WARM MIX ASPHALT AND TITANIUM DIOXIDE PHOTOCATALYST: ENGINEERING PROPERTIES AND ENVIRONMENTAL EFFECTIVENESS

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ABSTRACT

Warm Mix Asphalt (WMA) technology allows a reduction in temperatures at which asphalt mixes are produced and placed. This offers the benefits of reduced mixing and compaction temperature, reduced energy consumption, and greenhouse gas/toxic gases emission, extending cold paving season and long-hauling distance, and enhanced sustainability. On the other hand, nano anatase Titanium Dioxide (TiO_2) particles can trap and decompose harmful environmental substances like NOx, SO_2, and VOCs through photocatalytic oxidation. An infrastructure sustainable system that combines the benefits of WMA technology and photocatalytic properties of TiO_2 to capture and degrade organic and inorganic particles in the air was examined. A 19.0 mm wearing course warm mix asphalt mixture containing PG 70-22 binder was considered. A chemical additive was incorporated into PG 70-22 binder to produce WMA. Four levels (0-, 3-, 5-, 7% by the weight of the binder) of crystallized anatase-based titanium dioxide powder were blended with the WMA binder. The binder blends were rheologically characterized through the PG binder grading system. In addition, mixture laboratory performance tests conducted included loaded wheel test (LWT) and semicircular bend (SCB) test. The environmental efficiency of the proposed sustainable infrastructure system that combines WMA and TiO_2 was measured by quantifying the mixture's ability in removing part of the NO_x pollutants in the air stream before and after durability testing. Results indicated that the proposed sustainable infrastructure system achieved a NOx reduction efficiency ranging from 39% to 52%. The addition of TiO_2 to the asphalt binder did not affect the resulting PG classification of the evaluated binder. Results from the LWT and SCB tests exhibited positive performance due to the addition of TiO_2.

Keywords: Titanium Dioxide, Sustainable Asphalt Pavement Construction, Photocatalyst, WMA

1. INTRODUCTION

The US faces a significant challenge in controlling air pollution resulting from transportation activities. Although attempts are made to lower vehicle emission standards, a method is needed to remove these pollutants once they are emitted to the atmosphere. The potential of titanium dioxide (TiO_2) as an air purifier in urban and metropolitan areas, which suffer from high concentration of air pollutants, has been widely recognized in literature [1, 2]. Evaluation of concrete pavement treated with TiO_2 provided promising results as recent research by the authors and others show that a thin surface coating is able to remove a significant portion of nitrogen oxides (NOx) and volatile organic compounds (VOC) pollutants from the atmosphere when placed as close as possible to the source of pollution [2 - 4]. However, with 94% of the US road network covered with asphalt, it appears that widespread use of titanium dioxide in air purification applications can only be achieved by the development of a novel asphalt mixture that does not affect the mechanical properties of the mix while incorporating a photocatalytic compound into current highway construction practices [5]. In addition, the use of Warm Mix Asphalt (WMA) will have the added benefits of reduced energy and the associated pollution emissions during production.

The objective of this study is to test the hypothesis that TiO_2 can function as a photocatalytic compound when used in the preparation of WMA. To achieve this objective, a crystallized anatase-based titanium dioxide powder was blended with an elastomeric polymer modified WMA binder classified as PG 70-22M at three percentages by binder weight (3, 5, and 7%). In addition, a second application method was also evaluated, specifically useful for coating existing pavements, by spraying a water-based solution of TiO2 on the pavement surface at three coverage levels (0.026, 0.05, and 0.074 l/m2). Prepared blends were characterized using fundamental rheological tests (i.e., dynamic shear rheometer, rotational viscosity, and bending beam rheometer), the semi-circular bend (SCB) test for intermediate temperature, the loaded wheel tracking (LWT) test for high temperature, and by measuring the environmental efficiency of the mixture in removing part of the NOx pollutants in the air stream before and after durability tests.

2. BACKGROUND

Initial interest in environmental photocatalysis began in the 1970s, initiated by Fujishima and Honda's research in photo-electrochemical solar energy conversion. Through biomimicry of plant photosynthesis, the researchers attempted to replicate the photo-induced redox reactions, by oxidizing water and reducing carbon dioxide, using a semiconductor irradiated by UV light [6]. To accomplish this, the semiconductor is used as an electrode, which is connected to a counter electrode to generate electrical work while driving the redox chemical reactions [7]. TiO_2 was the semiconductor chosen, due to a positive valence band edge that theoretically can oxidize water to oxygen [8]. Fujishima and Honda found that when the surface was irradiated, a current was created such that oxidation occurred at the TiO_2 electrode and reduction at the counter electrode [7]. This proved that water could be decomposed into oxygen and hydrogen from solar irradiation, preferred since solar energy equates to roughly 5 x 1024 J per year [9].

The photo-electrochemistry concepts described were extended to research in heterogeneous photocatalysis applications by removing the external circuit [6]. In 1977, Frank and Bard were one of the first to demonstrate this, by illustrating the decomposition of cyanide in water. Since then, increased interest in environmental photocatalysis was realized which caused TiO_2 to be applied to glass, tile, paper, and pavements for self-cleaning materials, water purification, air purification, sterilization, and oil spill remediation. From these studies, it has been shown that organic and inorganic compounds can be completely decomposed and that the TiO_2 surface has the ability to self-regenerate [6]. Therefore, rather than an absorption of pollutants that is common to traditional air purification methods, heterogeneous photocatalysis can decompose pollutants to nonhazardous waste products with little energy requirements [10]. In the presence of UV light, TiO_2 produces hydroxyl radicals and superoxides, which are respectively responsible for oxidizing and reducing environmental contaminants including VOC and NO_x [8]. A proposed mode of oxidation of NO_x via hydroxyl radical intermediates in the presence of the photocatalyst is described by the following equations:

$$NO + \dot{O}H \xrightarrow{T_iO_2} NO_2 + H^{\cdot} \quad (1)$$

$$NO_2 + \dot{O}H \xrightarrow{T_iO_2} NO_3^{\cdot} + H^{\cdot} \quad (2)$$

Based on this heterogeneous photocatalytic oxidation process, NO_x are oxidized into water-soluble nitrates; these substances can be washed away by rainfall.

3. EXPERIMENTAL PROGRAM

The Asphalt cement binder blends were prepared by mixing a conventional WMA binder (WMA additive Evotherm was used at 1% by weight of the binder) classified as PG 70-22M with a commercial crystallized anatase-based TiO_2 powder at three percentages 3, 5, and 7% by weight of the binder. The blends were prepared at a mixing temperature of 163°C. Short-term aging was simulated using the rolling-thin film oven (RTFO), long-term aging was simulated using the pressure aging vessel (PAV). The RTFO test simulated construction hardening and asphalt binder aging by subjecting the material to a stream of 163°C air for 85 min. The PAV test simulated long-term oxidative aging for a period ranging from 5-10 years by subjecting the binder to pressurized air for 20 hrs and a temperature maintained at 100°C.

Prepared blends were characterized using fundamental rheological tests (i.e., dynamic shear rheometry, rotational viscosity, and bending beam rheometer) and by comparing the Superpave Performance Grade (PG) of the modified blend to the unmodified WMA binder. To assess the influence of the photocatalytic compound on the binder aging mechanisms and to ensure that TiO2 does not oxidize the binder, both the control and modified prepared blends were subjected to UV light for a period of seven days. Binders were characterized using the entire suite of PG grading system as per AASHTO M 320-09 (Standard Specification for Performance-Graded Asphalt Binder). Using the same experimental mix design parameters, two replicas of asphalt concrete samples were prepared for both the fracture and environmental tests. The blends were prepared at a mixing temperature of 143°C and compacted by a gyratory compactor according to AASHTO TP4 'Standard Method for Preparing and Determining the Density of Hot Mix Asphalt (HMA) Specimens by Means of the Superpave Gyratory Compactor.'

High temperature performance of the mixes was assessed using a Hamburg-type LWT, manufactured by PMW, Inc. of Salina, Kansas. This test was conducted according to AASHTO T 324. The test applies a repetitive load on slab specimens that have a length of 320 mm, a width of 260 mm, and a thickness of 80 mm. This test is considered a torture test that produces damage by rolling a 703-N steel wheel across the surface of a slab which is submerged in 50°C water for 20,000 passes at 56 passes a minute. A maximum allowable rut depth of 6 mm after 20,000 passes at 50ºC is recommended by LADOTD specification. The rut depth at 20,000 cycles was measured and used in the analysis.

Intermediate temperature performance was assessed using the semi-circular bending (SCB) test using the procedure developed by Wu et al. [11]. This test characterizes the fracture resistance of HMA mixtures based on fracture mechanics principals, the critical strain energy release rate, also called the critical value of J-integral, or J_c. To determine the critical value of J-integral (J_c), three notch depths of 25.4, 31.8, and 38 mm were selected based on an a/r_d ratio (the notch depth to the radius of the specimen) between 0.5 and 0.75. Test temperature was selected to be 25°C. The semi-circular specimen is loaded monotonically till fracture failure under a constant cross-head deformation rate of 0.5 mm/min in a three-point bending load configuration. The load and deformation are continuously recorded and the critical value of J-integral (J_c) is determined using the following equation [11]:

$$J_c = \left(\frac{U_1}{b_1} - \frac{U_2}{b_2} \right) \frac{1}{a_2 - a_1} \qquad (3)$$

where,
b = sample thickness;
a = the notch depth; and
U = the strain energy to failure.

A second application method consisting of applying a thin surface coating was also evaluated at three coverage rates (0.11, 0.21, and 0.31 kg/m^2). The spray coat used was a mixture of TiO_2 anatase nanoparticles suspended in an aqueous liquid at 2% by volume. A thin film was spray coated on each sample in layers using in a cross hatch formation for each of the three defined coverage rates.

3.1. Environmental test setup

The environmental benefit of the fabricated asphalt blends in trapping and degrading NO_x pollutants from the air stream through a photocatalysis mechanism was investigated. A laboratory test setup that is capable of quantifying the photocatalytic efficiency of asphalt and concrete specimens was used, Figure 1. The test setup was adapted from the Japanese standard JIS TR Z 0018 "Photocatalytic materials – air purification test procedure." The developed experimental setup consists of a pollutant source, zero air source, calibrator, humidifier, photoreactor, and a chemiluminescent NO_x analyzer as shown in Figure 1. The setup simulates different environmental conditions by allowing for control of light intensity and air humidity. The pollutants are introduced through an inlet jet stream to the photoreactor, a photocatalytic testing device. A zero air generator is used to supply the air stream, which is passed through a humidifier to simulate the desired humidity level.

Figure 1: Experimental Laboratory Setup

The photoreactor creates an enclosed controlled environment where the light and the atmosphere can be simulated. Fluorescent lamps, attached to the photocatalytic device, are used to imitate natural sunlight radiation required for photocatalytic activity. The pollutants measured from the recovered air before and after the photoreactor allowed for determination of the absorbed level of pollutants. In this study, NO_x and removal efficiency was measured using the Thermo 42i chemiluminescent NO_x analyzer. Nitrogen oxides were blown over the surface of the asphalt specimens at a concentration of 450 ppb. All tests were conducted at room temperature while the relative humidity was kept constant at 20%.

3.2. System Calibration

Scanning Before testing, the Thermo 42i was calibrated in accordance to the EPA calibration procedures using the gas phase titration (GPT) alternative. This technique uses the rapid gas phase reactions between the NO and O to produce NO_2 using the following chemical reaction.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4)$$

The Thermo 146i gas calibrator follows this principle to supply known concentrations of NO and NO_2 used in the NO_x analyzer. The NO_x analyzer was calibrated at five different spans for NO calibration and four different ozone settings for NO_2 calibration to confirm linearity and ozone converter efficiency. The calibration points were chosen

between the accuracy ranges that were set from 0 and 500 ppm, typical settings of ambient air monitoring equipment.

4. RESULTS AND ANALYSIS

The samples with the TiO_2 in the binder were tested at 1 l/min flow rate and 1 mW/cm^2. The results presented in Table 1 show low NOx reduction suggesting that the method of incorporation of TiO_2 into the asphalt binder mix may not be environmentally-effective. The low efficiencies could be attributed to the fact that only a small amount of TiO_2 is actually present at the surface. Other possible explanations could be that the asphalt binder inhibits the photocatalytic reaction at the surface. Future research is underway to support the understanding of these results.

Table 1: Average NO_x reduction and NO reduction for TiO_2 incorporated into binder mixes.

Sample	NO_x Reduction %	NO Reduction %
3% TiO_2 70-22	3.8%	5.4%
5% TiO_2 70-22	4.9%	5.5%
7% TiO_2 70-22	2.9%	4.5%

For the second application method consisting of applying a surface spray coating, samples were tested using a flow of 1.5 l/min and a luminosity of 2 mW/cm^2. Figure 2 illustrates the variation of NO_x concentration during the course of the environmental experiment for the asphalt sample treated with a TiO_2 surface spray coat with a coverage rate of 0.21 kg/m^2. The UV light is turned on 2 hours after the start of the experiment in order to ensure equilibrium condition. The inlet concentration reached equilibrium at 430 ppb before the light was turned on. After the light is turned on, a fast drop of NO concentration in the outlet air stream is exhibited and NO_2 is created from the NO oxidation. During the photocatalytic experiment, the NO_x concentration slightly increased. After 5 hours of testing, the light and gas supply was turned off allowing for any desorption to occur. For the test condition shown in Figure 2, the use of TiO_2 photocatalyst coating had an NO removal efficiency of 83% and the overall NO_x reduction was 69%.

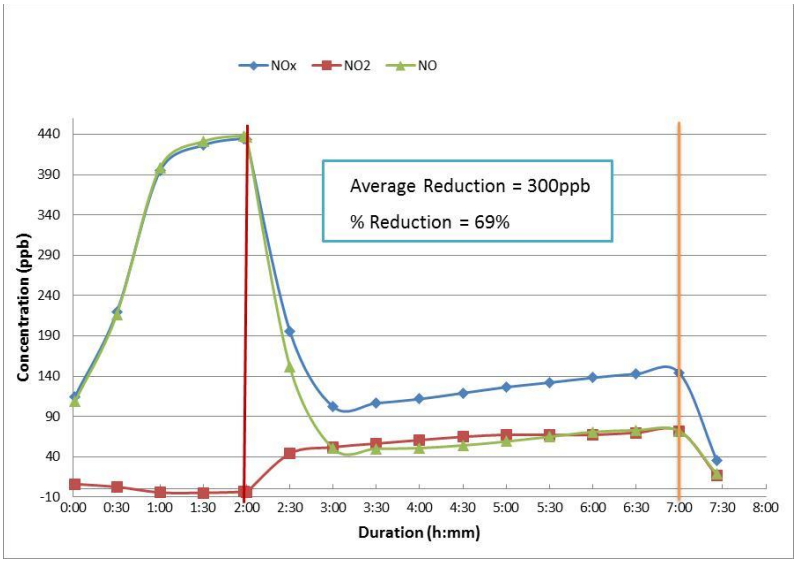

Figure 2: Variation of NOx Concentration during the Environmental Experiment (TiO_2 applied at a 0.21 kg/m^2 coverage)

The rest of the results for all of the samples are shown in Table 2. Table 2 also presents the measured NO efficiency for the asphalt sample that was not treated with TiO_2. As shown in this figure, the efficiency of the sample without TiO_2 was negligible validating the efficiency of the photocatalytic compound in removing part of the NO pollutants in the air stream when used as a spray coating. By comparing the effect of the TiO_2 coverage rate, it appears that the improvement of NO_x reduction is not linear. In fact, the maximum environmental performance was

achieved at the 0.21 kg/m2 coverage rate. The increase in TiO_2 application rate beyond an optimum coverage rate may block nanoparticles' access to light and contaminants, and therefore, decrease NO_x removal efficiency.

Table 2: Average NO_x reduction and NO reduction for TiO_2 used in a thin surface coating.

Coverage (kg/m2)	NO_x Reduction %	NO Reduction %
Control PG (70-22)	8.5%	9.6%
PG (70-22) 0.11kg/m^2	51%	73%
PG (70-22) 0.21kg/m^2	66.2%	76.6%
PG (70-22) 0.32kg/m^2	54.3%	56%

4.1. Effects of TiO_2 on Rheological Properties:

Table 3 presents the measured rheological properties of the TiO_2 modified and unmodified WMA binders based on laboratory testing conducted using rotational viscometer, dynamic shear rheometer, and bending beam rheometer. Results are presented for four types of specimen: PG 70-22 conventional WMA binder, PG 70-22 + 7% TiO_2, and PG 70-22 conventional and + 7% TiO_2 subjected to UV light for seven days. Since UV light will only influence the long-term behavior of the binder, rheological testing of specimens subjected to UV light was only performed on the aged samples (RTFO + PAV). Ultra-violet light initiates the photocatalytic process for the sample with TiO_2. Results presented in Table 3 indicate that the addition of TiO_2 only marginally affected the rheological properties of the conventional binder.

Table 3: Rheological Test Results of TiO_2-modified Asphalt Binder.

TiO_2 Binder Testing	**Spec**	**Test Temp**	**PG 70 W70CO**	**PG 70 W70CO + UV**	**PG 70 + 7%TiO_2**	**PG 70 + 7%TiO_2 + UV**
Test on Original Binder						
Dynamic Shear, G*/Sin(δ), (kPa), AASHTO T315	1.30^+	70°C	1.25	NA	1.44	NA
	1.00^+	70°C	0.63	NA	0.73	NA
Rotational Viscosity (Pa·s), AASHTO T316	3.0^-	135°C	0.7	NA	0.9	NA
Tests on RTFO						
Mass Loss, %	1.00^-	----	0.1	NA	0.7	NA
Dynamic Shear, G*/Sin(δ), (kPa), AASHTO T315	2.20^+	70°C	2.69	NA	2.88	NA
Tests on (RTFO+ PAV)						
Dynamic Shear, G*Sin(δ), (kPa), AASHTO T315	5000^-	25°C	3845	3935	4610	4460
BBR Creep Stiffness, (MPa), AASHTO T313	300^-	-12°C	163	142	189	152
Bending Beam m-value AASHTO T313	0.300^+	-12°C	0.304	0.310	0.305	0.301
Actual PG Grading			**70-22**	**70-22**	**70-22**	**70-22**

Results presented in Table 3 also show that exposing the binder to UV light did not accelerate the aging mechanisms in the material as compared to the sample that was not subjected to UV light. In addition, the use of TiO_2 as an air purification agent did not accelerate the aging mechanisms in the binder. This trend was desirable to ensure that UV light, which is necessary to initiate the photocatalytic process, did not negatively affect the binder rheological properties.

4.2. Effects of TiO_2 on the Mix Rutting Resistance

Figure 3 shows the results of the loaded wheel tracking test. As shown in this figure, the use of TiO_2 at 5 and 7% improved the rutting resistance of the mix as compared to the control mixture.

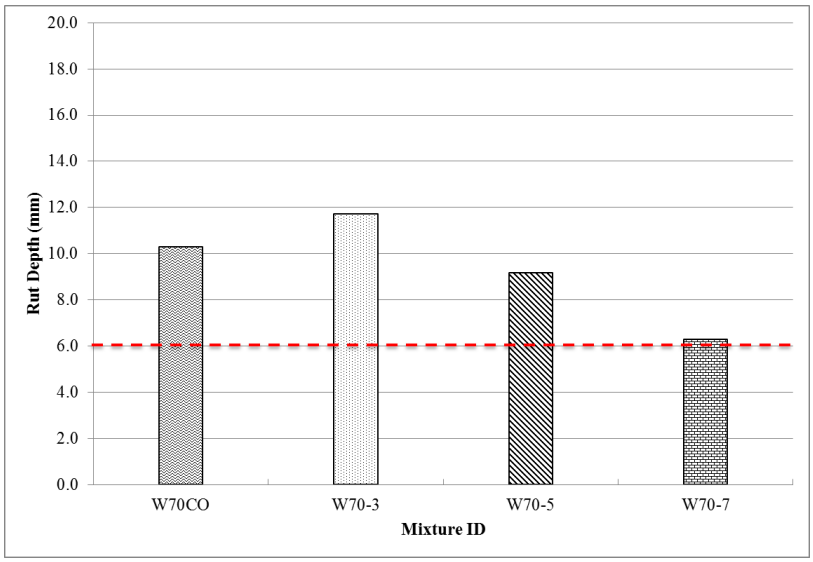

Figure 3: LWT test Results for TiO_2 incorporated into WMA mixtures.

4.3. Effects of TiO_2 on the Mix Fracture Resistance:

Table 4 presents a comparison of the critical strain energy (J_c) data for the mixtures evaluated in this study. High J_c values are desirable as indicative of fracture-resistant mixtures. As shown by these results, the use of TiO_2 as a binder modifier improved the mix fracture resistance at 3, and 5% while it did not have a noticeable effect when used at a content of 7.0%.

Table 4: SCB test Results for TiO_2 incorporated into WMA mixtures.

TiO_2 Content	J_c (kJ/m^2)
Control	0.54
3.0 %	0.54
5.0 %	0.36
7.0 %	0.30

5. SUMMARY AND CONCLUSIONS:

This study evaluated the benefits of incorporating titanium dioxide (TiO_2) as an additive to asphalt binder in the preparation of WMA. Two commercial crystallized anatase-based titanium dioxide powder were blended with an elastomeric polymer modified WMA binder classified as PG 70-22M at three modification rates (3, 5, and 7%). Prepared blends were characterized using fundamental rheological tests, the LWT test, and the SCB test. Two application methods to integrate TiO_2 were evaluated, a water-based titanium dioxide solution applied as a thin coating and using TiO_2 as a modifier to asphalt binder in the preparation of WMA. Based on the results of the experimental program, the following conclusions may be drawn:

- When used as a modifier to asphalt binder in the preparation of WMA, the photocatalytic compound was not effective in degrading NO_x in the air stream. This could be attributed to the fact that only a small amount of TiO_2 is present at the surface.
- When used as part of a surface spray coating, TiO_2 was effective in removing NO_x pollutants from the air stream with an efficiency ranging from 38 to 77%.
- Rheological test results indicated that the addition of TiO_2 did not affect the physical properties of the conventional binder. In addition, exposing the binder to UV light did not appear to accelerate the aging mechanisms in the binder.
- The use of TiO_2 as a binder modifier improved the mix fracture resistance at 3, and 5% while it did not have a noticeable effect when used at a content of 7.0%. In addition, the use of TiO_2 at 5 and 7% improved the rutting resistance of the mix as compared to the control sample.

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