

Barrier, Mechanical and Thermal of Polyvinyl Alcohol/Microcrystalline Cellulose Composites in Packaging Application

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To cite this article:

Nadia A. Ali, Seena I. Huseen, Harith I. Jaffer. Barrier, Mechanical and Thermal of Polyvinyl Alcohol/Microcrystalline Cellulose Composites in Packaging Application. *American Journal of Physics and Applications*. Vol. 5, No. 4, 2017, pp. 46-51. doi: 10.11648/j.ajpa.20170504.11

Received: April 20, 2017; **Accepted:** April 28, 2017; **Published:** June 28, 2017

Abstract: In this study Polyvinyl alcohol (PVA) and (3, 5, 10%)wt microcrystalline cellulose (MCC) were prepared using a solution-casting method. The films that were produced characterized with Fourier Transform Infrared Spectrometry, Differential Scanning Calorimetric, Tensile test, and Barrier properties. The results from FTIR shows that PVA and MCC were considered miscible and compatible owing to hydrogen bonding interaction. Results for Thermal analyses increased in the glass transition temperature (T_g) thermal stability of polyvinyl alcohol. Tensile strength of the films were increased with the increased loading of MCC to a composites films. Water vapor permeability of the MCC composites was increased with increasing with content of MCC in the films but oxygen transmission rate was decreased.

Keywords: Polyvinyl Alcohol, Microcrystalline Cellulose, FITR, T_g , OTR, WVTR

1. Introduction

PVA is a water-soluble and biodegradable polymer with excellent chemical resistance and an interesting material for biomedical applications, and PVA has no toxic action on the human body, so that PVA being used to manufacture medicines cachets. New fields of application of development of ecofriendly packaging materials are still a challenging area and many studies are focused on the improvement of PVA mechanical and barrier properties for PVA by combination with other polymers or fillers composites in order to use it in the packaging industry. For many other applications, mechanical properties of PVA should be substantially improved without damaging its valuable properties. The composites materials should be able to recycled, reused, reprocessed or biodegradable, to minimize its impact to ecosystem. At the same time, the supply of the materials should be sustainable and renewable [1, 2].

The structure of PVA molecule has many hydroxyl groups, which can form hydrogen bonds; this hydrogen bonding gives PVA many excellent properties. But the PVA film has the defects of low elongation at break, poor decomposition temperature and low glass transition temperature. The defects

affect the application of PVA widely, Compared with any other known polymer, PVA demonstrates remarkably superior features as an oxygen barrier; however, to avoid the degradation of its permeability toward gas, it must be protected from moisture when use in packaging application[3,4]. PVA presents remarkable barrier properties against oils and fats, aromas and perfumes, and small molecules (nitrogen, oxygen, etc.). It is one of the few semi crystalline polymers soluble in water and has good interfacial characteristics due to being a hydroxylated polymer capable of forming both intra-and intermolecular hydrogen bonds with other materials (blends or composites). This biopolymer has excellent film-forming properties and causes no toxic effects in the human body for it is biocompatible. Films made of this material are transparent, have good chemical and thermal stability, and good mechanical strength, are biodegradable and do not represent a threat to the environment. However, the highly hydrophilic nature of these films (which renders PVA a poor barrier to water) critically limits wider application of this polymer and PVA based composites [5, 6, 7].

MCC is biomaterials produced by using hydrochloric acid hydrolysis to dissolve the amorphous region of cellulose and hence the cellulose microcrystals are separated. These free cellulose microcrystals tend to aggregate again by strong hydrogen bonding to form MCC and show spongy, porous and random fine structures with the size ranging from several microns to several tens of microns [8]. Furthermore, cellulose is hygroscopic and interacts with water vapor, resulting in swelling. Its hydrophilic nature facilitates the absorption of water, but high gas or aroma barrier [9, 10]. When MCC has strong interfacial interaction with PVA the inter chain hydrogen bonds are formed mainly between the glucose ring ether oxygen and hydroxyl groups (OH) in polyvinyl alcohol while other bonds are also formed between secondary OH at either the C-2 or C-3 positions and the OH of the polyvinyl alcohol component that led to improves the modulus and tensile strength compared to unfilled PVA is of interest in the development of novel or improved applications for this polymer, for example in food and biomedical packaging [11, 12].

2. Experimental Part

2.1. Materials and Samples Preparation

PVA used in this study was PVA (BIO) of Sigma Aldrich Hydrolysed (98 to 99%) weight. It had an average mol. weight 1000 kg/mol. Microcrystalline cellulose with molecular weight of 95 kg/mol was supplied by Sigma Aldrich Co. The composites films were preared using solution casting method using PVA mixed with distilled water at 80°C for 3 hours then microcrystalline cellulose were added to PVA having (3, 5 and 10)% wt and stirred at 80°C for 3 hours. Final stirred mixing was poured on the petri dishes to make films. After keeping the films at 25°C temperature for 2 hour, films were kept in hot air oven for 4hours at 80°C [9, 10]

2.2. Characterizations

2.2.1. Fourier Transform Infrared (FTIR) Analysis

The infrared spectra were recorded with the help of SHIMADZU FTIR -7600 in range 400 to 4000 cm^{-1} .

2.2.2. Differentials Scanning Calorimetric (DSC)

Thermal properties measure the difference in the heat required to increase the temperature of a sample and a reference as a function of temperature by Differential Scanning Calorimetric (Schimadzu DSC-60) from 20°C to 250°C. A heating rate of 5°C/min was used under nitrogen atmosphere and at a flow rate of 30 mL/min, the weight of the sample was 5 mg.

2.2.3. Mechanical Properties

The stress-strain properties were obtained at 25°C room temperature using Instron4467Universal testing machine equipped with a computerized data acquisition system. According to ASTM D-882 standard modulus of elasticity, tensile strength percent elongation at break, and percent elongation at yield. Tested films were cut in 11 mm width

and 80 mm in length and the initial gauge length and testing speed were fixed at 5 mm/min.

2.2.4. Barrier Properties

i. Oxygen Transmission Rate (OTR)

Oxygen Transmission Rate (OTR) of the films was measured according to the ASTM D-3985[13] using gas permeation instrument Qualities (Canada). In the testing method, Firstly nitrogen gas is passed over both surfaces to remove oxygen in the sample. The nitrogen on one side is then replaced by oxygen, and the nitrogen flow on the other side then sweeps the surface to extract any oxygen that diffuses through the material. The diffusing oxygen is measured by a detector that is sensitive only to oxygen, after 12 to 16 hours test was completed. Before each measurement, the samples were kept dry in vacuum oven. The measured time interval is then transformed into the gas permeability rate expressed in $\text{cm}^3/\text{m}^2.\text{day}$. Gas permeability of the films were determined at constant temperature (23°C) and relative humidity (0% RH) conditions with speedy flow of gas between 5–10 cm^3/min and test Area 50 cm^2 and thickness ≤ 3 mm. Oxygen Permeability is based on the equal pressure method, and is professional applicable to the determination of oxygen transmission rate of film and package products, including plastic films, composite films. OTR is applicable in the measurement of gas permeability rate and permeability coefficient at various temperatures. The normalized unit for gas permeability is ($\text{cm}^3.\text{mm}/\text{m}^2.\text{day}.\text{atm.}$)

ii. Water Vapor Transmission Rate

The water vapor transmission rate WVTR of the films was measured according to the ASTM E-96[14] using water permeation instrument Qualities (Canada). Film specimens were mounted horizontally on poly (methyl methacrylate) cups filled with distilled water up to 1 cm under the film. The cups were placed in an environmental chamber at 25°C and 50% RH with air current movement at 60 cm^3/min exposed to a continuous flow of air across the upper side, while bottom side was exposed to water vapor from the moistened pad in the humid cavity. The cups were weighed every hour for a period of value was noted usually after 6-8 hours. The slopes of the steady state (linear) portion of weight loss versus time curves were used to calculate WVTR. An average of four values has been reported by the computer monitors on the screen as the water vapor transmission rate measurements were performed at conditions of 37°C and 90% relative humidity. Water Vapor Transmission Rate stady of the steady water vapor flow transmitted in 24 hours through 50 cm^2 area of a body and thickness is ≤ 3 mm, with unit $\text{gm}/\text{m}^2.24\text{h}$

3. Results and Discussion

FTIR of microcrystalline cellulose and PVA/MCC composites

The FTIR analysis of pure PVA (Figure 1) the presence of a large peak at 3400 cm^{-1} . This peak is linked to the stretching

of O-H from the intramolecular and intermolecular hydrogen bonds. The peaks observed at 2840 cm^{-1} and 2920 cm^{-1} are

respectively related to the symmetric and antisymmetric stretching vibrational of C-H from alkyl groups

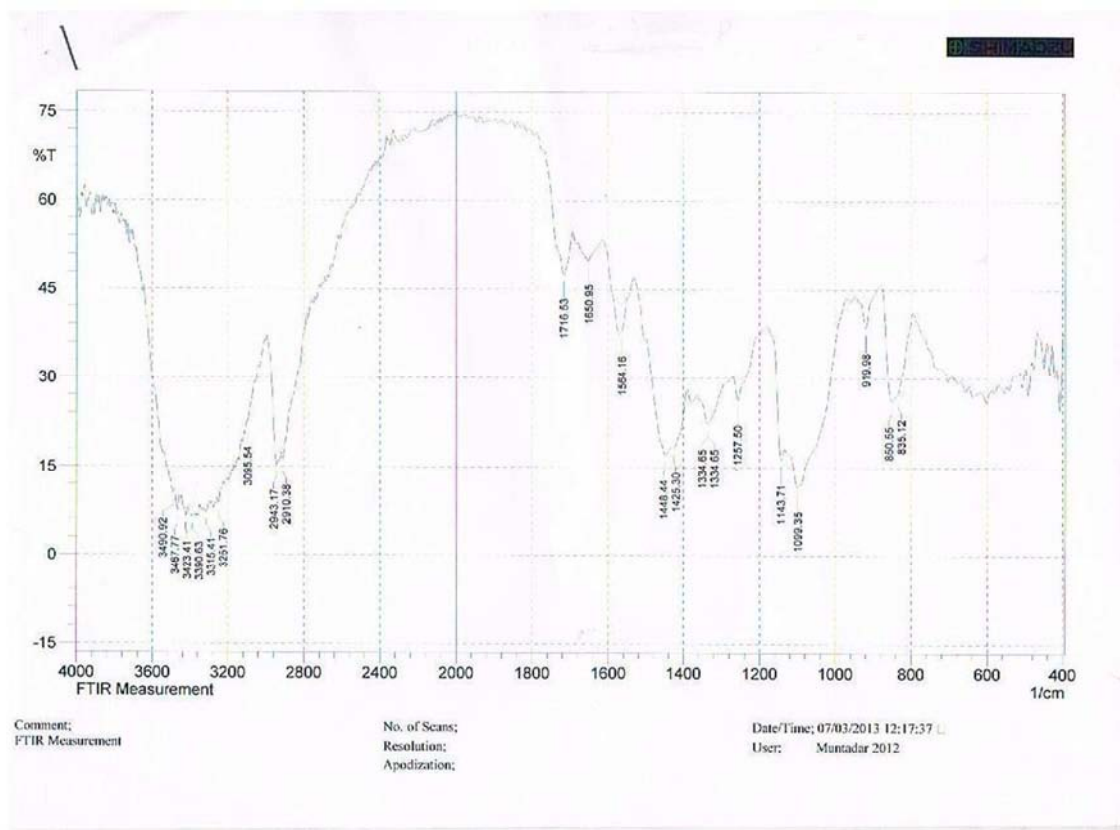


Figure 1. FTIR of polyvinyl alcohol film.

FT-IR spectra of MCC were shown in Fig (2). The spectrum of MCC was exhibited band in the region of $3500 - 3200\text{ cm}^{-1}$, which indicated the inter hydrogen bonded O-H stretching vibration of the OH groups in cellulose molecule [7]. The spectra also showed the peak in the region of about 1730 cm^{-1} which was attributed to glycosidic C-O bonds. Furthermore, the peaks around 1430 cm^{-1} were associated with the C-H in plane bending of MCC and 933 cm^{-1} for a –

OCH₂COO- group into the cellulose molecule.

The FTIR spectra Fig (3) of PVA/MCC composites showed the dominant transmission peaks between ($3420 - 3247$) at (–OH stretching) and at 2916.81 cm^{-1} due to CH stretching. 1411 , 1736 , 1090 and 847 cm^{-1} , which were respectively attributed to the $\nu(\text{CH O H})$, $\nu(\text{C O})$, $\nu(\text{C O})$ and $\nu(\text{C C})$ of PVA/MCC composites

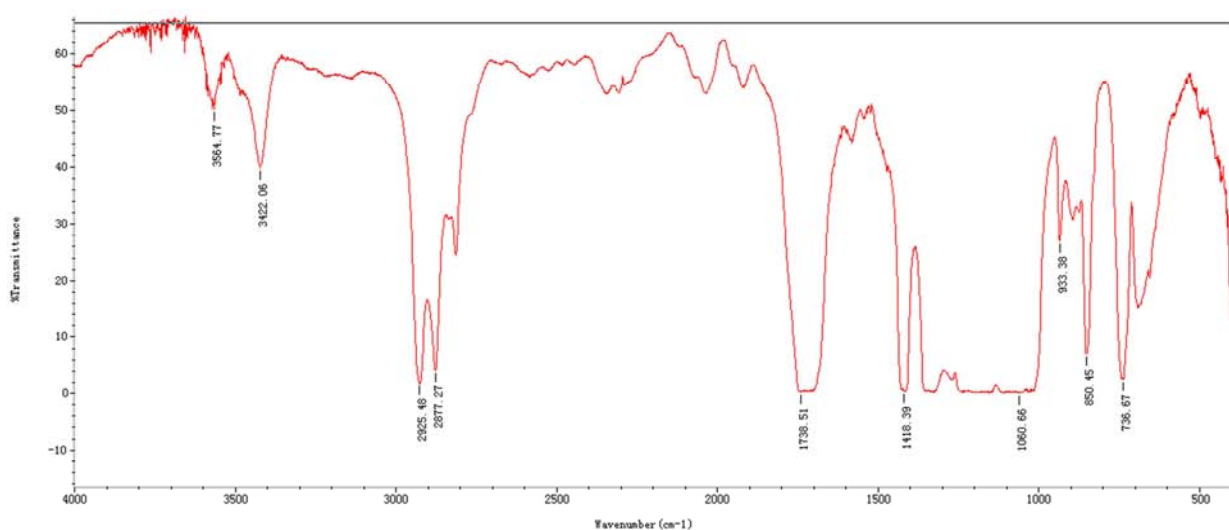


Figure 2. FTIR of microcrystalline cellulose (MCC).

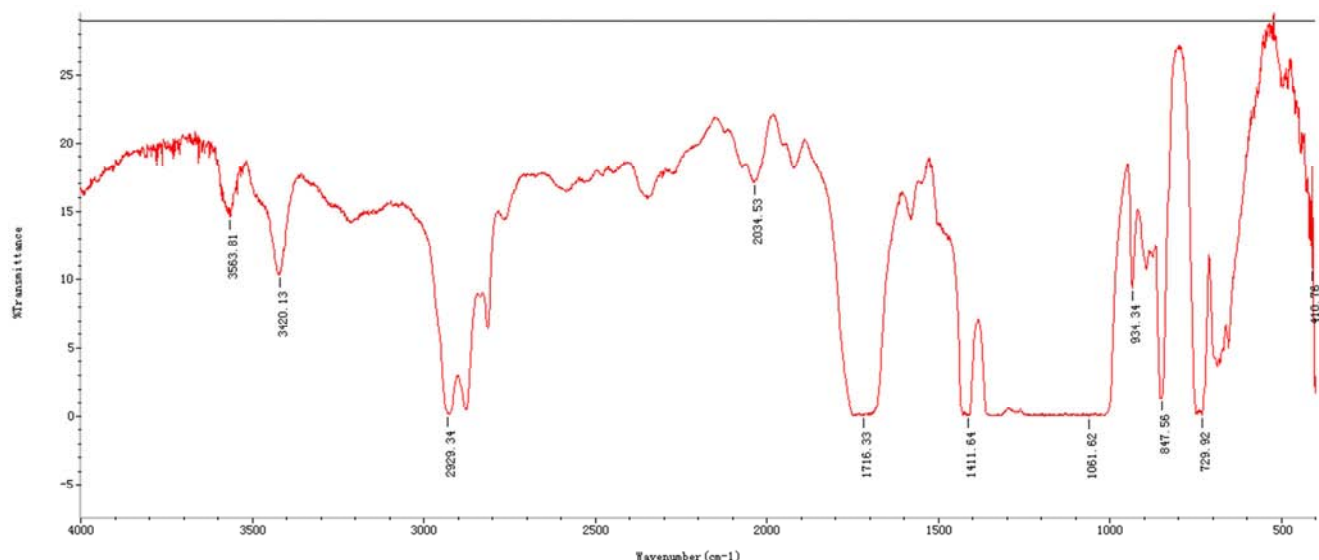


Figure 3. FTIR PVA/MCC composites at 10%.

Mechanical properties of microcrystalline cellulose and PVA/MCC composites

The Tensile Strength and Tensile Modulus of the PVA/MCC composites increased compared with PVA are shown in Fig (4) and improvement at amounts (3%) in sample PVA/MCC. Tensile moduli of PVA and PVA/MCC were 2.16 and 3.20 GPa, respectively. This behavior can be explained by creation of strong hydrogen bonds between cellulose and PVA which contributes to good dispersion in the matrix appear in FTIR [8, 9].

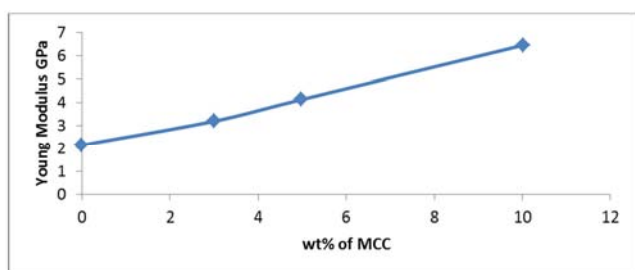


Figure 4. Mechanical properties of PVA and PVA/MCC composites.

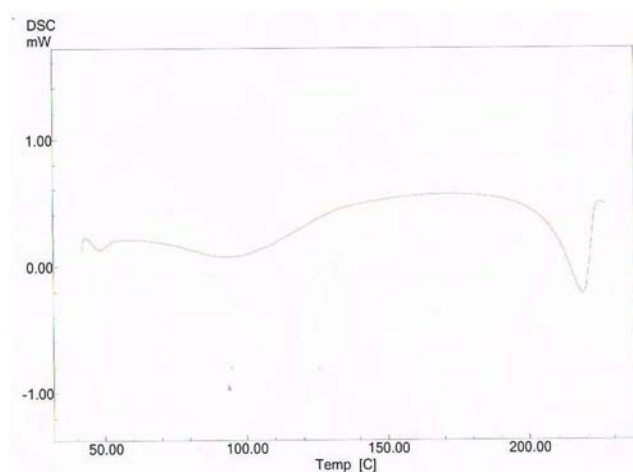
When increase in concentration of the microcrystalline cellulose up to 10% also increased stiffness of composites substantially. Tensile moduli is 6.45 GPa, which show improvement over pure PVA that because micro crystalline cellulose chains are linked by hydrogen bonds between the hydroxyl groups that yield high stiffness and structural strength to the materials that mean the bonding ability between matrix and reinforcing phase is one of the key factors in deciding the properties of composite material. The composites based on PVA and cellulose is likely to produce materials with excellent mechanical properties since both materials are polar polymer with high compatibility reactions, this is because most of the hydroxyl groups in cellulose molecules have already formed either intra- or inter-molecular hydrogen bonds within each other. Therefore, the micro-cellulose is commonly used in their primary

application as excipient for solid dosage forms in pharmaceutical production, due to their carrying capacity and compressibility [15, 16]

Thermal properties of microcrystalline cellulose and PVA/MCC composites

In fig(5) shows pure PVA that have high glass transition temperatures (T_g) is 85°C because PVA have hydroxyl groups are highly interconnected by hydrogen bonding, leading to high (T_g) [17].

The transition temperature T_g for the composites are increased to 100°C compare with pure PVA that mean in PVA/MCC composites other functional groups may support this bonding and increased T_g values to maximum in the 10% wt% composites samples, this means that the addition of MCC increases the thermal stability of PVA. This is due to the increase in crystallinity of the polymer after the addition of MCC.



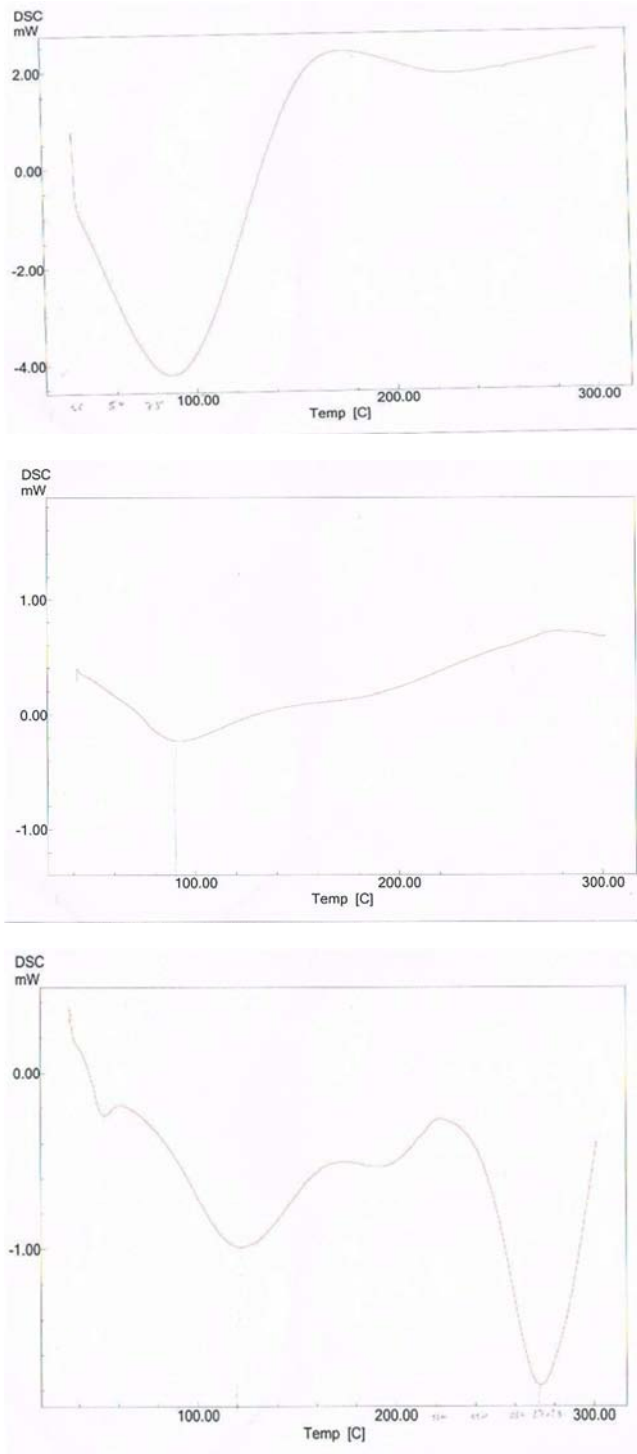


Figure 5. Thermal properties of pure PVA and PVA/MCC composites.

The $-OH$ group in microcrystalline cellulose (MCC) are able to bond with PVA, and thus change the interactions between PVA chains, which affect the T_g and crystallization behavior of PVA [10]. The polymer chain flexibility affected on T_g , so that the addition MCC to PVA with restricted the motion of chain so that the chains needed more heat to move and this will increase the T_g of composites.

Table 1. Thermal properties of pure PVA and PVA/MCC composites.

Samples	T_g (°C)
PVA	85
PVA/MCC 3%	88
PVA/MCC 5%	90
PVA/MCC 10%	95

Barrier properties of microcrystalline cellulose and PVA/MCC composites

Barrier properties is one of the main permeates relevant to packaging applications; they may transfer from the internal or external environment through the polymer package wall affecting the product quality and shelf life of packaging polymer.

Table 2. Barrier properties of pure PVA and PVA/MCC composites.

Samples	OTR ($\text{cm}^3 \cdot \text{cm}^2 / \text{day} \cdot \text{Bar}$)	WVTR (gm^2 / day)
PVA	12	4.3
PVA/MCC 3%	9	7.1
PVA/MCC 5%	7.5	8.7
PVA/MCC 10%	3.8	10.99

In table 2 shows that barrier properties (oxygen transmission rate OTR, water transmission rate WVTR) of pure PVA is high value due to PVA is hydrophilic and very sensitive to moisture which adversely affects its oxygen transmission rate, that means (lower contact angle) with increasing degree of hydrolysis because the higher number of polar groups (hydroxyl groups) at a higher degree of hydrolysis and the subsequent greater interaction between polar groups on the surface and the water droplet [15, 18]. The hydrophilic PVA is sensitive to moisture and thus its barrier properties are strongly affected by the surrounding relative humidity (RH). For instance the oxygen permeability of PVA films generally increases on going from 0% to 100% RH. This is typical of hydrophilic (bio) polymers in which their oxygen permeability increases exponentially with increased relative humidity.

In table 2 the increased of WVTR in PVA/MCC composite films due to swelling constraints and due to high hydrogen bonded of MCC network and strong molecular interactions between microcrystalline cellulose and polyvinyl alcohol. The results of water vapor transmission rate is increase when increased of MCC content in composite films because hydrogen bond interactions between MCC and PVA increased the availability of the hydrophilic groups, increased their interactions with water molecules, and consequently water vapor transmission rate (WVTR) is increased.

In PVA/MCC composites increased water transmission rate with increasing degree of hydrolysis because of hydrophilic of microcrystalline cellulose and PVA are combined; it is inevitable to consider their poor moisture resistance due to the presence of hydroxyl groups this reason is the higher number of polar groups (hydroxyl groups) lead to a higher degree of hydrolysis that useful in degradation.

4. Conclusion

1. Composite consists of PVA a biopolymer, with microcrystalline cellulose are improve the mechanical and thermal according to the presence of –OH active groups and their hydrophilic nature to give high compatibility materials with PVA because of their good interaction between MCC and PVA resulting a good composite properties and satisfactory performance

2. These green composites have demonstrated remarkable properties and thereby emerged as a new generation of composites, and advantageous characteristics, that suitable to for many fields including consumer, agriculture and biomedical.

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