EFFECT OF PEG LOADING ON THE MICROSTRUCTURE AND PHOTOCATALYTIC ACTIVITY OF TiO_2 FILM ON CERAMIC TILE

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ABSTRACT: TiO_2 films have been used and deposited on various substrates due to its potential application in photocatalysis. However, when deposited on ceramic substrates, TiO_2 films commonly resulted in a cracked morphology of the film which lead to delamination and peel off of film from substrate. Therefore, a binder needs to be added into the composition of TiO_2 solution in an effort to improve TiO_2 film structure. In this work, polyethylene glycol 2000 (PEG2000) was added into TiO_2 sol as an additive to act as a binder, in order to improve the microstructure of TiO_2 films on unglazed ceramic tiles and glass substrate by sol-gel dip-coating. The crystalline phases were characterized by XRD, while film morphologies were analyzed by SEM. The photocatalytic activity was evaluated by degradation of methylene blue (MB) under UV-radiation. The use of PEG successfully eliminated cracks and delamination of TiO_2 films even at the smallest amount of PEG added (1 mol%). Also, the addition of PEG creates pores on the surface of the films. This contributes to a higher degradation of MB and enhanced photocatalytic activity. The best degradation of MB observed was at 3 mol% PEG due to bigger pores on the surface of the film.

KEYWORDS: *TiO_2; Sol-Gel; Dip-Coating; Ceramic Tile; Photocatalytic Activity*

1.0 INTRODUCTION

TiO_2 has received special attention due to its stable chemical structure, biocompatibility, and optical properties [1]. It exists in three crystalline phases; anatase, rutile, and brookite. Among these, anatase was found to be the most used among TiO_2 crystalline phases due to its high photocatalytic activity [2-3]. Aside from using TiO_2 in powder suspension form, it can be immobilized by different deposition techniques on different substrates such as glass [2, 4], stainless steel [5], aluminium alloy [6], and ceramic tiles [6–8].

However, when TiO_2 films are deposited on ceramic tiles, the common problem faced by past studies was the crack and peeling off of the film from the substrate. It is due to the tensile stress during heating stage of the films [6, 9]. Therefore, adding additives to act as a binder is a promising approach in an effort to produce a microstructure that is crack free with continuous layer that covers the substrate, henceforth improving the properties of the TiO_2 film.

In general, polyethylene glycol (PEG) was introduced as an additive in TiO_2 sol-gel in numerous methods, followed by heat treatment, one can obtain porous films with desired porosity. The pores created on the surface of the film is due to decomposition of PEG [2]. PEG is an oligomer of ethylene oxide with molecular weight (MW) less than 10,000 units [10]. In coating formulations, low MW PEG is mainly used as a plasticizer while higher MW is useful as hydrophilic polishing material [11]. In addition, PEG is utilized in TiO_2 films as a pore-forming reagent commonly used to form porous TiO_2 films [12].

During TiO_2 sol-gel synthesis, PEG was introduced into the TiO_2 sol to evaluate the effect of PEG on the TiO_2 film properties. Various studies had been carried out to investigate the potential of PEG in TiO_2 films by varying its MW. It was reported that the use of higher PEG MW will create a rougher film surface and increase in pore size [3, 13]. On the other hand, there are also studies carried out using PEG with constant MW at various amount. It was reported that adding a low amount of PEG gives smaller sized pores and as amount of PEG increased, the pores shapes become irregular and fluctuating [14]. It is also highlighted that using high amount of PEG will cause overlapping of pores and cause significant fractures that could affect TiO_2 films photocatalytic activity [15-16]. Based on the review conducted, it should be highlighted that most work reviewed on the effect of PEG on TiO_2 film is conducted on glass substrate. Therefore, it is of our interest to study on the potential of PEG on ceramic substrate, particularly on unglazed ceramic tile. The photocatalytic activity of the film is also tested. In this paper, the influence of PEG content on the microstructure and photocatalytic activity of TiO_2 coating on unglazed tile is reported.

2.0 METHODOLOGY

2.1 Preparation of TiO_2 Films

The method of making TiO_2 sol with PEG are as follows. Titanium (IV) isopropoxide (TTIP) (Sigma Aldrich Co.) was used as TiO_2 source. Ethanol as solvent, hydrochloric acid as catalyst, and water for hydrolysis. Separate sols, sol A and sol B, were prepared with water, ethanol and hydrochloric acid in sol A and TTIP and ethanol in sol B. Next, sol B were added dropwise into sol A. PEG2000 was added in different amounts (1, 3, 5 mol%), and maintaining molar ratio of TiO_2, to study the effect of PEG on the films. Then, the solution was kept at room temperature for 48 hours for ageing process.

The films were prepared by dip-coating using above prepared TiO_2 sol on glass ($R_a = \pm 3.72$ μm) and unglazed ceramic tile ($R_a = \pm 6.55$ μm) with a withdrawal rate of 0.5mm/s and 5s dwelling time. The dipping step was repeated for 5 dipping times. Then the films were heat treated at 500˚C for 1 hour with heating rate of 2˚C/min. It should be noted that films on glass substrate is to act as control sample.

2.2 Characterization of TiO_2 Films

The crystal phase composition of the TiO_2 films was studied by Glancing Angle X-Ray Diffraction (GAXRD) method in the 2θ range of 10˚-80˚ at a grazing angle of 4˚ by using the PANalytical X'PERT PRO MPD Model PW 3060/60 with Cu $K\alpha$ of 1.54060Å and generator settings at 30 mA and 40 kV. The average crystallite size, L, were calculated at strongest XRD line [(101) at 25˚], [(110˚) at 27˚] by Scherrer's Equation [17] such as

$$L = \frac{K\lambda}{\beta \cos(\theta)} \tag{1}$$

Film surface microstructure was examined by Scanning Electron Microscope (SEM) (JEOL model JSM-6010PLUS/LV). Film thickness was determined by cross-section SEM analysis.

2.3 Photocatalytic Activity

Degradation of methylene blue (MB) was performed following the ISO 10678:2010 [18]. The samples were exposed under UV radiation for 24 hours in order to decompose any possible remaining organic contaminants by photocatalytic oxidation. Then, the samples were immersed in aqueous MB solution and left in the dark for another 24 hours for pre-adsorption of substrates. This process is necessary because the substrates tend to absorb the dye molecules. Next, the adsorbed solution was replaced by a new solution each (25 mL, 10ppm) and the samples were exposed to UV-light (Sankyo Denki, 20 W, intensity, E_p = 124.34 W/m^2). The degradation of MB was measured every 1 hour for 5 hours using a spectrophotometer (SHIMADZU UV-1700, cell length, d = 10 mm) by determining the absorption spectrum at 664nm wavelength. A reference sample (blank) was kept in the dark and the absorption spectrum was also measured at the same time interval. The specific degradation rate R was determined by

$$R = \frac{\Delta A_{\lambda} \times V}{\Delta t \times \varepsilon \times d \times A} \tag{2}$$

where ΔA_λ is the absorption difference, V is the volume of MB solution, Δt is the time difference, ε is the MB molar extinction coefficient at 664nm, d is the cell length used in the spectrophotometer, and A is the contact area from the MB solution and the catalyst.

The degradation rate, R, of the irradiated and dark samples makes it possible to calculate the specific photocatalytic activity, P_{MB} by the following equation:

$$P_{MB} = R_{irr} - R_{dark} \tag{3}$$

Finally, the photonic efficiency, ζ_{MB} can be calculated using

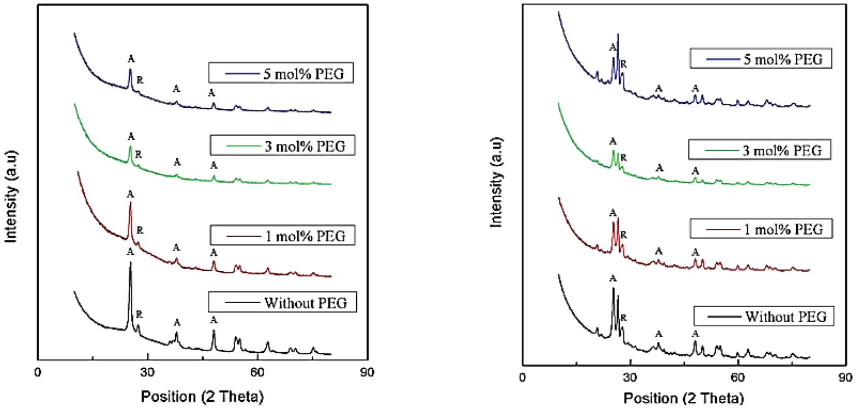
$$\zeta_{MB} = \frac{P_{MB}}{E_p} \times 100 \tag{4}$$

where E_p is the UV intensity.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of TiO_2 Films

Figure 1 shows XRD pattern of TiO_2 film with different PEG content on glass slide and unglazed tiles. XRD patterns show all samples exhibit a mixture of anatase and rutile crystalline phase after 1 hour heat treatment at 500°C. Peaks identified as anatase (1 0 1) are at 25.28°, 37.80° and 48.05° while rutile (1 1 0) are at 27.50°, 36.04° and 54.23°. Note that for films on unglazed tile, crystallized peak observed at 26.64° represents quartz which is attributed to the substrate's element.



(a) (b)

Figure 1: XRD pattern of TiO_2 films with different PEG content on (a) glass slide and (b) unglazed tile

It was observed that as the amount of PEG is increased, the intensity of anatase peak decreased at 25.28° for both substrates. This observation is much more obvious with films on glass slides. Besides that, the reduction of rutile peak intensity at 54.23° was similarly detected. The decreased in crystalline phase intensity was due to the porosity introduced crystal structure caused by the addition of PEG into the film. This is inconsequence to the burn out of PEG during heat treatment at 500°C [12] which resulted in crystal defects and changes in crystal intensity. Other than that, the addition of PEG also inhibits the formation of rutile phase hence decreasing the rutile peak intensity [3].

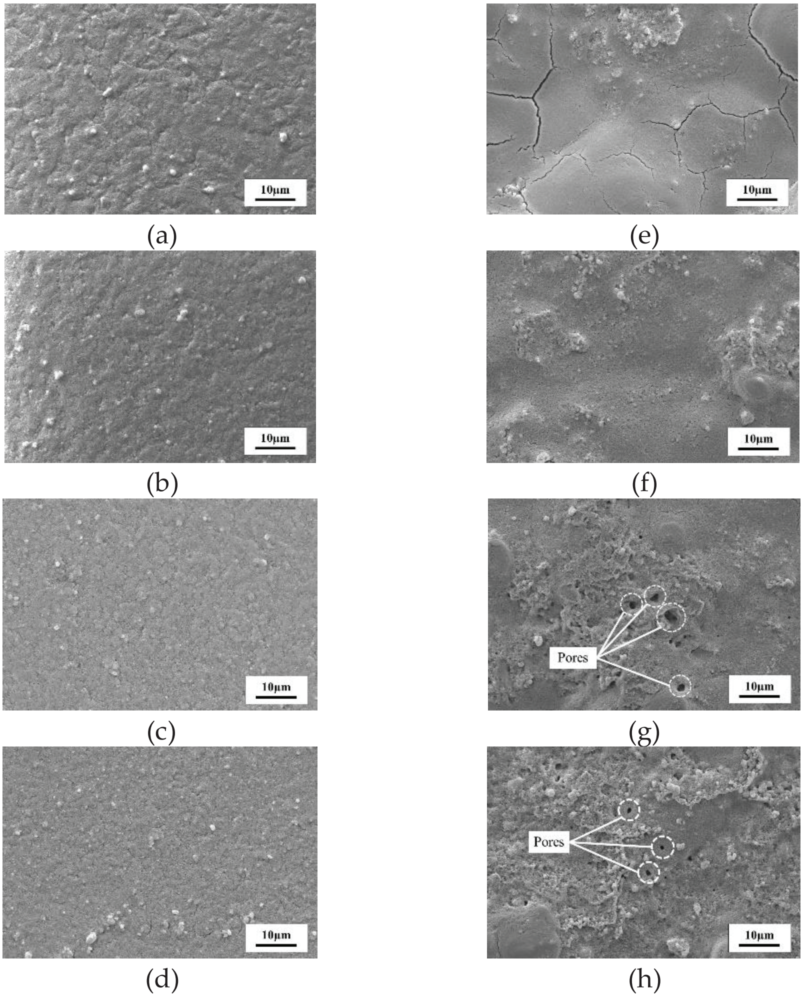
Table 1 shows the crystallite sizes of anatase and on glass slide and unglazed tile. It reveals that, as the amount of PEG is increased, the crystallite size of anatase is decreased. It is detected that 3 mol% and 5 mol% of PEG gives smaller anatase crystallite size which is comparable to the anatase crystallite size without PEG added. The decrease in crystallite size is due to the PEG reaction in the TiO_2 sol which slows down TTIP hydrolysis speed, which reduce the formation of TiO_2 phase hence does not enlarge the crystallite size of TiO_2 phase [3].

Table 1: Anatase crystallite sizes on glass slide and unglazed tile with different amount of PEG

Sample	Glass				Unglazed tile			
	No PEG	1mol% PEG	3mol% PEG	5mol% PEG	No PEG	1mol% PEG	3mol% PEG	5mol% PEG
Anatase crystallite size (nm)	22.45	27.63	21.80	19.00	19.75	23.89	19.74	18.66

Figure 2 shows SEM surface images of TiO_2 films with different amount of PEG2000 on glass slides and unglazed tiles. It was observed that TiO_2 films on glass, Figure 2(a-d), showed a smooth surface in contrast to films on unglazed tile, Figure 2(e-h), due to the nature of the substrates. It is seen that the surface microstructure of TiO_2 films with the addition of PEG on both substrates has less to none cracks when compared to films without PEG addition. For example, obvious cracks were seen on the surface of the film when TiO_2 is deposited on unglazed tile where no PEG is added as shown in Figure 2(e). In contrast, as PEG is added by 1 mol%, cracks were reduced and eliminated as shown in Figure 2(f). However, with further addition of PEG (3 and 5 mol%), pores were seen on the surface of the films. Thus, it can be deduced that adding PEG has successfully eliminate cracks however it has to be compromised with the presence of porosities. Besides from creating porous films, PEG also acts as a binder to immobilize Degussa P25 crystallite and TTiP precursors to the substrate [5, 16].

In conjunction with the presence of pores due to PEG addition, it is much more noticeable with TiO_2 films deposited on unglazed tile. Little to no porosity was observed in 1 mol% PEG TiO_2 film. However, for 3 mol% PEG, pores were formed in a cluster with average size of 4.70μm whereas at 5 mol%, pores became more distributed with average size of 2.07μm. The higher PEG content allows more amount of PEG to be embedded on the surface of the films, hence having higher chance to create more pores after burnout. The formation of pores on TiO_2 films is caused by the decomposition of PEG at 250˚C during heat treatment at 500˚C [16] and air released from the burn out of PEG creates and leaves pores on the surface of the films. In contrary, films deposited on glass have very small pore size which were unable to be identified as reported by Anastasescu et al. [2].



(a) (e)

(b) (f)

(c) (g)

(d) (h)

Figure 2: SEM images of the surface of TiO_2 films with (a, e) without PEG, (b, f) 1 mol% PEG, (c, g) 3 mol% PEG and (d, h) 5 mol% PEG with (a-d) glass slides and (e-f) unglazed tile

Figure 3 shows cross-sectional SEM images of TiO_2 films with different amount of PEG on glass and unglazed tile at 5 dipping times. It is clearly seen that the films' thickness on the tiles are greater than glass slides. The greater thickness on tile is due to the nature of the ceramic substrates utilized. Generally, the rough surface of the tile would ensure better hold onto the TiO_2 colloids during dip-coating until heat treatment. In contrast to the smooth surface of glass when dip-coated, TiO_2 colloids slip from the surface due to gravity [6].

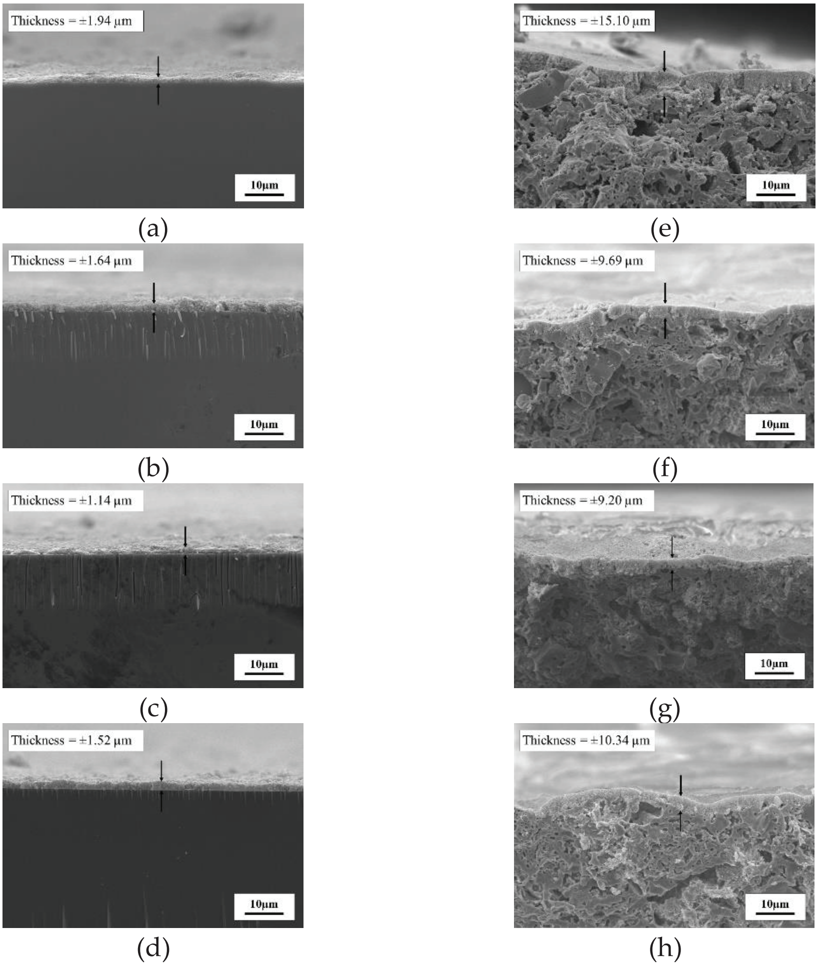
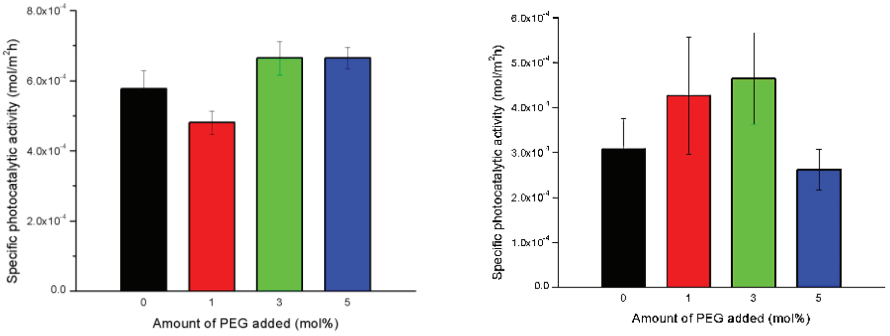


Figure 3: Cross-sectional SEM images of TiO_2 films with (a, e) without PEG, (b, f) 1 mol% PEG, (c, g) 3 mol% PEG and (d, h) 5 mol% PEG with (a-d) glass slide and (e-h) unglazed tile

3.2 Photocatalytic Activity

The specific photocatalytic activity, P_{MB} is shown in Figure 4, and Table 2 represents the photonic efficiency, ζ_{MB}. The P_{MB} and ζ_{MB} are the standard expression of photoactivity according to ISO 10678. It was observed that the addition of PEG had improved the photocatalytic activity of MB degradation by films on both substrates. For instance, the P_{MB} for TiO_2 film with 3 mol% PEG is higher than TiO_2 film without PEG addition on both substrates. When the amount of PEG is at 3 mol%, the degradation of MB is increased. Therefore, it was determined that the highest photocatalytic activity of TiO_2 film is by adding 3 mol% of PEG on both substrates. The improved photocatalytic activity of TiO_2 film added with PEG is due to the pores created by the decomposition of PEG during heat treatment which helps to reduce the diffusion resistance for targeted contaminants entering the interior part of the films [3].



(a) (b)

Figure 4: Specific photocatalytic activity, P_{MB}, of TiO_2 films with different amount of PEG on (a) glass slides and (b) unglazed tile

Table 2: Photonic efficiency of TiO_2 films, ζMB

Sample	Substrates	Film thickness (μm)	P_{MB} (mol/m²h)	$ζ_{MB}$ (%)
TiO_2 film	Glass	1.94	5.77e-4	3.09e-4
1P-TiO_2 film		1.64	4.81e-4	2.58e-4
3P-TiO_2 film		1.14	6.65e-4	3.56e-4
5P-TiO_2 film		1.52	6.64e-4	3.56e-4
TiO_2 film	Unglazed tile	15.10	3.07e-4	1.65e-4
1P-TiO_2 film		9.69	4.27e-4	2.29e-4
3P-TiO_2 film		9.20	4.65e-4	2.49e-4
5P-TiO_2 film		10.34	2.62e-4	1.41e-4

Moreover, the high photocatalytic activity is also influenced by the size of pores present. For example, the highest P_{MB} on unglazed tile was detected at 3 mol% of PEG addition compared to TiO_2 film with 5 mol% PEG added. This is due to the larger pore size observed at 3 mol% which is 4.70 μm (Figure 2(g)), compared to the smaller pore size with 5 mol% which is 2.07 μm (Figure 2(h)). The larger pore size will effectively decrease the diffusion resistance for the targeted MB entering the interior part of the films. In addition, 1 mol% PEG TiO_2 film has higher P_{MB} than 5 mol% due to its higher anatase crystallite intensity as shown in Figure 1, and the exception of pores does not destroy the anatase crystallite formation [15-16]. The higher the intensity of anatase crystallites, the higher the number of active sites for photocatalytic degradation to take place in the film. Furthermore, Mejia et al. [15] mentioned the high amount of PEG will cause overlapping of pores and crystallite fractures that could affect photocatalytic activity.

On the other hand, the P_{MB} is not correlated with the thickness of TiO_2 films. Both films on glass and unglazed tile with 3 mol% PEG, has lower thickness had a higher P_{MB} compare to film with 5 mol% PEG, that has higher film thickness yet the P_{MB} is lower. Here, it can be deduced that the photocatalytic activity is not dependent on the thickness of the TiO_2 films [19]. Therefore, it can be concluded that thickness of the film does not significantly affect the photocatalytic activity of the films. With the aid of pores in the film, only a thin layer could be applied on substrates as long as it covers completely the surface of substrates, hence reducing deposition cycle and time.

4.0 CONCLUSION

The addition of PEG had successfully eliminated cracks and delamination of TiO_2 films deposited on unglazed ceramic tiles. Nevertheless, it has to be compromised with the creation of pores due to the decomposition of PEG during thermal treatment which turned out to be beneficial for photocatalytic activity. XRD of the films showed anatase and rutile crystalline phase. The films with higher PEG content show higher photocatalytic performance than films without PEG content. The highest degradation of MB was TiO_2 films with 3 mol% PEG due to larger pores on the surface of the films deposited on unglazed tile. Likewise, TiO_2 films with 3 mol% PEG deposited on glass also exhibit highest degradation of MB. Further work will be done on the adhesion properties of the films.

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