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RELATIONSHIP BETWEEN THE STRUCTURE OF POLYMER NETWORK USING GLUTARALDEHYDE CROSSLINKING AGENT AND PHYSICO-MECHANICAL PROPERTIES OF BIOPOLYMER MEMBRANE BASED ON POLYVINYL ALCOHOL (PVA) MODIFIED WITH CASSAVA STARCH

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Abstract

The relationship between network structure and the properties of starch modified PVA membrane, such as the relationship between the crosslinking density (n), the average molecular weight of crosslinks (Mc), the mesh size (ξ) to the crystallinity were investigated. The increasing of glutaraldehyde crosslinking agent decreases the molecular weight between crosslinks (M_c) rapidly from 8985 g/mol to 1950 g/mol and the mesh size from 613 Å to 227Å. Salicylic diffusion coefficient of the membrane was determined to be $4.15\times10^{-6}cm^2/s$. This was proven that PVA/TBS membrane was able to have permeable molecules that contained bulky functional groups.

Keywords. Polyvinyl alcohol, cassava starch, biopolymer membrane, crosslinking density, mesh size, salicylic diffusion coefficient.

1. INTRODUCTION

Wounds are usually treated with two common ways using the old dressings (dry conditions) or network structural membranes known as hydrogel membrane to keep the moisture (wet conditions). In the traditional method, to avoid infection, the injuries have to be cleaned with saline and change the dressing every day. This process causes new exfoliation, delays the healing and gives a pain to the patient. Therefore, new material has been developed to solve such problems and simplify treatment. Depending on structure network, polymer can keep a large amount of water due to hydrophilic groups such as hydroxyl (OH) and carboxyl (COOH) [1, 2]. Thin membrane of PVA modified with starch using glutaraldehyde (GA) crosslinking agent has good mechanical properties and compatibility with skin, ... Starch modified PVA membrane had a good moisturizing effect, translation permeability, decrease pain during treatment for patients, helps faster skin regeneration [3-5]. This work studies the relationship between parameters of network structure using glutaraldehyde (GA) crosslinking agents such as: crosslinking density (n), the average molecular weight between crosslinks (Mc), the mesh size (ξ) and the physical properties of biopolymer membranes PVA modified with cassava starch.

2. EXPERIMENTAL

2.1. Raw materials and chemicals

- Polyvinyl alcohol (PVA): PVA fibrous (Japan) with melting temperature of 180-230 ^oC, the average molecular weight of 120.000 g/mol and hydrolysis of 98 %.
- Cassava starch (TBS): (Vietnam), starch content of 79.6 %.
- Glycerol (Gl): density of 1.261, boiling temperature of 290 ^oC (The Netherlands).
- Glutaraldehyde (GA), (50 % solution), Merck (Germany).
- The another necessary chemicals for analysis.

2.2. Systhesis of PVA/TBS membrane using glutaraldehyte (GA) crosslinking agents

2.2.1. Preparing modified starch by chemical methods

Adding 100 ml HCl 0.5 M into 500 g cassava starch solution (the ratio of starch/distilled water is 1/3 by volume) and tirring for 6 hours. Then the mixture was clarified, neutralized to pH 7 by NaOH 0.1 N, filtered and vacuum dried at 45-50 ^oC to constant weight.

+ Glutaraldehyde solution (GA) was prepared by dissolving 1 ml of GA 50 % in 10 ml of ethanol.

2.2.2. Crosslinking PVA and cassava starch

16 grams mixture of PVA, 4 grams of modified starch (TB), 6 grams of glycerol (Gl) and 100 ml of distilled water were given in 3 neck flask with reflux condenser were stirred about 1 hour to form homogeneous solution. Then 1.2 ml glutaraldehyde (GA) were dropped into the reactor. The reaction was kept stirring at 80 °C for 3 hours at 400 rpm to get starch modified PVA.

2.2.3. Casting film and finishing

The membrane was prepared from reacted solution on glass plate with dimension of 120×180×1 mm by casting method. Bubble in the membrane was removed by rolling. Membrane samples were dried at 50 °C in a vacuum of 120 mmHg for 8 hours to constant mass, then samples were prepared for determining the physico-mechanical properties.

2.3. Research methodology

2.3.1. Network density, molecular weight between two nodes, mesh size were determined by saturation swelling method [6]

The sample size 20×20×1 mm membrane was soaked in water, after a certain period of time, wiped sample with clean cotton cloth, dried at temperature of 50 °C to constant mass. Stage of network density (n) is defined by the formula Flory Rehner:

$$-[\ln(1 - \upsilon_2) + \upsilon_2 + \chi_1 . \upsilon_2^2] = \upsilon_1 . n . (\upsilon_2^{1/3} - \upsilon_2/2)$$

In which χ_1 is the coefficient of the interaction of solvent with the polymer, (χ_1 = 0.49 for water solvent); υ_1 is the partial molar volume of the polymer, the solvent water (18.1 cm^3/mol); υ_2 = Vo/V_{bh} (with Vo is the initial volume of the polymeric form, V_{bh} is the volume of polymeric samples soaked in pure water, n is the density of the network (mol/cm^3). average molecular weight between crosslinks (Mc) is determined by the formula:

$$M_c = \rho / (2.n)$$

where: ρ is the density of the network polymer (g/cm^3).

2.3.2. Define the mesh size (ξ)

The mesh size was calculated from Mc via following formula:

$$\xi = \nu_{2m}^{-1/3}\left[C_n\left(\frac{2\bar{M}_c}{M_r}\right)\right]^{1/2} l$$

where: Cn: Flory characteristic ratio = 8.3 for denatured PVA; M_r: average molecular weight of one repeat unit of [-CH_2-CHOH-] = 44; one repeating unit of starch = 144; l = length links C-C = 1.54 Å.

2.3.3. Determine the density of the polymer network

The density of the network polymer is defined by ISO 1183-1: 2004, calculated by the formula:

$$\rho_g = (W_a . \rho_h)/(W_a - W_h)$$

Where: W_a: volume of the sample in air, [g]; W_h: volume of the sample in liquid (*n*-heptane); ρ_h: density of the fluid (ρ_h of *n*-heptane = 0.684); ρ_g: density of the polymer network

2.3.4. Determination of crystallinity of the polymer network

Crystallinity of the network polymer (semi-crystalline form) was determined by the formula [2]:

$$\frac{1}{\rho_g} = \frac{X}{\rho_c} + \frac{(1-X)}{\rho_a}$$

Where: ρ_g = density of the polymer network; ρ_c = 1.345 g/cm^3 corresponding to 100 % crystalline; ρ_a = 1.269 g/cm^3 corresponding to 100 % amorphous. It follows that formula crystallinity of PVA membranes modified starch (polymer network) was:

$$X = [\rho_c \times (\rho_g - \rho_a)/[\rho_g \times (\rho_c - \rho_a)] = 17{,}697 \times [1 - (1{,}269/\rho_g)]$$

2.3.5. The swelling of the PVA membrane modified starch was determined according to TCVN2752-78

+ Identify the diffusion coefficient of salicylic acid

Diagram cell was used to measure diffusion coefficients as follows [3]:

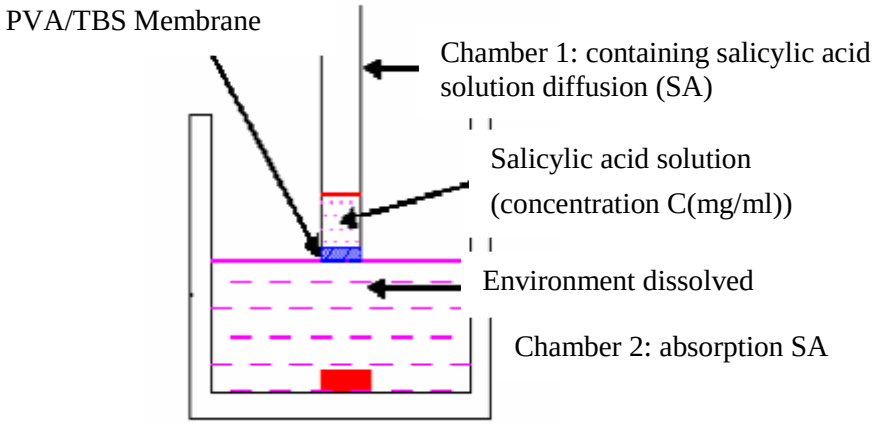

Figure 1: Diagram cell used to measure diffusion coefficient of salicylic acid

The cell consisted of two chambers separated by the PVA/TBS membrane (~ 0.2 mm thick). In the first chamber contained 10 ml SA solution (8 mg/ml). The chamber 2 contained 100 ml of distilled water. The system was placed in a water bath with constant temperature (30 °C). A pipette was used to withdraw 0.5 ml sample solution from the first chamber and 1 ml samples from the second chamber. The recovered sample was replaced with distilled water. Then, samples were analyzed by absorption spectrophotometer UV-Visible Spectrometer Cintra 40 GBC (Canada) at a wavelength of 294 nm to determine the concentration of SA in the first chamber and second chamber.

The diffusion coefficient (D) was calculated according to the following equilibrium equation*:*

$$D = \frac{1}{\beta t} \times \ln \frac{C_D(t) - C_R(t)}{C_D(0) - C_R(0)}$$

with:

$$\beta = \frac{A_H}{W_H} \times \left[\frac{1}{V_1} + \frac{1}{V_2}\right]$$

where: $C_D(0)$: initial concentration of the solution in the first compartment; $C_R(0)$: initial concentration of the solution in the second chamber; $C_D(t)$: Concentration of the solution in the first Compartment after time period t; $C_R(t)$: concentration of the solution in the second chamber after time period t; A_H: cross-sectional area of the effective diffusion membrane PVA/TBS; W_H: The width of the membrane

3. RESULTS AND DISCUSSION

3.1. The effect of GA concentration on molecular weight between the network nodes and mesh size PVA/TBS membrane

Stage of network density (n), the average molecular weight between network nodes (Mc) and mesh size (ξ) were determined by the swells saturated immersion method (at room temperature).The effect of GA concentration on average molecular weight between network nodes (Mc) and mesh size (ξ) was shown more clearly in figure 2.

The results in Fig. 2 showed that the GA content increased from 0.1 % to 0.3 %, the molecular weight between network nodes (M_c) decreased rapidly from 8985 g/mol to 1950 g/mol, the mesh size(ξ) decreased rapidly from 613 to 227 Å. When GA content was over 0.3 %, molecular weight between two nodes of PVA/TBS membrane and the mesh size(ξ) slightly effected.

From these results we can build relationships between structure and properties of PVA/TBS membrane created by glutaraldehyde crosslinking agent as follows: With increasing content of glutaraldehyde (GA) crosslinking agent, the network density increased. Stage of network density higher average molecular weight between two nodes (M_C) was declined, the average size between the mesh (ξ) also decreased.

3.2. The relationship between the average molecular weight between network nodes with crystallinity and density of the PVA/TBS membrane

A series of samples of the starch modified PVA membrane was synthesized according to the procedures in section 2.2 to generate different average molecular weight between crosslinks samples. The relationship between the average molecular weight between crosslinks (M_c) and the crystallinity and density of the polymer network formed are shown in table 1.

The results in table 1 show that the average molecular weight between different network reduced from 8985 g/mol to 1070 g/mol, the crystallinity of PVA/TBS membrane increased from 22 to 78.6 %; density of PVA/TBS membrane increased from 1.285 g/cm^3 to 1.328 g/cm^3. The reason was that when the average molecular weight between network nodes (M_c) reduced, the crosslinking between the polymer molecules thicker, the mesh generation molecule polymer crystals increased, leading to increased crystallinity.

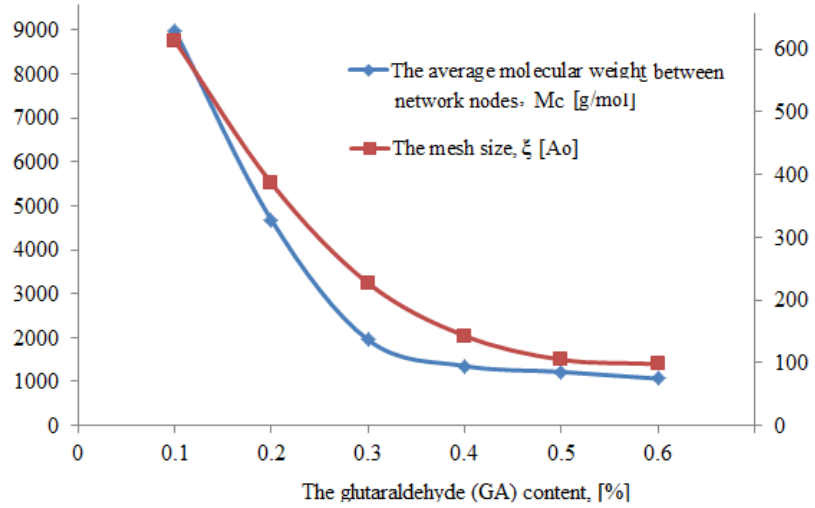

Figure 2: The effect of GA concentration on average molecular weight between network nodes (M_c) and the mesh size (ξ)

Table 1: Effect of the average molecular weight between network nodes (M_c) to crystallinity and density of the polymer network

No	The average molecular weight between network nodes (M_c), g/mol	Density of PVA/TBS polymer network, g/cm^3	Crystallinity of PVA/TBS polymer network, %
D1	8985	1.285	22.0
D2	4680	1.300	42.2
D3	**1950**	1.320	68.4
D4	1355	1.325	74.8
D5	1220	1.326	76.1
D6	1070	1.328	78.6

3.3. The relationship between crosslinking density and the swelling of the PVA/TBS membrane

Because PVA/TBS network structure should be able to swell in the solvent, the nature of the swelling is a adsorption characteristic of the PVA/TBS membrane making PVA/TBS membrane ability to hold moisture, prevent dehydration and electrolyte surface of the skin wound, enabling the recovery process, reducing irritation to the patient and wound healing. Therefore, the crosslinking density affected to the swelling of the PVA modified starch membrane. The PVA/TBS membrane samples were synthesized according to 2.2 to the same ratio PVA/TB/Gl = 80/20/30, catalyst concentration HCl 0.1 N was 0.05 %; concentration GA was changed from 0.1 to 0.6 % respectively according to total volume of PVA/TBS; The reaction was stirring at speed of 400 rpm for 3 hours at 80 ^oC. The dependence of the swelling of PVA/TBS membrane on the crosslinking density (n) was presented in figure 3.

The results in figure 3 showed that when the crosslinking density was increased from 0.707×10^4 mol/cm^3 to 5.935×10^4 mol/cm^3; the swelling of the membrane decreased from 295.5 % to 145.8 %. This is due to the increasing crosslinking density, distance between network nodes (M_c) decreases, leading to the decline of swelling of PVA/TBS membrane.

3.3. Diffusion coefficient of salisilic acid (SA) of PVA/TBS membrane

Salicylic acid diffusion coefficient was determined by calculating the concentration of

salicylic acid found in two compartments as described in the experimental section. Results in determination of salycilic acid content in the first chamber and second chamber, setting graph salicylic acid concentrations in first chamber and second chamber according to times in figure 4 and build graph –lnX in figure 5, -lnX was calculated using the formula:

$$-lnX = -ln\ [\{C_1(t) - C_2(t)\}/\{C_1(0) - C_2(0)\}]$$

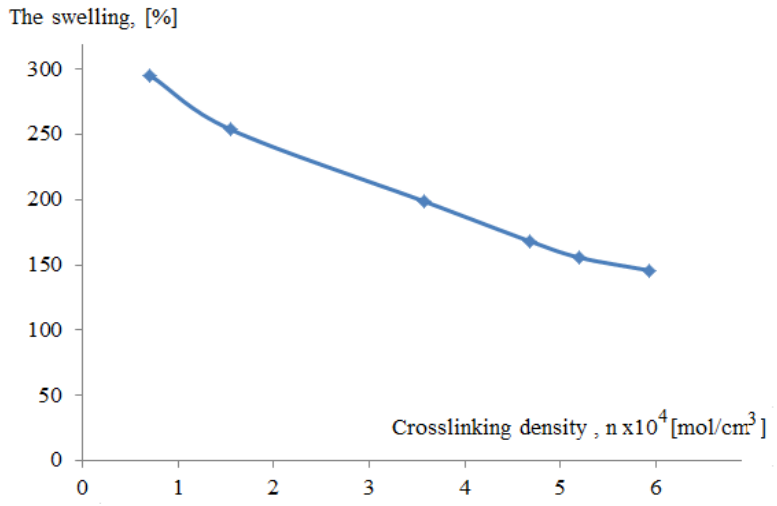

Figure 3: Effect of crosslinking density(n) to the swelling of PVA/TBS membrane

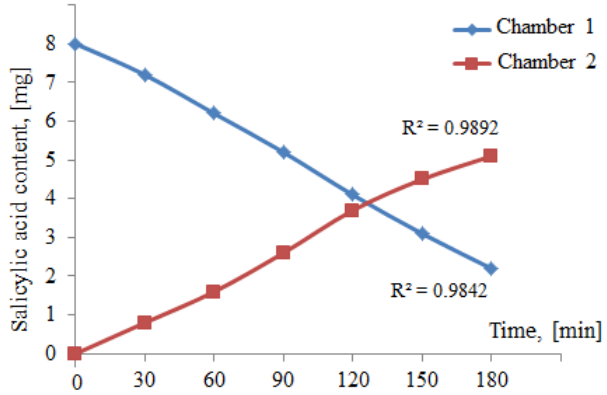

Figure 4: The concentration of salicylic acid in first chamber and second chamber according to times

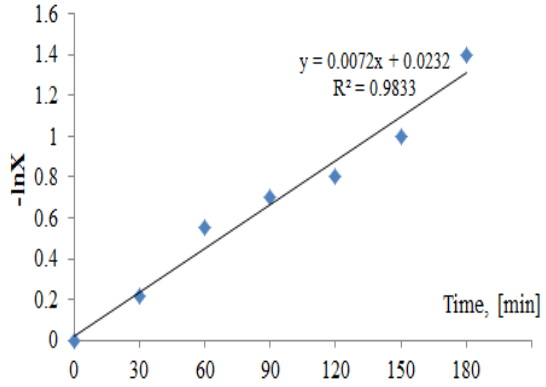

Figure 5: Graph determined diffusion coefficient of salicylic acid

Applying the formula for calculating the diffusion coefficient (D) according to the value of the two chambers in concentration according to the balance equation, the salicylic acid diffusion coefficient of PVA/TBS was identified as 4.15×10^{-6} cm^2/s, proved that the membrane was able to have permeable molecules containing bulky functional groups.

4. CONCLUSIONS

The GA content increased from 0.1 to 0.3 %, the molecular weight between network nodes (M_c) decreased rapidly from 8985 g/mol to 1950 g/mol, the mesh size decreases rapidly from 613 to 227 Å. When the glutaraldehyde (GA) content increased from 0.3 % to 0.6 % molecular weight between two nodes of PVA/TBS membrane decreased slowly from 1950 g/mol to 1070 g/mol and the mesh size (ξ) decreased from 227 to 98 Å.

The average molecular weight between network nodes down from 8985 g/mol to 1070 g/mol, crystallinity of PVA/TBS membrane increased from 22 to 78.6 %; density of PVA/TBS membrane increased from 1.285 g/cm^3 to 1.328 g.cm^3.

The crosslinking density increased from 0.707×10^4 mol/cm^3 to 5.935×10^4 mol/cm^3; the swelling of the membrane decreased from 295.5 to 145.8 %.

The salicylic acid diffusion coefficient of

PVA/TBS had been identified as 4.15×10^{-6} cm^2/s, proved that the membrane was able to have the permeable molecules containing bulky functional groups.

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