The Effect of Polyethylene Glycol (PEG) on TiO₂ Thin Films via Sol-Gel Method

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Abstract. This research focus on the effect of polyethylene glycol (PEG) on TiO₂ thin film. Sol-gel method is the best method which tends to be used due to its simplicity, good chemical homogeneity and high purity of the product. Titanium (IV) isopropoxide, isopropanol and acetic acid are the three different chemical which being used to make sol solution. The samples was then will annealed at three different temperature which are 400 °C, 500 °C and 600 °C to observed the phase composition of TiO₂ added PEG thin film and pure TiO₂ by using x-ray diffraction (XRD) analysis and the structural surface by using scanning electron microscope (SEM) analysis. The XRD analysis show the anatase phase present for the sample of pure TiO₂ thin film and rutile phase present for the sample of TiO₂ added PEG thin film. The micrograph of SEM show that with the addition of PEG at high temperature will give the analysis of flaky large cracked which is not separated to each other on the surface coating. Meanwhile, pure TiO₂ give the result of irregular shape structure of the film.

1. Introduction
Titanium dioxide (TiO₂) has a variety of crystal structure which were anatase, brookite and rutile. The least stable of crystal structure is the distortion of brookite [1]. Titanium dioxide (TiO₂) is a nontoxic which has no harmful effects. Besides, TiO₂ gives a unique chemical, physical and electro-optic properties which it is become famous and well researched materials [2]. TiO₂ can be applied in many fields such as environmental including the self-cleaning surface, anti-fogging surface also energy fields. TiO₂ also widely used as photocatalyst. Based on research, TiO₂ has some limitations where high refractive index of TiO₂ will reduce the glass of transmittance. In addition, the self-cleaning efficiency will negatively affected because of the rapid reestablishment of hydrophobicity in the dark environments of TiO₂ films [3].
Photocatalysis is a clean technology, efficient and attractive which has been used for pollutant abatement [4]. There are many method that can be used to prepare the TiO₂ film. In preparing the TiO₂ thin film, sol-gel process was considered to be used because of its own advantage in order to save the cost. It is an attractive technique because of its advantages and the preparation method is easier which just need less completing instrument and less time consuming. Sol-gel method also have been used for preparation of TiO₂ thin film where it can be utilized in many fields applying on superhydrophilic properties, photocatalytic properties and also antibacterial properties [5]. The phase of anatase will be produce at a low temperature because of the high activity in photocatalytic applications. Based on previous researchers, the photocatalytic decomposition of an aqueous acetic acid was affected by the morphology and crystal structure of TiO₂ coatings [6].

This research was focus on the effect of the additive Polyethylene Glycol (PEG) on TiO₂ thin films which play an important role in resulting the desired result. The TiO₂ thin film was fabricated by using spin coating of sol-gel method. Then, the thin film will characterized by using x-ray diffractometer (XRD) to observe the crystalline structure and the phase composition of TiO₂ film and Scanning Electron Microscopy (SEM) was used to determine the surface morphology.

Figure 1. Flowchart preparation for TiO₂ thin film.
2. Methodology
The solutions of TiO₂ was prepared by using titanium (IV) isopropoxide (TTIP) as a source of TiO₂ and then, mixed together into the isopropanol by using a molar ratio mixture of 1:20 (TTIP:isopropanol). The solution was then stirred for 5 minutes. During stirring process, several drops of acetic acid was added into the mixing solutions which give the function of catalyst. The solutions were continuous mixing for about 1 hour by using magnetic stirrer. The clear and homogeneous solutions will be formed after 1 hour. Figure 1 show the flowchart preparation of TiO₂ thin film.

The final solution which was formed will be deposited on the silica wafer with a spin rate of 1000 rpm for about 30 seconds. The sample will dry in the oven for about 10 minutes at the temperature of 60°C. Then, the samples will annealed at three different temperatures which are 400 °C, 500 °C and 600 °C for about 1 hour. Then, the preparation of TiO₂ thin film with the 10 drops of PEG was prepared with the same steps as the previous one. PEG will be dropped into the solution of TiO₂ for about 10 drops after clear solution of TiO₂ was formed. Then, it will continuously stirred for 30 minutes at room temperature.

3. Results and discussion
Figure 2 show the XRD pattern of pure TiO₂ sample. It can be seen the diffraction pattern shows anatase phase and the diffraction peak was assigned at 61.20° and 69.12° which is corresponds to (2 1 3) and (1 1 6) as shown in Figure 2 (a) and (b). Meanwhile, Figure 2 (c) show the diffraction pattern at 25.8°, 61.20° and 69.12°. The diffraction pattern observed is labeled according to standard XRD pattern of JCPDS No. 21-1272. The phase corresponds to (1 0 1), (2 1 3) and (1 1 6) directions. Muthukumarasamy et al. (2010) was studied at high temperature of annealing process, the formation of anatase phase will be present where the film will oxidized and turn into oxide. This will affect the increasing of grain size. The formation of anatase phase and the grain growth were the results diffusion of titania species towards nucleated grain [7].

Figure 2. XRD pattern of pure TiO₂ film which annealed at 400 °C, 500 °C, 600 °C.
Figure 3. XRD pattern of TiO$_2$ added PEG film which annealed at 400 °C, 500 °C, 600 °C.

Figure 3 (a), (b) and (c) show the XRD pattern of 10 drops PEG which undergoes the annealing process at temperature of 400 °C, 500 °C and 600 °C. It is clearly seen that there is a rutile phase with a tetragonal structure existed. Based on Figure 3 (a) and (c), the diffraction peak at 61.799° and 69.927° was assigned to the diffraction pattern of rutile phase which corresponds to (0 0 2) and (1 1 2) direction. From Figure 3 (b) show the diffraction pattern 61.799° and 69.442° which have a plane of (0 0 2) and (3 0 1), respectively. The pattern observed with the agreement of XRD standard pattern of JCPDS No. 88-1172. Liu et al. (2005) was reported that the relatively large agglomerate tends to the formation of rutile phase [8]. Rutile is the most stable phase which has a large chemical stability, cheaper production cost also has high refractive index compared to anatase and brookite phase [9].

Figure 4 shows the SEM micrograph of pure TiO$_2$ thin film and TiO$_2$ added PEG thin film which annealed at 400 °C, 500°C, 600°C, respectively. The SEM micrograph in Figure 4a-400 revealed that there is a very tiny of irregular shape of structure on the crack surface. This might happen due to the low annealing temperature. This result is well agree with Mayabadi et al. (2014) [10]. Figure 4b-400 show there are many crack present with a large size of crack. Shuhui et al. (2014) was reported, the mismatch of thermal expansion coefficient between substrate and films, the evaporation of a solvent and also the precursors decomposition leads to formation of cracks [11].

Figure 4a-500 show the microstructure of pure TiO$_2$ is in irregular shape of crystal which was the solution is not added with any additive. Meanwhile, in Figure 4b-500 show the microstructure is crack free and exhibit a huge agglomeration. Regarding to Thomas et al. (2002), agglomeration occur when the combination of three set rate processes which involved the consolidation and growth, wetting and nucleation and attrition and breakage. The large agglomerate size is affected by the higher of PEG concentration was used [12]. From the Figure 4a-600 the microstructure of irregular shape start to merge with one another due to the increasing in annealing temperature, this can be proved by Bakri et al. (2017) [13]. Besides, the microstructure of the large flaky cracks which is not separated to each other can be seen...
in Figure 6b-600. The cracked film present may be due to the temperature increase from 400 °C to 600 °C. It is also can reduce the coating of lucidity and transparency and happen because of the surface tension between film and air during drying process [14-15]. Zhang et al. (2004) was studied that the addition of PEG will improve the surface roughness also the cracking-free films [16]. Hence, from the results of the crack obtained might be due to the insufficient of molar ratio of PEG to prevent the film from crack.

![Figure 4](image)

**Figure 4.** SEM image of: (a) pure TiO$_2$ thin film (b) TiO$_2$ added PEG thin film, which was annealed at 400 °C, 500 °C, 600 °C, respectively.

4. **Conclusions**

This research was focus on the effect of polyethylene glycol (PEG) on TiO$_2$ thin films via sol-gel method. There are three different annealing temperature were carried out for every samples which are 400 °C, 500 °C and 600 °C. The samples were then characterized by using X-Ray Diffraction (XRD) analysis and Scanning Electron Microscope (SEM) analysis. The different concentration of PEG and three different annealing temperature has been affected the XRD analysis and also the surface morphology of the thin film. Based on the XRD analysis, basically all of the samples with the PEG show there is a TiO$_2$-rutile phase existed. Meanwhile, the TiO$_2$-anatase phase exist for the samples of pure TiO$_2$. From the SEM micrograph, when the annealing temperature was increased from 400 °C to 600 °C, the films were non-uniform with an irregular shape and also have an agglomeration. At 600 °C, it can be clearly seen, there was no agglomeration but having a large flaky crack. At higher temperature, a small island will coalesce and channel each island.
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