°C and 159°C. It is proven that is has a lower viscosity compared to unmodified asphalt which has a compaction and mixing temperature of 157°C and 168°C.

Acknowledgement

The research was carried out at Advanced Highway Engineering Laboratory, Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia.

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