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Chinese Society of Pavement Engineering

International Journal of Pavement Research and Technology 11 (2018) 867-874

http://www.ijprt.org.tw/

Study on air-purifying performance of asphalt mixture specimens coated with titanium dioxide using different methods

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Received 23 April 2016; received in revised form 9 June 2018; accepted 23 August 2018

Abstract

Titanium dioxide (TiO_2) has been employed to degrade hazardous materials since its photocatalytic ability was discovered. In recent years, attempts have been made to apply TiO_2 onto road surfaces to degrade the harmful compounds (such as NO and NO_2) from vehicle emissions. As a photocatalyst, the NO_X degradation efficiency of TiO_2 largely depends on its surface area exposed to sunlight. However, the effective coating methods to enlarge the contact area between the coated TiO_2 and sunlight have not been well studied, especially for asphalt pavements. To fill this gap, this study aims to investigate the photocatalytic performance of three TiO_2 coating methods for asphalt pavements, including the conventional water-solution-based TiO_2 (WT) coating, and the innovative glass-bead-based TiO_2 (GT) coating and porous TiO_2 (PT) coating. A custom-designed environmental test setup was used to determine the NO_X degradation efficiency of the specimens with TiO_2 coating, and the durabilities of the coating materials were characterized by measuring their NOx degradation efficiency subjected to different numbers of lab-simulated tire abrasion. It was found that the PT and GT methods provided not only better NO degradation efficiency but also improved durability compared to the conventional WT method.

Keywords: Titanium dioxide; Photocatalytic asphalt pavement; NOx removal efficiency; Coating method

1. Introduction

Nitrogen oxide (NO_X) is one of the main hazardous components of vehicle emission, which is also an important precursor of particulate matter 2.5 (PM2.5) [1]. Furthermore, exposure to the air with high NO_X content may cause problems to human health, especially the respiratory system [2]. The high traffic densities in megalopolises like Hong Kong often lead to high NO_X concentrations in urban areas. Research showed that the main hazardous components of the automobile exhaust that pollute the atmosphere are NOx, CO, and SO_2. It was reported that 60% of CO, 50% of NOx and 30% of hydrocarbons in the air in the large and medium cities in China are caused by automobile exhaust emissions [3]. Thus, effective and efficient approaches to degrade the NO_X as soon as they are emitted from vehicles are keenly desired.

Titanium dioxide (TiO_2) has been successfully applied as an air-purifying material since its photocatalytic oxidation property was discovered by Fujishima and Honda in 1972 [4]. With the aid of ultraviolet (UV), the photocatalyst, TiO_2, can significantly accelerate the degradation process of NO_X. The photocatalytic process starts with the light irradiation on TiO_2 particles. Once TiO_2 absorbs a photon containing the energy larger than or equal to its band gap,

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Peer review under responsibility of Chinese Society of Pavement Engineering.

https://doi.org/10.1016/j.ijprt.2018.08.003

3.2 eV, an electron will be promoted from the valence band to the conduction band, leaving a hole behind and creating electron–hole pairs, which are also known as excitons (Eq. (1)). The generated h^+ and e^- are powerful oxidizing and reducing agents, respectively.

$$TiO_2 \xrightarrow{hv} h^+ + e^- \quad (1)$$

The strong oxidation power of h^+ enables it to react with water to generate the highly active hydroxyl radical ($OH^{\cdot}$), which is also a powerful oxidant. In addition, the power of the electrons can induce the reduction of molecular oxygen (O_2) to superoxide anion (O_2^-), which also has the strong capacity of degrading pollutants. These two processes can be illustrated by Eqs. (2) and (3), respectively.

$$h^+ + OH^- \rightarrow OH^* \quad (2)$$

$$e^- + O_2 \rightarrow O_2^- \quad (3)$$

The superoxide anion can further react with H^+ dissociated from water to generate the HO_2^* radical, as Eq. (4) shows.

$$H^+ + O_2^- \rightarrow HO_2^* \quad (4)$$

Most organic air pollutants can be degraded completely by either the OH^- or the holes themselves to innocuous final products. For example, NO can be oxidized to NO_2, and then both the hazardous gases (NO and NO_2) can be degraded to water soluble nitrates, as Eqs. (5) and (6) show:

$$NO + HO_2^* \rightarrow NO_2 + OH^* \quad (5)$$

$$NO_2 + OH^* \rightarrow HNO_3 \quad (6)$$

After the above reactions, the final product, nitric acid (HNO_3), can be easily washed away by rainwater.

In recent years, various studies have been conducted to investigate the feasibility of a technology called "TiO_2 on road", which applies TiO_2 onto pavement surface for air-purifying purpose [5–9]. The mechanism of this technology is to make the NOx emitted from vehicles quickly degraded by TiO_2 particles on road surface, and the NOx removal efficiency is largely determined by whether the TiO_2 particles are activated or not, i.e., whether the catalysts can have direct contact with UV and the pollutants [10,11]. However, the application of TiO_2 coating onto asphalt pavement surface is in general not quite successful so far, mainly because of the following limitations: (1) the NOx removal efficiency of asphalt pavements with TiO_2 coating is not very satisfying; and (2) the ability of asphalt pavements with TiO_2 coating to maintain NO_X removal efficiency is relatively poor [12,13]. Correspondingly, more effective methods to coat TiO_2 onto asphalt road are keenly desired to make "TiO_2 on road" a more successful technology.

The main objective of this study is to assess the performance of TiO_2 coatings prepared by two innovative methods, namely porous TiO_2 (PT) coating and glass-bead-based TiO_2 (GT) coating, against the conventional water-solution-based TiO_2 (WT) coating. To achieve this objective, laboratory Marshall specimens were first prepared and coated using the three methods. Then, their NOx removal efficiency before and after lab-simulated abrasion were measured using a custom-designed environmental test system.

2. Background on TiO_2 coating methods

Conventionally, the TiO_2 particles have been coated to asphalt pavements by first dissolving them into water solution and then spraying the TiO_2 water solution onto pavement surface. This method is denoted as WT coating method in this study. Recently, a number of new coating methods, such as the PT coating method and the rubber-based TiO_2 coating method, have been developed to improve the pollution removal efficiency and the durability of TiO_2 coating [10,13–16].

The PT method is mainly based on the so called Breath Figure (BF) process [17], which fabricates numerous micro pores on pavement surface (Fig. 1). The mechanism of the BF process can be described as follows: (1) the polymer is dissolved in a low boiling point solvent, and then cast onto a solid substrate in a high-humidity environment; (2) the water droplets nucleate on the surface and grow subsequently due to the evaporative cooling; (3) driven by the surface convection and capillary force, the condensed water droplets self-assemble into hexagonal arrays; and (4) templated by the formed droplet arrays, micro pores are formed on the polymer film surface as soon as the solvent evaporates. The researchers in Hong Kong first applied this method to build micro-porous structures on asphalt binder surface and accommodate TiO_2 particles inside, which allows larger contact area among TiO_2, NO_X and UV [14]. They found that the specimens with PT coating provided satisfying performance in terms of both NO removal efficiency and durability of the efficiency.

The researchers in Nanjing, China proposed a novel coating method based on Rubber/TiO_2 (RT) composite structure [15]. The TiO_2 particles were coupled into crumb rubber surface by coupling agent. They found that the rubber-based TiO_2 coating method allowed the test specimens to achieve similar NO_x removal efficiency as the conventional WT coating method with fewer amounts of TiO_2 particles (Fig. 2).

Inspired by this idea, attempts were made in this study to use glass beads as a replacement of rubber. Glass beads and TiO_2 particles were cross-linked by a suitable coupling agent, which was Silane coupling agent KH570 in this study. The oil-wet hydrophobic properties of glass beads enable them to be dispersed in the absolute ethyl alcohol easily. Thus, the TiO_2 particles coated on the glass beads are beneficial for the dispersion. In addition, since TiO_2 and glass beads are both in light color (Fig. 3), the coated asphalt pavement surface will have better reflection to sunlight, thus lower temperature. Fig. 4 presents the SEM images of the glass bead/TiO_2 (GT).

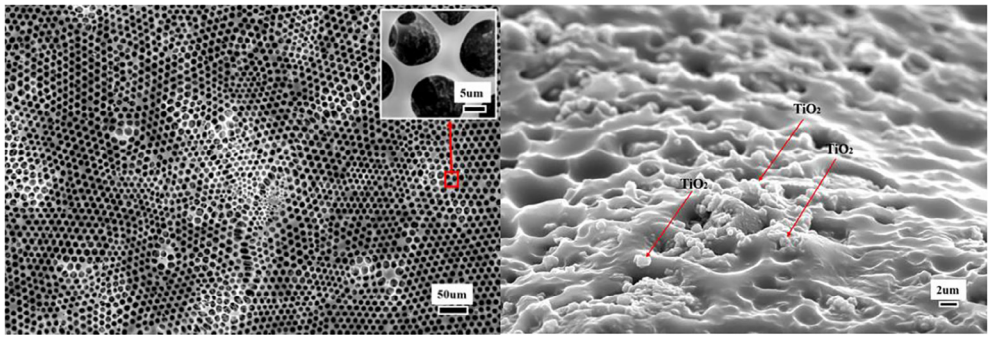

Fig. 1. SEM images of porous coating: top-view (left); cross-sectional view (right).

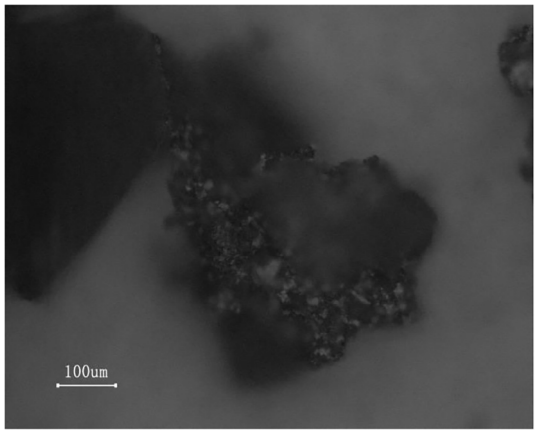

Fig. 2. SEM images of rubber/TiO_2 (RT) composite structure.

Fig. 3. Nano-TiO_2 particles (left) and glass beads (right).

3. Experimental program

3.1. Sample preparation

Table 1 describes the process for preparing the coating solutions using WT, PT, and GT methods. All coating solutions were prepared at room temperate (20 ± 3 °C) and humidity ($60 \pm 5\%$). For PT and GT, solutions with two TiO_2 contents were prepared. Specially, L-PT and H-PT correspond to PT solutions with low TiO_2 content (mass ratio of TiO_2, asphalt, and PS = 0.5:1:1) and high TiO_2 content (mass ratio of TiO_2, asphalt, and PS = 2:1:1), respectively, while L-GT and H-GT correspond to GT solutions with low TiO_2 content (mass ratio of TiO_2, glass bead, and KH570 coupling agent = 0.2:1:0.32) and high TiO_2 content (mass ratio of TiO_2, glass bead, and KH570 coupling agent = 0.8/1/0.32), respectively.

Standard Marshall specimens (101.6 mm in diameter and 63.5 mm in height) were prepared as the substrates for the coating solutions. The mixture used to prepare Marshall specimens was 10 mm stone mastic asphalt (SMA10), which is commonly used in Hong Kong [18]. The dosages of solutions applied to each Marshall specimen were controlled so that the designed amounts of TiO_2 practices were applied to each specimen. Certain amount of TiO_2 solution was placed into a watering can first and then the solution was sprayed on Marshall specimen surface. Table 2 describes the mass of TiO_2 applied to each group of specimens (Fig. 5). Fig. 6 shows the pictures of the specimens coated with TiO_2 using different methods. For all groups except for CG, three replicate specimens were prepared and tested to ensure the reliability of the test results.

3.2. NOx removal efficiency test

A custom-designed environmental testing system was used to measure the NO_X removal ability of the prepared specimens. As shown in Fig. 7a, the system consists of three main parts, namely air supplier (NO and zero air), reacting chamber with ultraviolet light, and NO_X analyzing equipment. During the test, NO and zero air supplier provides continuous flow stream into reacting chamber, and the data analyzer system records the NO and NO_2 content data inside the chamber. The reacting chamber (Fig. 7b) is equipped with two UV-A fluorescent lamps, which were positioned parallel to each other on the glass cover of the reactor to provide UV radiation for the photocatalytic process. The testing system was made according to the specifications of JIS R1701-1 with slight modifications. The parameters in this study follows the Japanese standard and they are generally consistent to previous publications conducted in the same laboratory [14,19–21], the original NO content inside the reacting chamber was 1200 parts per billion (ppb) and the flow rate was 3 L/min. During the testing process, the condition inside

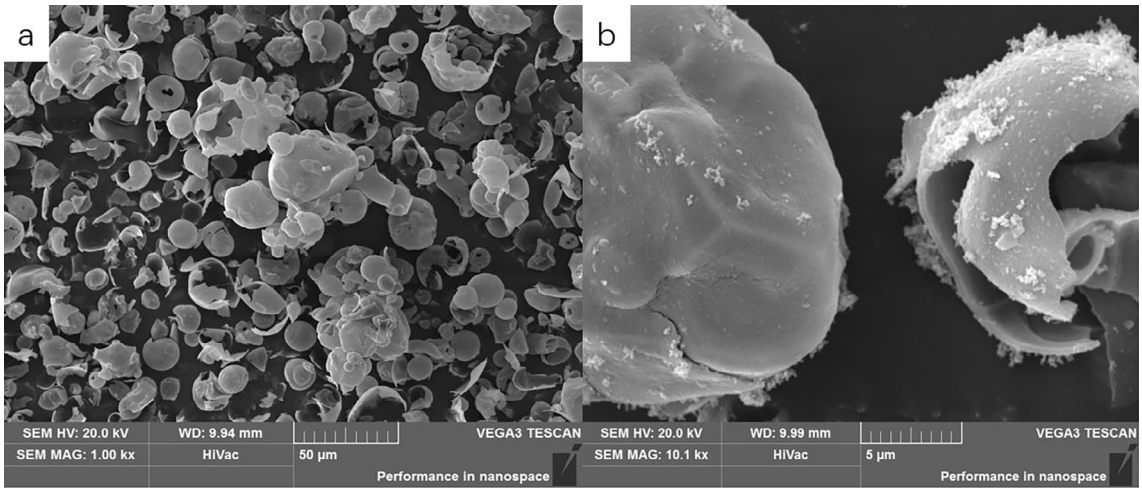

Fig. 4. SEM images of glass bead/TiO_2 (GT) composite structure: (a) magnified 1000 times; (b) magnified 10,000 times.

Table 1
Preparation of the three coating solutions.

Coating method	Materials	Preparation process
WT	Water and TiO_2	Mixing TiO_2 particles directly with water by magnetic stirring for 40 min
PT	Tetrahydrofuran (THF), polystyrene (PS), asphalt binder, and TiO_2	Mixing asphalt binder, THF, PS, and TiO_2 together by ultrasonic dispersion and magnetic stirring for 40 min and 2 h, respectively
GT	Glass bead, coupling agent, ethyl alcohol and TiO_2	Mixing TiO_2 and coupling agent KH570 and enough amount of alcohol at 60 °C, followed by ultrasonic dispersion for 1 h

Table 2
Marshall specimens with different coating solutions.

Group ID	TiO_2 content on each sample	Number of samples
CG (control group)	0 g	3
WTM (mixture with water-based TiO_2 coating)	0.4 g	3
L-PTM (mixture with low rate porous TiO_2 coating)	0.1 g	3
H-PTM (mixture with high rate porous TiO_2 coating)	0.4 g	3
L-GTM (mixture with low-rate glass-bead-based TiO_2 coating)	0.1 g	3
H-GTM (mixture with high-rate glass-bead-based TiO_2 coating)	0.4 g	3

Fig. 5. The spraying process of TiO_2 solution.

the chamber was controlled at a temperature of 20 °C and a humidity of 10%. The wavelength and intensity of the UV light were 365 nm and 10 W/m^2, respectively.

At the beginning of test, the sample was first placed into the reacting chamber, and then the air supplier was turned on. The gas streams were adjusted by the flow controllers to obtain the initial NO concentration ($X_{initial}$), which is approximately 1200 ppb. Usually it takes 30 min to reach the first equilibrium inside reacting chamber. Afterward, the NO_X removal test was started by turning on the UV lamps, activating the photocatalytic process. After another 30 min, the second stable status was reached, and its corresponding NO concentration inside the chamber was recorded as X_{stable}. Finally, the NO removal rate (E%) was calculated according to Eq. (7). A larger E% value indicates higher NO removal efficiency.

$$\%NO\,Removal\,Rate\,(E\%) = \frac{X_{initial} - X_{stable}}{X_{stable}} \times 100\% \qquad (7)$$

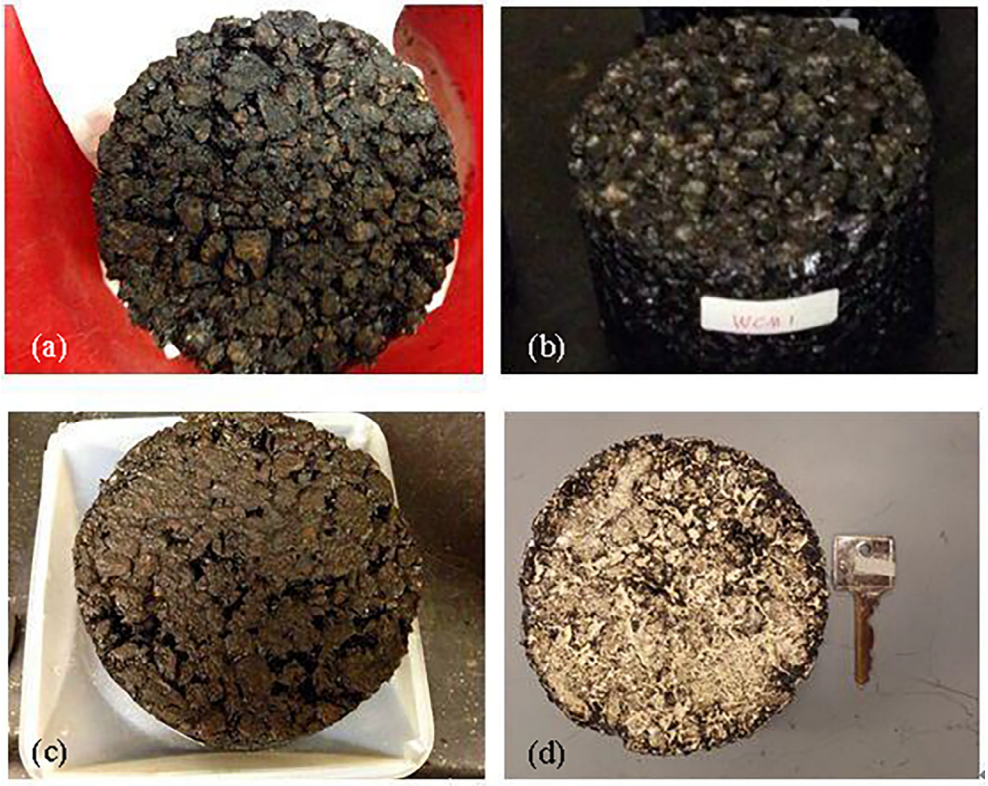

Fig. 6. Marshall specimens: (a) CG; (b) WT; (c) PT; (d) GT.

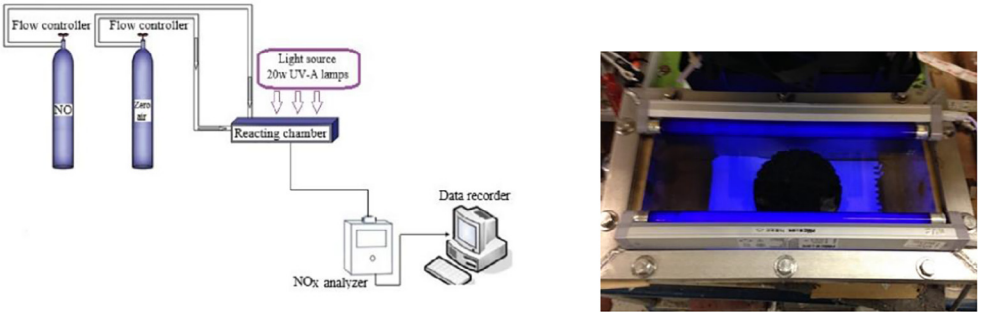

Fig. 7. Equipment for NOx removal efficiency test: (a) sketch of the whole system; (b) test sample in reacting chamber.

3.3. Durability test

Since the TiO_2 coating on asphalt pavement surface is subjected to repeated vehicle tire abrasion, satisfactory durability of the coating material is necessary to maintain its photocatalytic degradation efficiency. In this study, the British Pendulum Tester (BPT) was used to simulate the field tire abrasion on different types of TiO_2 coating layers.

As Fig. 8 shows, the test specimen was fixed on the ground, and the pendulum slider was adjusted to the position that barely in contact with the specimen surface. The simulated abrasion was started by raising the pendulum to the horizontal lock position and then releasing it, allowing the rubber slider to make contact with and pass the specimen surface. After 50 passes and 200 passes of simulated abrasion, the NOx removal efficiencies of each specimen were measured again. The residuary NO removal ability (RA%) was calculated using Eq. (8).

$$\%\,Residuary\,NO\,removal\,ability\,(RA\%) = \frac{E_x}{E_0} \times 100\% \qquad (8)$$

where E_x represents the NO removal rate after X passes of abrasion and E_0 is the original NO removal rate without

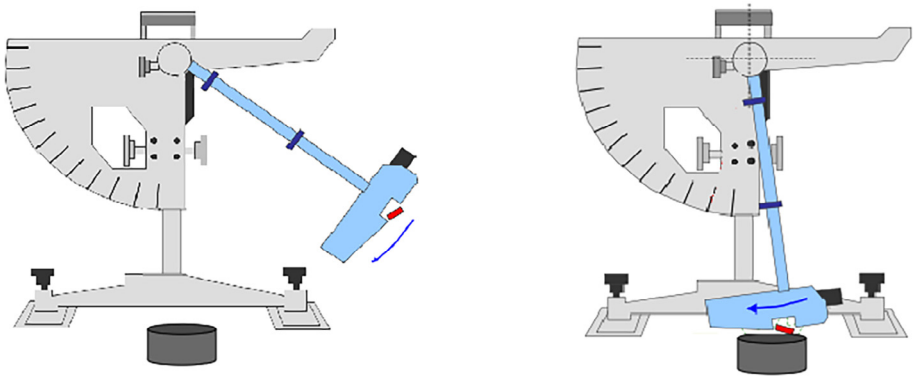

Fig. 8. Lab-simulated abrasion test.

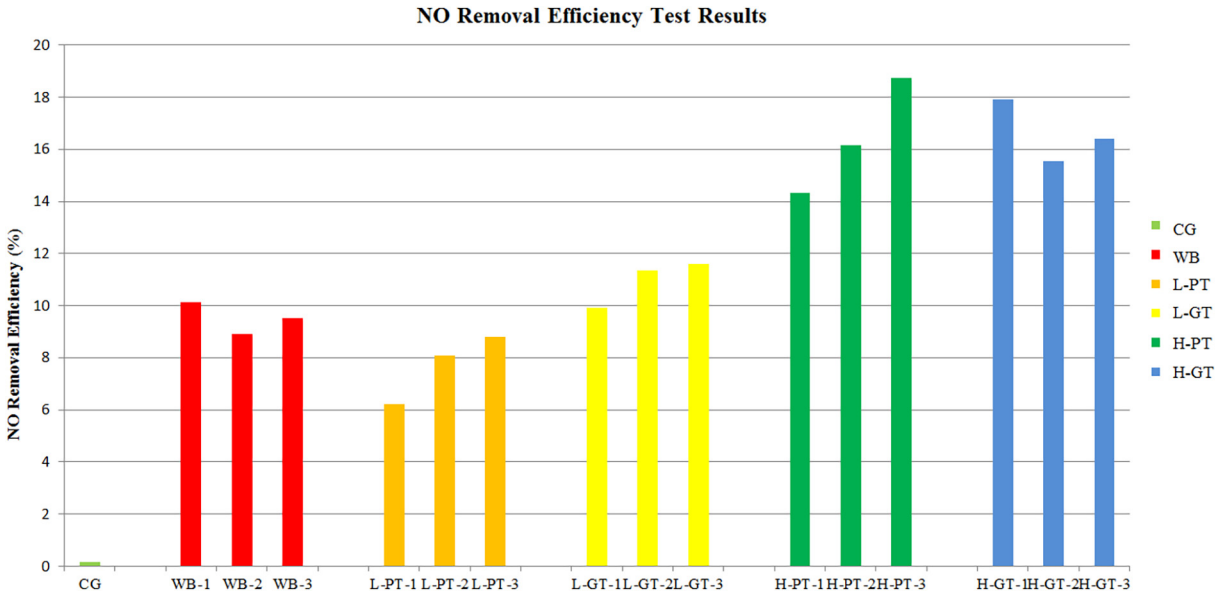

Fig. 9. NO removal efficiency test results.

abrasion. A higher value of RA% indicates better durability of the TiO_2 coating material.

4. Results and discussion

4.1. NO removal efficiency

Fig. 9 summarizes the NO removal efficiency of all test specimens before lab-simulated abrasion. It can be observed that the specimens from the same group provided very close NO removal rates, indicating good test repeatability. The NO removal efficiency of the control specimen is almost zero, suggesting that the effect of UV light on degrading NOx without TiO_2 is minimal. The specimens with 0.4 g TiO_2 particles on surface, i.e., the H-GT and H-PT specimens, provided similar E% values (16.6% and 16.4%), both of which are much higher than that of the WT specimens (9.5%). In addition, the specimens in the L-GT group and L-PT group, which had only one fourth of the TiO_2 particles on surface compared to WT specimens, obtained 11.0% and 7.7% NO removal rates, respectively. The NO removal efficiency test results indicated that both novel coating methods, PT and GT, provide higher NO removal efficiency than the conventional WT method. These two novel methods were also able to achieve similar photocatalytic performance as the WT method when much less TiO_2 materials were used.

For the PT specimens, the improved performance of NO removal efficiency is mainly due to the introduction of the micro porous structure on the coating surface. Based on the mechanism of photocatalytic activity, only catalysts exposed to UV provide the catalytic effect. Thus, the micro porous structures allow for larger contact area among TiO_2, UV, and NO, leading to higher pollution removal rates.

For the GT specimens, the enhanced photocatalytic performance mainly comes from the larger contact area provided by the TiO_2-glass bead structure. The diameters of the glass beads are approximately 100 μm, which are thousands of times larger than that of the nano-TiO_2

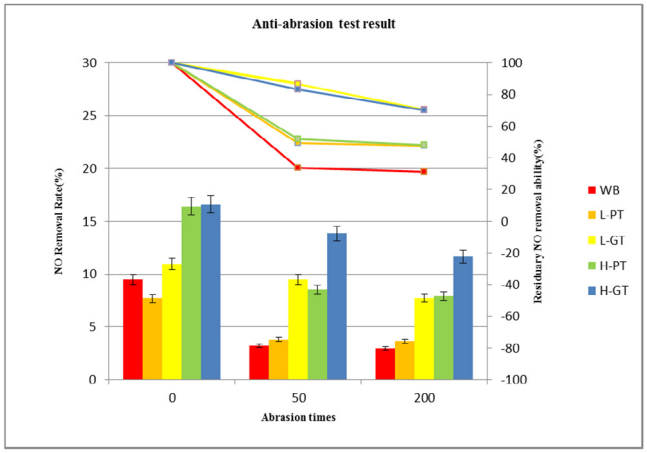

Fig. 10. Durability test results.

particles. When the catalysts are dispersed around the glass beads, the contact area among TiO_2, UV, and NO is also greatly increased, leading to better NO removal efficiency.

4.2. Durability

Fig. 10 shows the results of the durability tests. The columns in the figure represent the average NO removal rates (R%) while the dots represent the residuary NO removal ability (RA%) after various numbers of abrasion. It can be seen that compared to the initial state, i.e., the state without abrasion, there were obvious declines in R% for specimens in all groups after 50 passes of abrasion. However, after 200 times of abrasion, there were only minor drops for WT and PT specimens, but significant drops for GT specimens. The possible reason is that after 50 times of abrasion, the amount and distribution of the TiO_2 particles at the WT and PT specimen surfaces became relatively stable. In case of GT specimens, the TiO_2 distribution was not stable yet after 50 times of abrasion, therefore the subsequent abrasions still have obvious impact on the NO removal efficiency.

It can also be noticed the GT specimens provided the highest removal efficiencies at all stages. The durabilities of PT specimens are higher than those of WT specimens, which were the poorest. The average RA% values of the L-PT, H-PT, L-GT and H-GT specimens were 48.3%, 47.5%, 70.59%, and 70.12%, respectively, after 200 times of abrasion, while that of the WT specimens was only 31.1%. In other words, both the PT and GT coating methods provided better abrasion resistance than the traditional WT method.

5. Summary and findings

In this study, three methods of coating TiO_2 onto asphalt pavement surface (WT, PT and GT) were studied and compared. The NO removal efficiency tests and durability tests were conducted to evaluate these three methods. Based on the test results, the following findings were obtained:

- Both the two novel coating methods, PT and GT, provide better NOx removal efficiency than the conventional WB coating method.
- The GT method provides the coating material the best abrasion resistance, followed by the PT method and WB method.
- Considering the removal efficiency and durability, GT is the most promising coating method to incorporate nano-TiO_2 particles onto asphalt pavement.

However, it is worth noting that this study only assessed the performance of the three TiO_2 coating methods under dry and clean condition in the laboratory. It is recommended that further study should be conducted on the effects of moisture and dirt on different coating methods, and the feasibility and performance of each method in field application. In addition, the BPT was adopted in this study to manually simulate the field tire abrasion. It is expected that more realistic and objective testing results can be achieved by using more advanced laboratory abrasion tools, such as the Aachen Polishing Machine in Germany [22].

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