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Analysis of Distribution of Polyvinyl Alcohol Hydrogel Nanocrystalline by using SAXS Synchrotron

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Abstract: Polyvinyl alcohol (PVA) hydrogel has been successfully synthesized through freezing-thawing (F-T) process by using time-variation. This work is aimed to investigate the distribution of nanocrystalline from the hydrogel. Fourier Transform Infrared (FTIR) Spectroscopy, Differential Thermal Analysis/Thermogravimetric (DTA/TG), and Synchrotron Small-Angle X-ray Scattering (SAXS) were used as the instruments in characterizing the PVA hydrogel, respectively to observe the frequency of absorption, thermal degradation, and structural dimensions. The functional groups which represent the PVA polymer chains were verified on the wavenumber of 1450-1480 cm^{-1} and 850-870 cm^{-1} which is in accordance with the stretching of $–CH_2$ vibration mode. The absorption band of PVA polymer chains was also found on the wavenumber of 1090-1150 cm^{-1} which is in accordance with the stretching of carboxyl vibration mode (CO), and this wavenumber gave a contribution towards the crystallinity of PVA polymer. Furthermore, the PVA polymer only interacted with the distilled water in the sample of PVA hydrogel without experiencing any chemical interactions between the PVA polymer and other substances. Meanwhile, the graphic of PVA hydrogel thermal degradation shows three thermal decompositions which are indicated by three areas in which there was sample weight loss. The second decomposition with sample weight loss was equivalent to 61.62%-73.04% occurred at the temperature of 282-376 ^oC which became the highest sample weight loss due to polymer chain degradation. Teubner-Strey and Beaucage models were used to analyze the characterization of structural dimension and distribution of PVA Hydrogel nanocrystalline with SAXS Synchrotron. With a high compatibility between the model data and the experiment, the average structural dimension of PVA hydrogel

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nanocrystalline is the equivalent of 3.96 nm, with an inter-crystalline average distance of 16.9 nm. These results indicate that PVA hydrogel is very potential to be applied as a primary material for human implants.

Keywords: distribution, nanocrystalline, structural dimension, PVA hydrogel, SAXS

1. Introduction

Polyvinyl Alcohol (PVA) Hydrogel is a flexible material consists of polymer chain network structure. The network structure can be made of a physical cross-binding agent which hereinafter shall be referred to physical gel and a chemical binding agent which hereinafter shall be referred to as chemical gel. The physical gel is formed by an interaction between ion, water and hydrophobic, hydrogen bond, and Van der Walls force, while the chemical gel is formed by covalent bond [1]. On the other hand, PVA hydrogel can be formed by using various methods, such as γ-irradiation, cross-binding process, and freezing-thawing cycle.

The freezing-thawing method is one of the most used methods by researchers in fabricating PVA hydrogel. This method was chosen since it has a simpler process and it is easy to be conducted. The potential of PVA hydrogel to be utilized and developed in medical, industrial and nanotechnology fields has been reported for many times. In medical field, PVA hydrogel can be utilized and developed, among others, for implants of human body network system [2], artificial cartilage [3-5], contact lenses [6-8], heart valves [9-10], and cornea implants for rabbits [11]. However, PVA hydrogel has some disadvantages for its application in the medical fields, such as weak hydrogel network, weak hydrogel endurance in high temperature, high level of hydrogel porosity and the incompatibility of hydrogel network with human body network.

PVA hydrogel quality improvement is necessary to overcome such problems. One effort which can be done is fixing the fabrication process and PVA hydrogel network structure. The PVA hydrogel network structure can be observed by identifying the structural and dynamic nature of PVA polymer and PVA hydrogel by using a sophisticated tool such as Small-Angle X-ray Scattering (SAXS). Studies on PVA hydrogel network structure have been reported by the authors and several previous researchers. The authors have successfully characterized the PVA hydrogel structure for various numbers of freezing-thawing cycles. The results show that the dimension of nanocrystalline average diameter is 4 nm with an average inter-crystalline distance of 18 nm [12]. These results are similar to the results reported by previous researchers, such as the fact the isotropic PVA hydrogel structure consists of 3 nm structural dimensions and is distributed with approximately 19 nm distance [13]. Furthermore, PVA hydrogel consists of polymer crystal with the radius of approximately 2.8-3.3 nm and with the average inter-crystal distance of 15-17.5 nm [14]. However, the period of freezing-thawing cycles for fabricating the PVA hydrogel and the observation results on PVA hydrogel structure have not frequently been reported.

Therefore, this research focused on the fabrication and characterization of PVA hydrogel structure with various periods of freezing-thawing cycles. The structural dimension and nanocrystalline distribution inside the PVA hydrogel were characterized by using SAXS instrument and global fitting analysis technique. The fabrication method and data analysis technique used in this research is one alternative to improve the quality and characteristic technique of PVA hydrogel structure. The frequency of absorption and thermal degradation of PVA hydrogel were also reported.

2. Experimental Method

2. 1. Material

PVA and distilled water were used as the materials. PVA polymer used has a hydrolysis degree of ≥ 98%, and the weight of molecules is of approximately 60,000 g/molecule, purchased from Merck Schuchardt OHG, Germany. The distilled water is utilized as a cross-binding agent on the synthetic process of the hydrogel.

2. 2. PVA Hydrogel Fabrication

PVA hydrogel fabrication was initiated by dissolving the PVA polymer and distilled water with a certain composition of weight. The mixture was stirred by using a magnetic stirrer and heated on a hot plate magnetic stirrer with the temperature of 70-90 ^{o}C in order to enhance the level of solubility of the PVA polymer in the water; this step is similar to the previous research [15]. The mixture transformation from a liquid into paste indicated that the PVA polymer solution had been perfectly mixed with water. Furthermore, the mixture was poured into the mold, and the process of freezing-thawing was done by using 3 cycle process. The freezing process was performed with the temperature of – 10 ^{o}C, while the thawing process was performed with the temperature of 27 ^{o}C. The variation of time periods on the freezing process of 1, 2, 3, 4, 5, and 6 hours are the main objects of research to determine the distribution of PVA hydrogel nanocrystalline.

2. 3. Characterization

2.3. 1. Spectroscopy of Fourier Transform Infrared (FTIR). The FTIR spectroscopy was utilized to determine the chemical bond, chemical function, and organic compound structure consisted in PVA hydrogel. The FTIR spectrum had been recorded in the frequency range of 500-4000 cm^{-1} by using Shimadzu spectrometer.

2.3. 2. Thermogravimetric Analysis (TGA). TGA was used to characterize the thermal degradation of PVA hydrogel sample. TA TGA Q500 Analyzer was used to measure the thermal degradation. The sample measuring operation was performed by dynamic mode in the nitrogen with the heating rate of 10 ^{o}C/minute on the temperature of 25 until 600 ^{o}C. Similar with the XRD characterization, the sample of PVA hydrogel was drained under vacuum on the temperature of 37 ^{o}C in 48 hours and then characterized by using TGA.

2.3. 3. Small Angle X-ray Scattering (SAXS). SAXS Instrument was used to analyze the distribution of PVA hydrogel nanocrystalline. This instrument is a sophisticated tool which is capable of providing information on the size, morphology, inhomogeneity and interaction among the Nanocrystalline accurately. This is made possible since the SAXS instrument is a tool which will not damage the sample and this instrument has a characteristic of being capable to properly transmit the nanocrystalline light from the sample.

The SAXS measurement was performed in Siam Photon Laboratory of Synchrotron Light Research Institute (SLRI), Thailand. This measurement was made in order to observe the structural dimension and distribution of PVA hydrogel nanocrystalline. The distribution of PVA hydrogel Nanocrystalline was observed by using CCD detector with the sample-to-detector-distance (SDD) of 1.8 m and 4.5 m with the range of q momentum scattering of approximately 0.12 until 2 nm^{-1}. The SAXS initial data processing was initiated by the processes of normalization, calibration, and verification of the sample scattering intensity towards the background of the instrument by using SAXSIT Software [16]. The two SAXS data configurations which are resulted from two different SDD distances were combined and analyzed by using SASfit data analysis program [17].

3. Results and Discussion

As shown in Figure 1, FITR spectroscopy showed the configuration of absorption intensity of PVA hydrogel sample as the function of frequency. The PVA hydrogel absorption band was observed on five main peak areas which represent the mixture of PVA Polymer absorption band with the distilled water. The functional groups which represent the PVA polymer chains were verified on the frequency of υ = 1450-1480 cm^{-1} and υ = 850-870 cm^{-1} which are associated with the stretching of –CH_2 vibration mode and the absorption wavenumber of 2850-3000 cm^{-1} which is associated with the carboxyl of vibration mode stretching (C-O) and this wavenumber gives a significant contribution on the PVA crystallization [18-19].

Such five peaks of the absorption band which were observed from the PVA hydrogel were the real supports of the PVA polymer and distilled water. As we know, the chemical structure of PVA polymer was delivered by (CH_2-CH-OR) equation, where R = H and R = $COCH_3$ respectively for fully hydrolyzed PVA polymer and partly hydrolyzed PVA polymer. Therefore, the vibration mode stretching of –CH_2, C-O, and CH is in accordance with the characteristics of partly-hydrolyzed PVA polymer. It is confirmed by the material used in this research, namely PVA polymer with 98% hydrolysis. Furthermore, the intensity absorption support on the peak of υ = 3200-3570 cm^{-1} frequency is associated with the –OH vibration mode or hydrogen mode stretching. This result is equivalent with the cross-binding agent of the distilled water which is used in the production of PVA hydrogel. Of the most important matters to be paid attention to is that –OH stretching band is a connecting factor between the hydrogen intra-molecule and inter-molecule and the PVA polymer chain which is obtained from a high hydrophilic process [20]. But in the other side, PVA polymer only interacted with the distilled water in the PVA hydrogel sample without being continued by chemical interaction between PVA polymer and other substances.

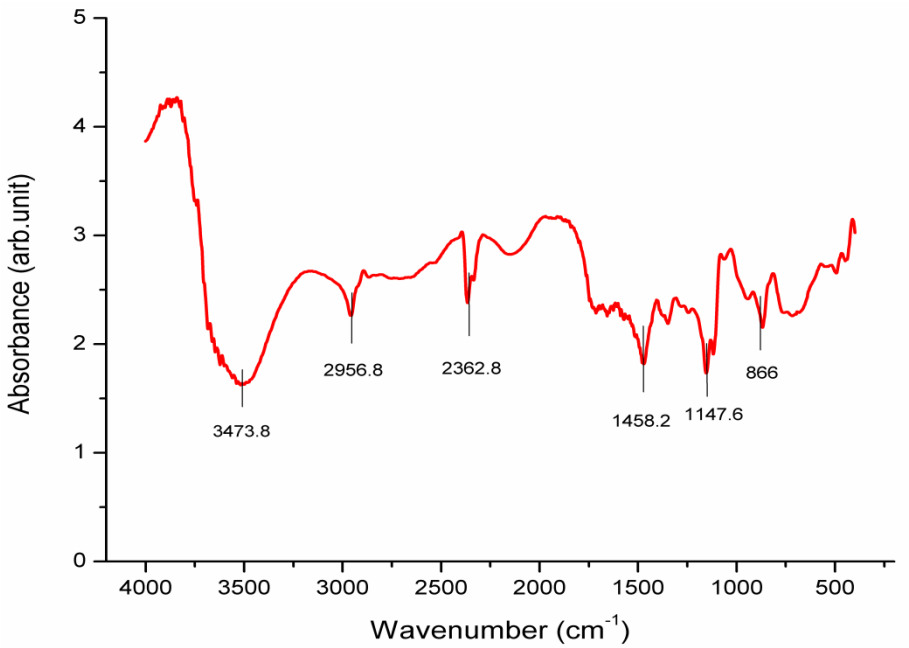

Figure 1. FITR Spectrum of PVA hydrogel for 3-hour freezing cycle

Thermal degradation on PVA hydrogel with various periods of the freezing-thawing cycle is shown in Figure 2. The graphic of PVA hydrogel thermal degradation shows three thermal decompositions which are indicated by three areas of sample weight-loss for all variation of cycle periods. The first decomposition with sample weight loss of 1.14-3.87% occurred in the temperature range of 181-192 ^oC. It can be clarified that the thermal decomposition on the first area was caused by crystal decomposition of water, condensation reaction, and evaporation of solvent trapped in the PVA hydrogel. This reaction is the process of water molecule release from the PVA hydrogel sample, where the group of hydroxyl (OH) moved from one sub-unit of PVA polymer chain and the hydrogen (H) atom was released from the other polymer chains.

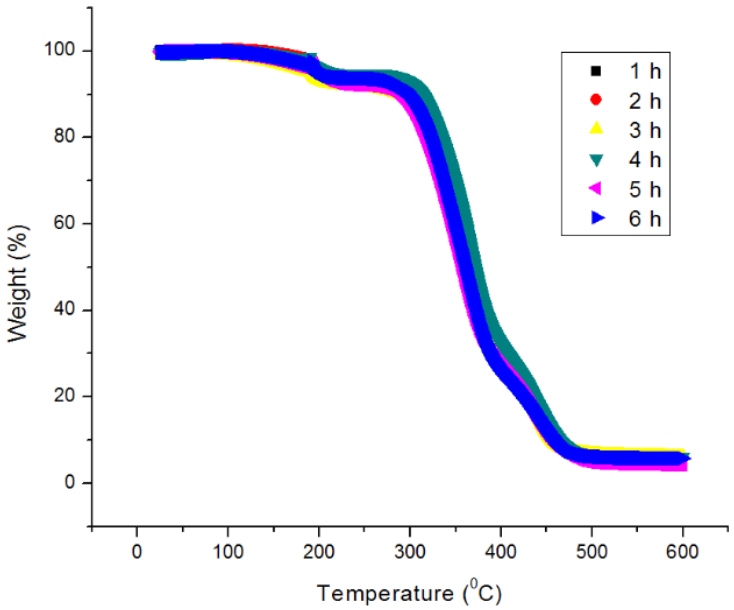

Figure 2. Profile of TGA thermogram of PVA hydrogel with the variation of freezing-thawing periods

For the second decomposition, sample weight loss of approximately 61.62-73.04% occurred in the temperature range of 282-376 °C. On this stage, the decomposition was resulted by the degradation of polyene structure from the polymer chain [21-22], while the third decomposition with sample weight loss of approximately 16.64-23.32% occurred in the temperature range of 390-460 °C. The third decomposition is the continuance of the polyene structure residue by producing carbon and hydrocarbon [22-24]. Besides research on sample decomposition, research on the temperature of maximum sample weight-loss level (T_p) was also reported. Based on the DTA/TG characterization results, the T_p value of the various cycle periods did not experience significant changes. The average T_p value of all samples is around 345.97 °C. However, such T_p value is higher than the T_p value of PVA polymer on about 230 °C [25]. It showed that the temperature of PVA hydrogel thermal degradation increased more significantly than PVA polymer. Such result indicated that the PVA hydrogel thermal stability was properly composed by the formation of hydrogen bond among the polymer [26]. The thermal stability of PVA hydrogel shows the orientation of stability of polymer chain and saturation of cross-binding agent diffusivity of the distilled water in the PVA hydrogel with a similar number of cycle. The thermal stability of the PVA hydrogel will be more stable along with the decreasing diffusivity of the distilled water cross-binding agent in PVA hydrogel by increasing the number of the freezing-thawing cycle [24-27]. Therefore, the period of the freezing-thawing cycle does not significantly affect the mobility of polymer chain and the diffusivity of the cross-binding agent.

The data of PVA hydrogel with various freezing-thawing cycle periods which are characterized by using SAXS instrument are shown in Figure 3 and Table 2. The combination of two model of data analysis, namely Teubner-Strey and Beaucage, was used in the scattering data analysis in order to observe the structure and distribution of PVA hydrogel nanocrystalline. The Teubner-Strey model provides a description on the inter-crystalline distance (d) and the length of correlation (ξ) of the PVA hydrogel sample. The scattering intensity equation is formulated as follow [28].

$$I(q) = \frac{8\pi\langle\eta^2\rangle\xi}{a^2 - 2bq^2 + q^4} \quad (1)$$

Where η^2 is contrasted scattering square with a long density contrast, a is positive quantity

$$a = k^2 + \frac{1}{\xi^2} \tag{2}$$

and b can be positive or negative, depends on the amount of wave vector $k = 2\pi / d$ and ξ.

$$b = k^2 - \frac{1}{\xi^2} \tag{3}$$

Meanwhile, the Beaucage model [29] is capable of determining the sample dimension structure with the following equation.

$$I(q) = G\exp(-q^2 R_g{}^2 / 3) + B\left[erf\,(qR_g / \sqrt{6})\right]^{3P} / q^P \tag{4}$$

Where R_g is the radius of gyration of the structure, P is the fractal dimension characteristic, G is big structured factor Guinier, B is the pre-factor of the scattering specification and the equation of $\left[erf\left(qR_g / \sqrt{6}\right)\right]^{3P}$ is the transitional factor between high q-range and low q-range.

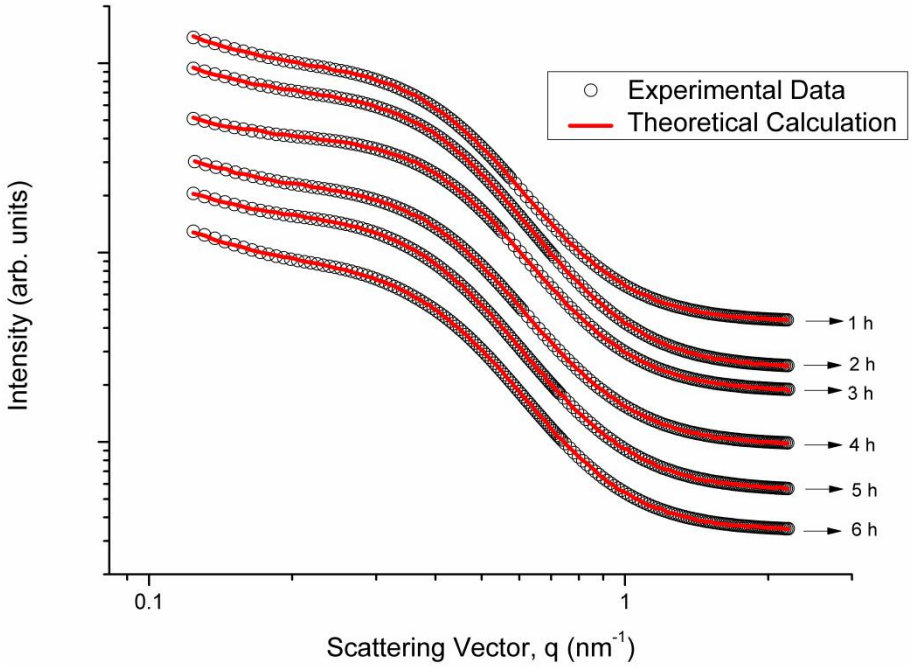

Figure 3. Data of PVA hydrogel with the variation of freezing-thawing cycle periods which is characterized by using the SAXS instrument

The data of PVA hydrogel has been successfully analyzed by using the Teubner-Strey and Beaucage models. The size of nanocrystalline structural dimension and distance has been properly confirmed by the data of *fitting* (Figure 3) between the data of experimental results (black circle line) from Teubner-Strey and Neaucage models which were improved by using the SASfit software. The results of SAXS data analysis show that the size of PVA hydrogel crystal experienced degradation along with the increasing period of F-T cycle from 1 hour (4.0 nm) up to 3 hours (3.8 nm) and which increased one more time on 6-hour cycle (4.1 nm) as shown in Table 2. Even though the crystal size on 1 hour cycle period was closed with the size crystal size on 6-hour cycle, the inter-crystal distance on 1-hour cycle (17.0 nm) is longer than the 6-hour cycle (16.0 nm). It can be confirmed that the sample homogeneity on 6-hour cycle has improved along with the degrading inter-crystal distance.

Therefore, the condition of PVA hydrogel structure with 6-hour cycle treatment was relatively more stable than the treatments with other cycle periods.

Such results show that the PVA hydrogel with 6 hour cycle period has an optimum crystal density which is produced from the decreasing amorphous phase in the *polymer-rich* domain. On the other hand, the PVA hydrogel with 3 hour cycle period has an optimum cross-binding power which can be seen on the smallest crystal. Such results are in accordance with the results reported by Millon *et al*. [13]. They revealed that the anisotropic mechanical nature of PVA-D_2O hydrogel was affected by big-scaled pore structure of the gel and not by the PVA crystal structure which acted as a physical cross-binding agent.

Furthermore, Table 1 shows that the average structural dimension of PVA hydrogel is about 3.96 nm and the average inter-PVA hydrogel nanocrystalline distance is 16.9 nm. These results are similar to the report of the previous researchers that, among others, the isotropic PVA hydrogel structure consisted of the structural dimension of about 3 nm and was distributed with the average distance of approximately 2.8-3.3 nm and the average inter-crystal distance was approximately 15-17.5 nm [14].

Table 1. Parameter of structural dimension (ξ) and inter-crystalline distance (d) of PVA hydrogel

The variation of time periods on the freezing process (hours)	ξ (nm)	d (nm)
1	4.00	17.0
2	3.89	17.1
3	3.84	17.5
4	3.93	17.1
5	4.07	17.0
6	4.12	16.0

Based on the above results of the discussion, it can be confirmed that PVA hydrogel has a fairly good thermal stability which is identified with its average maximum sample weight-loss (T_p) of 345.97 ^oC which is higher than the T_p value of PVA polymer of approximately 230 ^oC [25]. Such results were supported with the SAXS characterization which shows that the PVA hydrogel had an optimum crystal density along with the decreasing amorphous phase inside the polymer-rich domain. Therefore, the PVA hydrogel consists of a structure which consists of weak polymer chain which referred to as amorphous phase and combined with the nanocrystalline referred to as polymer-rich phase which forms the PVA hydrogel structure. With its unique natures, PVA hydrogel is very potential to be applied as a primary material of human implant [11].

4. Conclusion

The weight of PVA hydrogel sample experienced the most significant drop in the temperature range of 282-376 ^oC as a result of the PVA polymer chain degradation. The average T_p value of PVA hydrogel is much higher than the T_p value of PVA polymer. It showed that the temperature of PVA hydrogel thermal degradation increased more significantly than the PVA polymer. Such results were supported by the SAXS characterization which showed that the PVA hydrogel had the optimum crystal density along with the decreasing amorphous phase in the polymer-rich domain. Measured by using the Teubner-Strey and Beaucage models, the average structural dimension of PVA hydrogel nanocrystalline is in the range of about 3.96 nm with the inter-nanocrystalline distance of 16.9 nm.

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