



Effect of Pectin Addition on Mechanical Properties of Poly(vinyl alcohol) Membrane

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The effect of pectin addition on the mechanical properties of poly(vinyl alcohol) has been studied. The physical properties of the membrane studied from the membrane that gives the highest flux on acetone, *n*-butanol and ethanol (ABE) permeation, *i.e.*, membrane that have mol ratio of PVA:pectin (1:2), with addition of glutaraldehyde to form the crosslink at $n = 120$. That membrane composition is the optimum composition that exhibits the highest ABE flux value at permeation time range for 12 h. The membrane was characterized by scanning electron microscopy and Fourier transform infrared spectroscopy. The mechanical properties of membranes were examined by thermogravimetric analysis-differential thermal analysis, tensile strength and swelling degree. The result of characterization suggested that the PVA-pectin-GA membrane was non-porous membrane. The addition of glutaraldehyde (GA) to PVA membrane increasing the tensile strength and reducing the swelling degree. However, the pectin addition incross-linked PVA membrane with glutaraldehyde will increase the flux, decomposition temperature and swelling degree, while it would decrease the tensile strength of membrane.

Keywords: Poly(vinyl alcohol), Membrane, Pectin, Acetone, Glutaraldehyde, *n*-Butanol, Ethanol.

INTRODUCTION

Membrane is a thin layer to separate the two phases which acts as selective barrier to matter displacement¹. One of the polymers that used as membrane in separation or purification process of an organic solvent is poly(vinyl-alcohol) (PVA) that has a high chemical stability, capable to form a thin layer, low-cost and hydrophilic. It is a polymer that can be used to separate or purify an organic solvent. The high hydrophilic property of PVA leads to the low stability of PVA toward the water, so it is very easy to be swelled. Therefore, it needs to be modified to improve the characteristic of membrane by chemical methods, such as the formation of cross-links which is able to generate the membrane with high crystallinity degree and low swelling degree^{2,3}.

Formation of cross linking is done by reducing swelling index, so that the polymer becomes not easily dissolve in the water and produces higher resistance in the membrane⁴. If the cross-linker reagent is added in the polymer solution, then there are two models of cross-links predicted. The first, across-link between different polymer molecules, called intermolecular cross-link and the internal cross-link of a polymer molecule as well as intramolecular cross-link. Those can increase the viscosity and produce gel system⁵.

Another method developed to accelerate the permeation is blending method by mixing the non-covalent bond polymer

to obtain a membrane with a mixture of component with functional group as active agent that helps to accelerate the permeation process. As a type of natural hydrophilic polymer, pectin, can be added to the PVA synthetic polymer. The presence of pectin in the membrane mixture is expected to increase the functional group of carboxylic and hydroxide, which can form hydrogen bond with the sample acetone, *n*-butanol and ethanol (ABE) thus the permeation rate can be increased. This research will study the effect of pectin addition on the cross-linked basic polymer of PVA with glutaraldehyde.

EXPERIMENTAL

All chemicals used in this experiment were analytical grade, purchased from Merck (Germany), PVA, Pectin (citrus WAKO pure for chemical industry), glutaraldehyde, acetic acid glacial, NaOH, aquabidest (Analytical Chemistry Laboratory of Brawijaya University), filter paper.

Apparatus used in this experiment were Laboratory glassware, Thickness Mitutoyo 7301, Infrared Spectrophotometer Shimadzu FT-IR 8400S, Scanning Electron Microscopy (SEM) Hitachi SU8000, DTA-TGA Perkin Elmer, Digital Force GaudelMADA ZP-50N, Refractometer A. Kruss Optronic 881286,

Fabrication of cross-linked PVA-pectin membrane with glutaraldehyde (GA): The cross-linked PVA-pectin

membrane with glutaraldehyde was made by mixing 13.3 mg of pectin into the Petri dish ($\phi = 5$ cm) containing 10 mL of PVA 2 % so obtained mol ratio of PVA-pectin = 1 : 2, stirred for a day until homogeneous mixture. Cross-linking process was held by adding catalyst (1 % acetic acid and 14.3 μ L of glutaraldehyde 35 %) into membrane mixture and re-stirred for 0.5 h. Left at room temperature for a day, put in the oven at 80 °C for 5-6 h. Temperature was lowered to 40 °C for a day to remove the remaining water. Removing the membrane from the petri dish is done by immersing the membrane with 1 M NaOH for a while. The membrane was washed with aquabidest and aerated in 30-40 °C.

RESULTS AND DISCUSSION

Characterization of membrane: Scanning electron microscopy (SEM) used for determine the membrane thickness⁶. SEM micrograph shows either PVA or PVA-pectin-GA membrane are non-porous or dense membrane. The SEM micrograph with 800-7000x magnification (Fig. 1) shows that there is no pore, either cross-section or surface cross-section. The non-porous membrane has some pores, but the size of pore is too small, so it is called non-porous or dense⁷.

Fourier transform infrared (FTIR): Mechanical properties of PVA membrane can be improved by adding glutaraldehyde to prevent of swelling⁸. The presence of glutaraldehyde generate the formation of crosslink either intra or intermolecular PVA, because hydrophilicity of PVA is very high. The aim of pectin addition in the basic polymer of PVA generate the membrane with mixture component with functional group that can form a bond with ABE. The hydrogen bond has same polarity with the component (ABE) that will be separated or permeated. Because of permeation is done based on solution-diffusion, so the similarity of polarity between membrane and permeated component can accelerate the permeation process (exhibit high flux value).

The FTIR spectrum of PVA, PVA-GA and PVA-GA-pectin membrane are shown in Fig. 2. The spectrum of pure PVA has the main peak that can attributed to band of C-H alkyl at 3100-2900 cm^{-1} , strong and specific band of free alcohol hydroxyl at 3900-3600 cm^{-1} and band of bonded hydroxyl at 3570-3200 cm^{-1} . The important band is verified in 1200 cm^{-1} region.

The spectrum of PVA-GA has the main peak at 2860 and 2730 cm^{-1} is attributed to C-H stretching of aldehyde and duplet

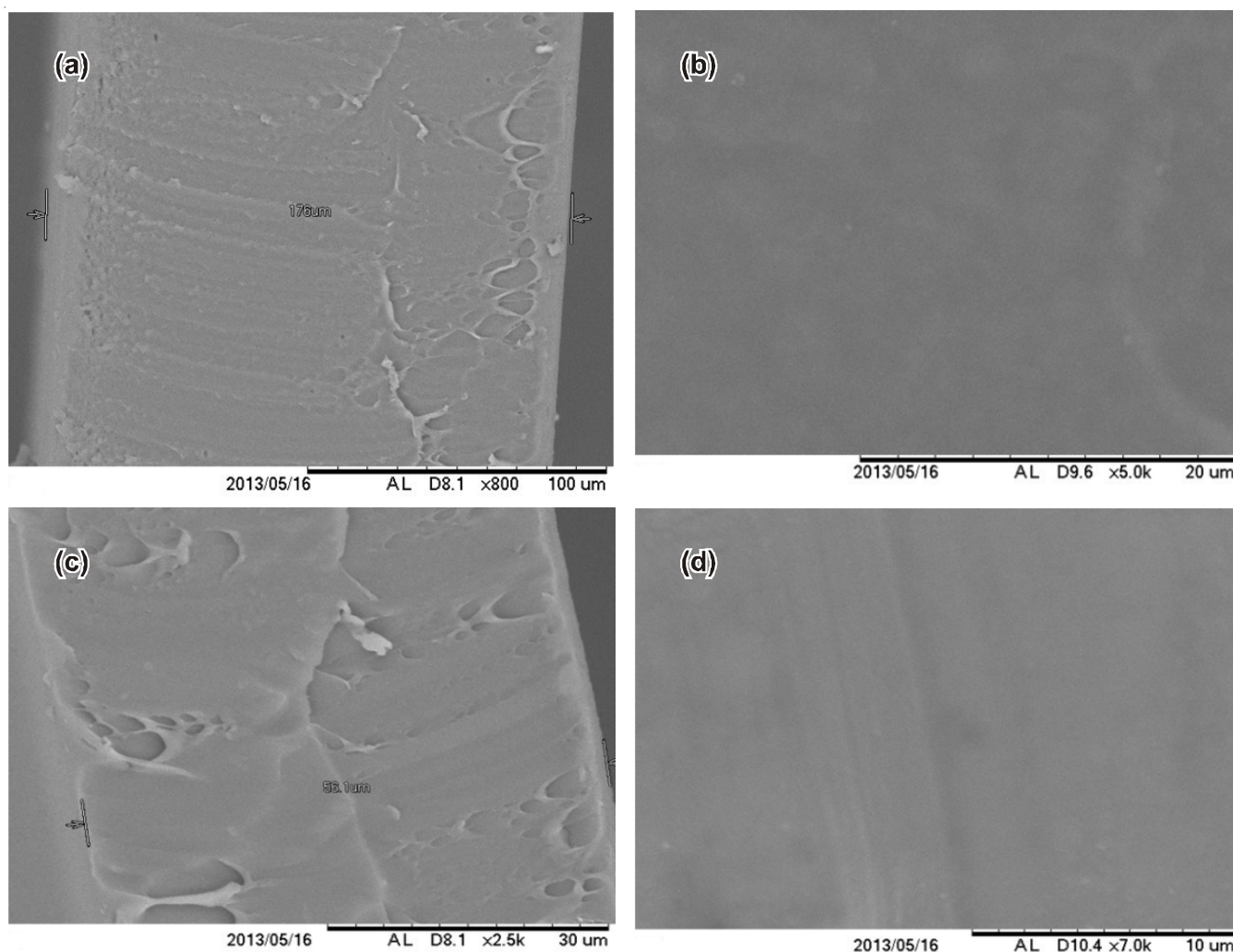


Fig. 1. SEM micrograph of cross-sectional PVA-pectin-GA membrane with a magnification of 800x (a) and cross-section of the outer surface of membrane PVA-pectin-GA with a magnification of 5000x (b), cross-section PVA membrane with a magnification of 2500x (c), outer surface cross-section of PVA membrane with a magnification of 7000x (d)

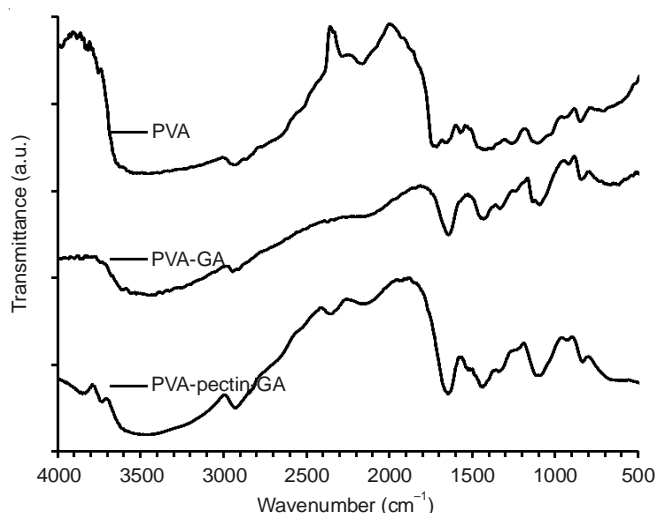


Fig. 2. FTIR spectrum of PVA, PVA-GA and PVA-pectin-GA membrane

absorption of alkyl chain. The lowering of -OH stretching peak (at 3600 cm^{-1}) compare with the pure PVA spectrum, because of cross-linked PVA with glutaraldehyde. It is due to the reaction between hydroxyl (-OH) in PVA and functional group of aldehyde (-CH=O) in glutaraldehyde to form the cross-linking by hydrogen bond formation. Hydrogen bond in PVA-GA is weaker than pure PVA, because of the lowering of -OH group total and formation of acetal (Fig. 3) that the absorption peak appears at $1300\text{--}900\text{ cm}^{-1}$, consecutively, is formation of acetal group (-C-O-C-O-) and ether group (-C-O-C-) in polymer chain⁹.

The spectrum of PVA-pectin-GA membrane shows that the absorption peak at $3000\text{--}3600\text{ cm}^{-1}$ will increase within the amount of pectin addition in this membrane. It may caused by the increasing amount of hydroxyl group which is donated by pectin. Another expansion peak at 1600 cm^{-1} region, carbonyl group peak of pectin either from carboxylic acid or ester. The peak of carboxylic acid at about 1200 cm^{-1} (C-O), whereas the peak of ether also expand at about 1100 cm^{-1} .

Tensile strength (TS): Mechanical properties of membrane depends on the fabrication process and constituent morphology of membrane¹¹. Basically, the material will be more rigid and tougher or crackier because of the increasing of tensile strength.

The addition of cross-linker in membrane leads the membrane to be rigid and it will influence the tensile strength¹².

Mechanism of cross-linking depends on polymer functional group and separation properties of membrane, that intend on increase the durability of membrane without losing selectivity and permeability¹³. The formation of crosslink in PVA membrane with glutaraldehyde is occurred by reaction as explained in Fig. 4.

The addition of cross-linking agent of glutaraldehyde leads to the increasing of tensile strength from 9.9 MPa to 12.9 MPa (Table-1). This may be due to glutaraldehyde able to form crosslink with PVA polymer either intra or intermolecular polymer. The formed crosslink will increase within glutaraldehyde addition, the membrane has more crystalline and not easily swollen. The tensile strength of PVA-pectin-GA membrane is lower than PVA-GA membrane. The decreasing of tensile strength from 12.9 MPa to 10.7 MPa due to pectin as hydrophilic compound is easy to attract the water molecule. The water molecule pulled-out by pectin occurs through formation of hydrogen bond between -OH group of pectin molecule and H atom of water molecule. Amount of bonded water depends on the number of free -OH group in pectin molecule¹⁴.

TABLE-1
TENSILE STRENGTH OF PVA, PVA-GA AND
PVA-PECTIN-GA MEMBRANE

Membrane	Tensile strength (MPa)	Fmax (N)
PVA	9.9 ± 1.6	4.0 ± 0.6
PVA-GA n = 120	12.9 ± 2.7	3.2 ± 0.7
PVA-pectin (1:1)-GA n = 120	10.7 ± 1.1	3.8 ± 0.4

Swelling degree (% S): Swelling degree occurs because of slowly solvent diffusion into the polymer chain. Interaction between membrane and solvent, especially water, leads to be swelling¹⁵. As reversible reaction, means that the membrane can re-shrink initially by heating, to reduce diffused solvent molecules in the polymer chain structure. The expansion of polymer chain occurs because of the interaction between polymer-polymer is stronger than polymer-solvent, therefore separation of membrane linked can be prevented¹⁶.

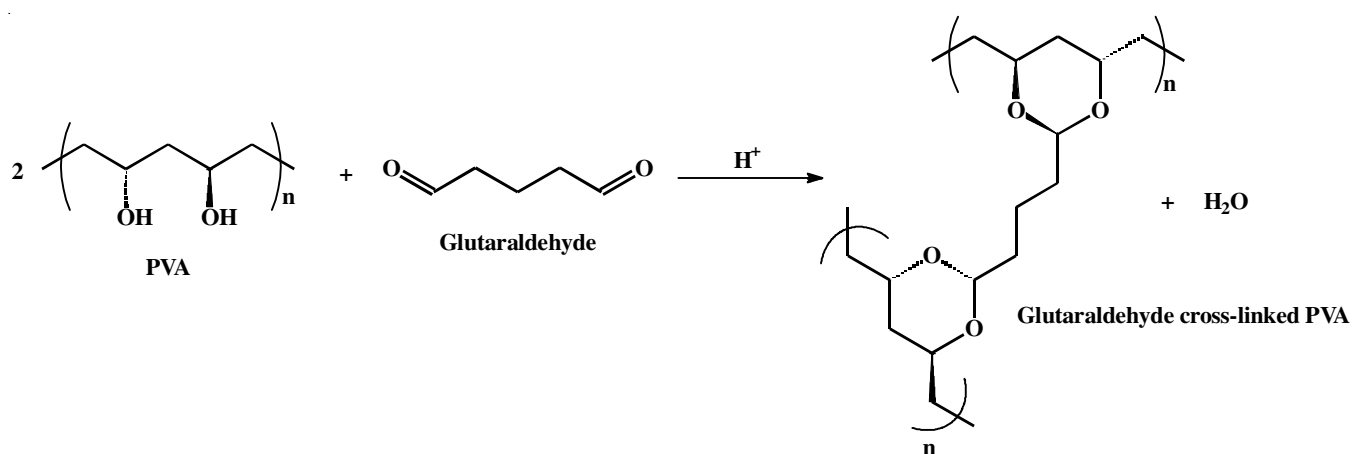


Fig 3. Cross-linking reaction of PVA with glutaraldehyde [Ref. 10]

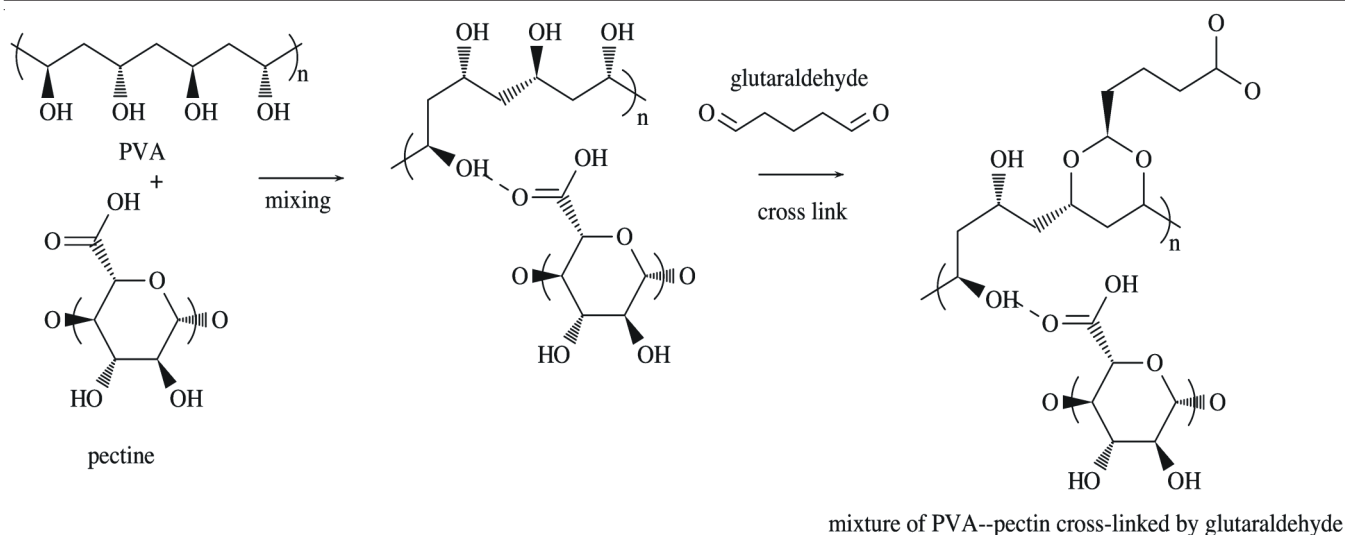


Fig. 4. Approximation cross-linking reaction between PVA, pectin and glutaraldehyde

The swelling degree of membrane can be analyzed to know the effect of membrane swelling toward ABE sample that will be permeated. Swelling degree depends on amount of cross-linking agent, crystallinity and intermolecular forces, thereby it needs to select a cross-linking agent and membrane combination in order to better performance and increasing permeation flux¹⁷. The swelling degree of some membranes in solvents are shown in Table-2.

$$\text{Swelling degree (\%)} = \frac{\text{Mass (wet)} - \text{Mass (dry)}}{\text{Mass (dry)}} \times 100$$

Membrane	Swelling degree (%)			
	Aquadest	Acetone	<i>n</i> -Butanol	Ethanol
PVA	322.1	265.5	414.2	346.0
PVA-GA (n=120)	209.9	173.9	230.6	207.1
PVA-pectin (1:1)	277.0	232.1	411.3	220.8

On the whole studied membrane, the addition of cross-linking agent glutaraldehyde leads the decreasing of swelling degree about 35-45 %, means that cross-linked membrane is stronger and hard to swell. This result is supported by the increasing of tensile strength in cross-linked membrane (Table-1). The level of tensile strength are caused by crosslink either intra or intermolecular of PVA, as explained previously. Instead, the addition of pectin leads to the increasing of swelling degree on whole studied membrane and solvent, each of water 32 %, acetone 34 %, *n*-butanol 78 % and ethanol 6 %.

Pectin is water soluble polysaccharide with D-galacturonate acid polymer as main component, that has α -1,4-glycosidic bond. Galacturonate acid has carboxyl group that can form ionic bonding with Mg^{2+} or Ca^{2+} ion become Mg-pectin or Ca-pectin salt. This salt has amorphous structure and would swell if there is solvent molecule, *i.e.*, water, trapped in among spaces then form a gel. Without the presence both of ion, pectin dissolve in water¹⁸. The solvent ability to enter

among the space in pectin structure leads to the increasing swelling degree and decreasing tensile strength of membrane containing pectin.

Polymer type of PVA and Pectin, both are hydrophilic and easy to be swelling when there is polar solvent. Overall studied solvent, *i.e.*, (water, acetone, *n*-butanol and ethanol), are polar solvent, therefore can permeate into the membrane and causes the membrane swollen. The increasing of membrane swelling degree gives negative impact to selectivity and permeation retention because it will increase the swollen and plasticized.

Thermogravimetric analysis and differential thermal analysis (TGA and DTA): Thermogravimetric analysis is a way to examine or characterize that intended to determine the thermal resistance of the material in consequence of heating, assessed based on the change in the weight-loss. DTA gives transition or change properties information, both physical and chemical properties during heating. A DTA thermogram (Fig. 5) depicts three types of membranes were analyzed at the heating temperature range 30-900 °C with increased rate of 10 °C/min.

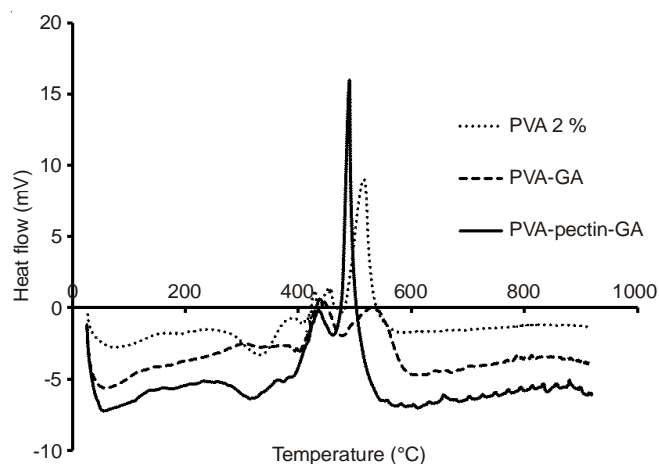


Fig. 5. DTA thermogram of PVA, PVA-GA and PVA-pectin-GA membranes

The DTA thermogram of PVA and PVA-pectin-GA membranes have a similar pattern, but PVA-pectin-GA membrane resulted a sharp exothermic peak which is higher than PVA

membrane whereas PVA-GA membrane does not show any sharp peaks. The TGA thermogram give supporting data from physico-chemical processes occurring in the membrane during the heating, therefore interpretation is also compared with the TGA thermogram (Fig. 6).

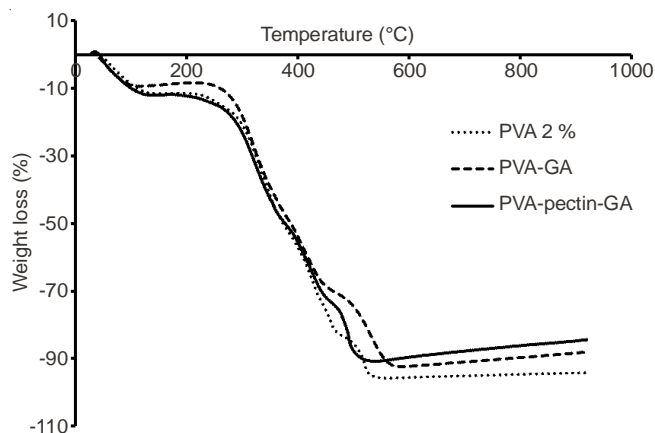


Fig. 6. TGA thermogram of PVA, PVA-GA and PVA-pectin-GA membranes

Based on the TGA thermogram of the three types of membranes, they showed that no glass transition point and have three transition phases. The first change occurred in temperature range 36-122 °C with weight loss up to 10 % and there is a broad endothermic peak on the DTA thermogram that indicating the dehydration process occurred. It is because PVA is hydrophilic membrane, that absorb water molecules. DTA thermogram shows that the first transition of PVA membrane removed the water in a large amount. The existence of cross-link agent glutaraldehyde resulting in free hydrophilic group and reducing the amount of absorbed water, the membrane becomes more hydrophobic and lower thermogram peak.

The second phase transition occurs at 200-450 °C which is indicated by the formation of an endothermic peak on the DTA thermogram and the case of weight loss in TGA thermogram. PVA and PVA-GA membranes have similiar peak, derived from the melting point in 297-306 °C. Transition of PVA-pectin-GA membrane occurs at 350-356 °C with greater enthalpy. Thus, the presence of third component in the membrane that increased the membrane cristallinity. Degradation temperature of all three types of membranes ranged between 489-524 °C, which is characterized by an exothermic peak in the DTA thermogram and TGA thermogram reduction to obtain a total weight loss ranges from 89-95 %.

A review of a sample temperature of the heat flow, the DTA thermogram, there are significant differences in the pattern of a PVA-GA membrane. The thermal stability of PVA-GA is higher than the PVA and PVA-pectin-GA. The presence of crosslinking agent is important for the results obtained. The first effect, crosslinking agents provide more resistance to the membrane, the flux of the sample becomes smaller. Second, crosslinking agents can arrange hydrophilic or hydrophobic properties of a membrane material¹⁹.

Poly(vinyl alcohol) membrane shrinks at 200 °C, biodegradable, it has bonds between molecules. Decomposition of PVA-GA membrane occurs at 280 °C, there are bonds between molecules and cross-link between PVA and glutaraldehyde, requiring greater energy for decomposition than that of PVA membrane. Decomposition temperature of PVA-pectin-GA membrane occurs at 200 °C, similar to PVA, possibly because PVA-GA membrane is more rigid than PVA membrane-pectin-GA.

Conclusion

The characterization results suggested that PVA and PVA-pectin-GA membranes are non-porous membrane. The glutaraldehyde addition into PVA membrane increases the tensile strength and reduces the swelling degree. While the pectin addition into cross-linked PVA membrane with glutaraldehyde increases the flux, decomposition temperature and swelling degree of membrane, but it decreases the tensile strength of membrane.

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