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WEATHER ACCELERATION DURABILITY OF BIOPOLYMER MEMBRANES PVA MODIFIED WITH CASSAVA STARCH USED IN THE TREATMENT OF WOUNDS

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Abstract

This research shows the results of accelerated weather durability of biopolymer membranes polyvinyl alcohol (PVA) modified with cassava starch (TBS) in biomedical uses, in order to evaluate the stability of biopolymer membranes PVA/TBS in the storage conditions. For the purpose of determining the using time of PVA/TBS membranes in the applications of covering, moisturizing, reducing pain in burn wound treatment. The characteristic properties of PVA/TBS biopolymer membranes and PVA membranes before and after accelerated weather testing were examined, such as: mechanical strength (tensile strength, elongation at break), infrared spectrum (IR) and the scanning electron microscope images (SEM). The results showed PVA/TBS biopolymer membranes aging resistant, against UV rays were better than ordinary PVA membranes. The using time of PVA/TBS membrane has been identified as 36 months.

Keywords. Biopolymer, polyvinylalcohol, cassava starch, weather acceleration.

1. INTRODUCTION

Biopolymer membrane polyvinylalcohol modified with cassava starch (PVA/TBS) was made from PVA, cassava starch, glycerol plasticizer and glutaraldehyde crosslinking agent (GA), which had excellent physico-mechanical properties like: high mechanical strength, good swelling, good compatibility,.... Therefore, the PVA/TBS membrane can be used to cover wounds having a moisturizing effect, permeability, infection control, pain during treatment for the patient, helps skin regeneration faster [1, 2]. Since this is product which related directly to skin wounds, in addition to the required standards to ensure the mechanical, indicators and sterile assurance level prescribed by the Ministry of Health, membrane PVA/TBS needed to assess the stability of the membrane, from which determined the using time of PVA/TBS membrane and preservation measures [3-5]. The purpose of this paper is to study the accelerated weather durability, the using time evaluation of membrane by the accelerated aging methods.

2. EXPERIMENTAL

2.1. Raw materials and chemicals

- Polyvinyl alcohol (PVA): PVA fibrous, white (Japan), melting temperature 180-230 ^{o}C, the average molecular weight 120.000 g/mol, hydrolysis of 98 %.
- Cassava starch (TBS): production in Vietnam, starch content of 79.6 %.
- Glycerol (Gl): density 1.261, the boiling temperature 290 ^{o}C (The Netherlands).
- Glutaraldehyde (GA), (50 % solution), Merck (Germany).

2.2. Synthesis of biopolymer PVA/TBS using glutaraldehyde (GA) as crosslinking agent

+ Cassava starch disconnected, using 0.5 M HCl at 50 ^{o}C. Proceed stirring for 6 hours, then clarified, washed and neutralized with sodium hydroxide to pH = 7. Collect of starch by filtration vacuum, then dried at 50 ^{o}C in a vacuum until reaching the constant weight.

+ Mixtures including PVA, starch, glycerol were given in 3-neck flask reflux water condenser, stirred about 1 hour to the most co-create solutions. Then the glutaraldehyde solution (1.2 ml of 5 % glutaraldehyde and 0.05 % HCl 0.1 N) dripped slowly into the flask. The reaction continued at 80 °C for 3 hours.

+ After the reaction was finished, the homogeneous solution was made the membrane by the casting method on the glass and then put in oven for drying at the temperature of 50 °C under vacuum conditions (~120 mmHg).

+ Disinfection stage: cut the membrane according to the standard size, brought to define the quality standards, preserved in plastic bags, and sterilized by gamma radiation.

The fabrication conditions of polyvinyl alcohol modified starch were presented in table 1.

Table 1: The sythesis of conditions of biopolymer membrane based on PVA/TBS, and process of applications in the treatment of wounds

No	Conditions	Unit	Value
I	*Single batching and technological conditions*		
I.1	PVA	%	80
I.2	Cassava starch (TBS)	%	20
I.3	Glycerin (by total volume of PVA + TBS)	%	30
I.4	GA content (by total volume of PVA + TBS)	%	0.3
I.5	HCl 0.1 N (by total volume of PVA + TBS)	%	0.05
I.6	Temperature mixing solution	^{o}C	80
I.7	Time to crosslinking reactions	hours	3
I.8	Stirring speed	r/min	400
I.9	The drying temperature (under vacuum ~ 120mmHg)	^{o}C	50
I.10	Conditions γ-ray sterilization		
	radiation dose	kGy	15-20
	Exposure time	hours	10
II	*The physico-mechanical properties and biochemical indicators of PVA/TBS membrane*		
II.1	Tensile strength	MPa	38.5
II.2	Elongation to break	%	520.9
II.3	Reliability puncture resistance	MPa	54.8
II.4	Concentration of heavy metals	-	Achieving QCVN 8-1: 2011 /BYT
II.5	The sterility	-	Achieving Pharmacopoeial Vietnam (2002)

2.3. Research methodology

+ Accelerated weather test ASTM G154-06, equipment UV Atlas / The Model UC-327-2, UVB-irradiated type 313 lamp, irradiation cycle test 4 hours, at 60 °C, humidity condensate 4 hours, 50 °C, test period 240 hours.

+ Tensile strength, elongation were determined according to ASTM D638-03, the Zwick machine 2,5N1S WN: 144 950 (UK).

+ Infrared spectra were measured on a BRUKER-tensor (Germany).

+ Identify the surface morphology of the membrane by a scanning electron microscope (SEM) JEOL JSM 6360LV (Japan).

3. RESULTS AND DISCUSSION

3.1. Mechanical properties of biopolymer PVA/TBS membranes in accelerated weather test conditions

Effect of the accelerated weather testing to the mechanical properties of PVA membranes and PVA/TBS membranes were presented in figure 1.

In experimental studies on the accelerated weather test, tensile strength and elongation at break as reliable indicators to assess the degree of aging. The results showed that PVA membranes under 10 cycles testing, the tensile strength of the PVA membranes decreased from 53.37 MPa to 34.33

MPa (35.7 %); elongation decreased from 872.5 % to 390.6% (55.2 %); it showed that PVA membrane after 10 cycles accelerated weather tests was partly degradable. After 20 cycles accelerated testing of PVA membranes, the tensile strength decreased from 53.37 MPa to 26.98 MPa (49.5 %); elongation was reduced to 242.3 % (72.3 %). Meanwhile, for the PVA/TBS membrane, after 10 cycles accelerated testing tensile strength decreased from 38.25MPa to 36.22 MPa (2.03 %); elongation at break decreased from 523.5 % to 492.6 % (5.9 %). After 20 cycles accelerated weather testing, PVA/TBS membrane had a tensile strength decreased from 38.25 MPa to 34,35 MPa (10.2 %); elongation to break was 460.5 % (12 %). It can be seen that independently on the time, the rate of PVA membrane aging was faster than PVA/TBS; or otherwise starch modified PVA membranes maintained tensile strength and elongation stability than pure PVA film. The reason was membrane PVA modified with starch using glutaraldehyde (GA) crosslinking agent coupling between PVA and starch to form a network 3D structure therefore polymer is more durable, its resistance to aging is better under effects of UV.

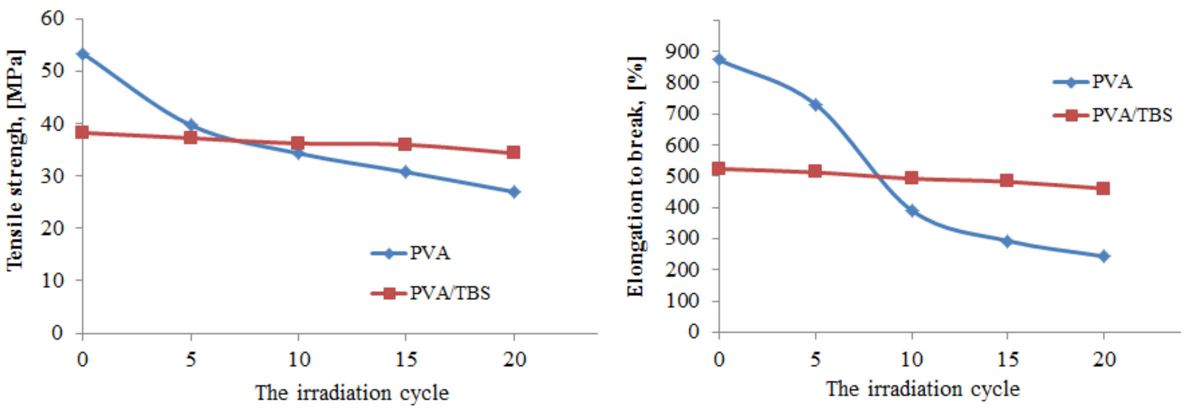
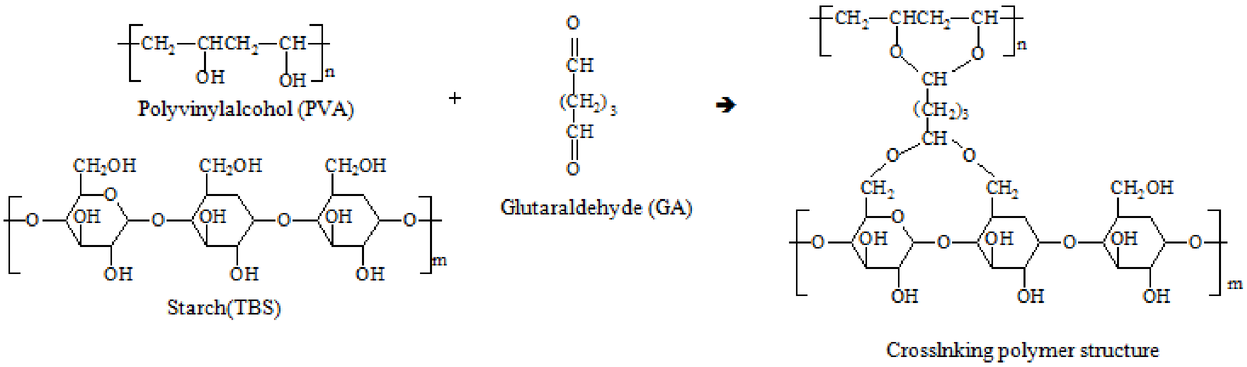


Figure 1: Effect of accelerated weather test on the tensile strength and elongation to break of PVA membranes and PVA/TBS membranes



3.2. Mechanical properties of polymers and biological membranes PVA/TBS in natural conditions in the laboratory

The stability of the PVA/TBS membrane was investigated in laboratory conditions (temperature from 25 °C to 30 °C; the humidity from 75 to 80 %). The results of elongation and tensile strength of membranes PVA and PVA/TBS membrane after each month were presented in table 2.

The results in table 2 showed that, for the PVA membrane after 18 months in the laboratory, tensile strength decreased from 53.37 MPa to 24.63 MPa (53.8 %); elongation to break decreased from 872.5 % to 329.8 % (62.2 %), according to the theory, membrane durability falls below 50 %, i.e. the membranes were broken; This suggested that the PVA membrane is only stable under 18 months. Meanwhile, the PVA/TBS membrane in the laboratory after 18 months, the tensile strength decreased from 38.5 MPa to 36.18 MPa (6.6 %); elongation decreased from 523.5 % to 496.5 % (5.15 %); decline in tensile strength and elongation to break of PVA/TBS membranes was not much. This showed that PVA/TBS membranes remained stable tensile strength and elongation to break better than pure PVA membrane after 18 months.

Table 2: Tensile strength and elongation to break of PVA membrane and PVA/TBS membrane in the laboratory

No	Time (month)	PVA membrane		PVA/TBS membrane	
		Elongation at break (%)	Tensile strength (MPa)	Elongation at break (%)	Tensile strengh (MPa)
1	0 (initial)	872.5	53.37	523.5	38.25
2	3	730.3	51.18	522.4	38.10
3	6	680.2	45.73	520.6	38.04
4	9	560.6	39.25	519.8	37.82
5	12	395.6	34.92	516.6	37.60
6	15	280.5	30.45	510.6	37.15
7	18	249.8	26.63	496.5	36.38

3.3. Infrared spectra of PVA membrane and PVA/TBS membrane after accelerated weather testing

The IR spectra of the PVA/TBS membranes after 10 cycles, and after 20 cycles accelerated test were shown in figures 2 and 3.

Figures 2 and 3 showed that the IR spectra of PVA/TBS after 10 cycles and 20 cycles accelerated weather testing did not see the peak 1701-1704 cm^{-1} wavelength characterized for the C=O group, which indicated that there is no oxidation process in PVA/TBS membrane.

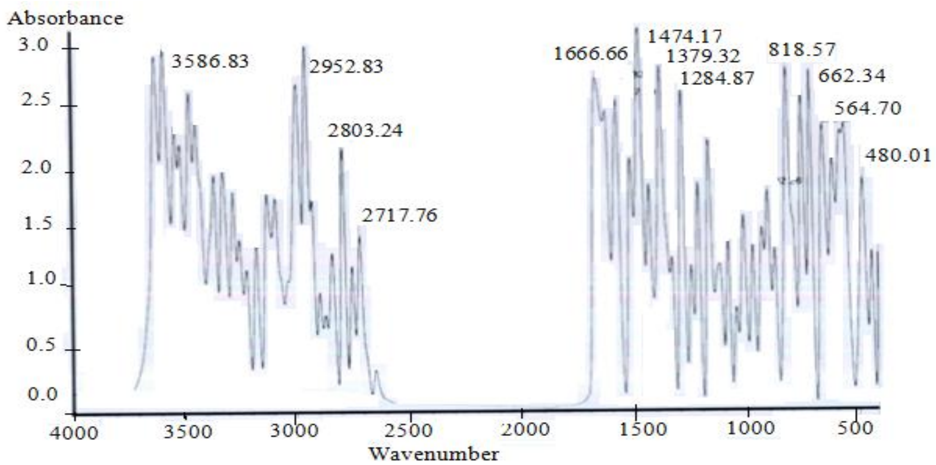


Figure 2: Infrared spectrum of PVA/TBS membrane after 10 cycles accelerated weather testing

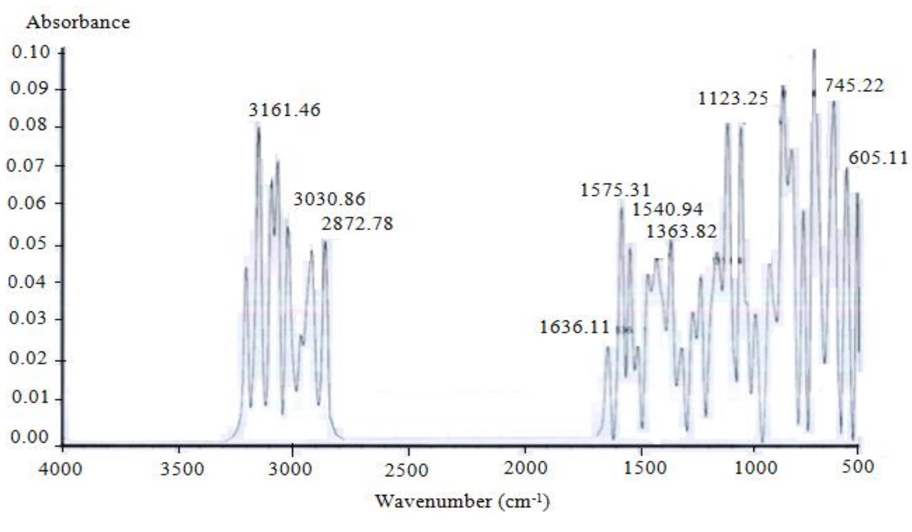


Figure 3: Infrared spectrum of PVA/TBS membrane after 20 cycles accelerated weather testing

3.4. Determining the surface structure of PVA/TBS biopolymers membrane by scanning electron microscopy SEM

Figures 6 and 7 were showed the SEM image capture surface morphological structure of the PVA membrane after 10 cycles and 20 cycles of accelerated weather testing. Figures 8 and 9 showed the SEM images of the PVA membrane after 10 cycles and 20 cycles of accelerated weather testing.

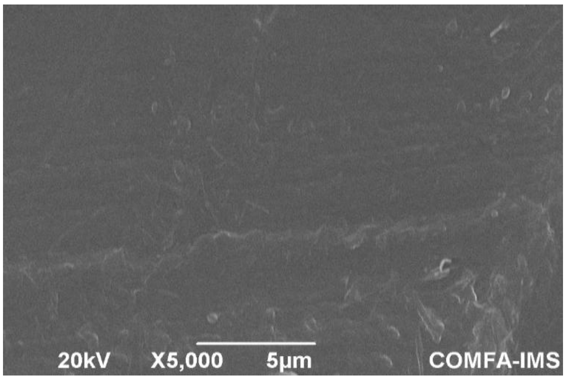


Figure 4: SEM images of original PVA membranes

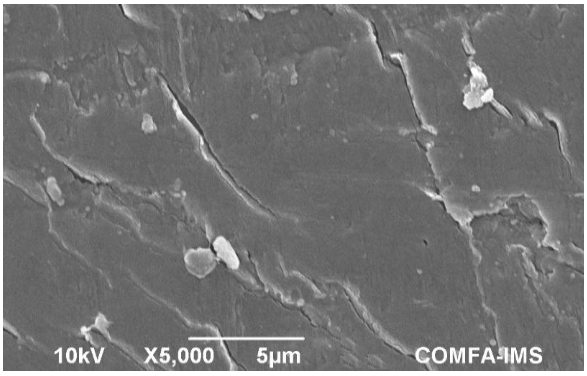


Figure 5: SEM image of PVA membrane after 20 cycles of accelerated weather testing

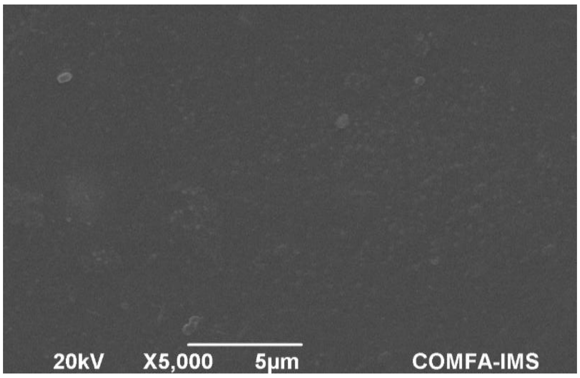


Figure 6: SEM images of original PVA/TBS membrane

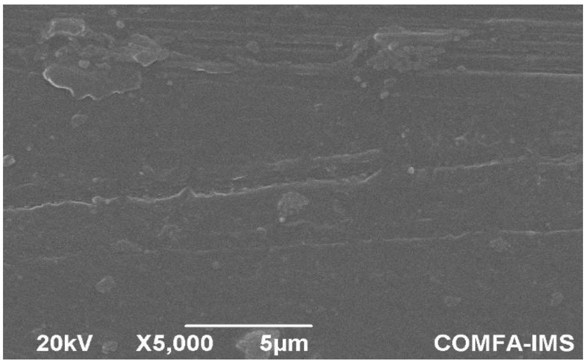


Figure 7: SEM image of PVA/TBS membrane after 20 cycles of accelerated weather testing

Figures 4 and 5 showed that the surface structure of PVA membrane after 20 cycles of accelerated weather testing had the appearance of cracks, fractures, indicating PVA membrane was destroyed. Meanwhile, figures 6 and 7 showed that the surface structure of PVA/TBS membrane after 20 cycles of accelerated weather testing had no the significant changes. This proved that PVA/TBS membrane was not destroyed after 20 cycles test, i.e. the PVA/TBS membrane was more stable than pure PVA membrane.

4. CONCLUSIONS

Membrane PVA modified with starch (PVA/TBS) maintained the tensile strength and the elongation. It was more stable than the pure PVA membrane.

After 20 cycles accelerated weather testing of PVA membrane, the tensile strength decreased by 49.5 %; tensile strength decreased by 72.3 %. Meanwhile, after 20 cycles accelerated testing, PVA/TBS membrane had the tensile strength which was decreased by 10.2 %; the elongation was decreased by 12 %.

For PVA membrane stored 18 months in the laboratory, tensile strength decreased by 53.8 %; elongation to break decreased 62.2 %. The PVA/TBS membrane in the laboratory after 18 months, the tensile strength was decreased by 6.6 %; elongation was reduced by 5.15 %.

The surface morphology of PVA membrnae after 20 cycles accelerated weather testing had more cracks up, indicating membrane was destroyed. The surface morphology of PVA/TBS membrane after 20 cycles accelerated weather testing had no the significant change. This proved that PVA/TBS membrane was not destroyed.

The stability of PVA/TBS membrane was 36 months, equivalent to the period of use of PVA/TBS membrane 36 months with preservation in cool dry conditions, avoiding sunlight.

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