Abstract

This chapter presents the development of bio-nanocomposites as barrier membrane for packaging applications. The barrier properties like, water vapour transmission rate, moisture uptake and gas barrier were examined. Water vapour transmission rate and moisture uptake were found to be decreased as the CNC concentration increases. On contrary to this, nanocomposite film showed increase in oxygen transmission rate as the CNC increases.
8.1 INTRODUCTION

Packaging materials are used for protection of consumer goods against physical, biochemical, and microbiological attack. They should provide enough barriers against oxygen, water vapour, grease, and microorganisms etc [1]. Majority of manufactured plastics are used as packaging material due to their desirable properties like high specific strength, lightness, resistance to water and water-borne microorganisms, long durability, transparency, availability in large quantities at low cost, tear strength, good barrier properties to O$_2$ and aroma compounds and heat sealability [2,3]. Therefore, they are replaced by the conventional packaging materials like glass, metals, and ceramics in many fields. However, unlike materials such as glass or metals, polymers such as polyolefin, polyesters, polyamides, etc., which have been used mainly as packaging materials are permeable to gases, water vapour and volatile organic compounds like hydrocarbons or food flavors etc [4]. Even though, these are credited with many desirable properties they are nonbiodegradable.

The indiscriminate use of plastics in our daily life resulted in generation of huge amount of plastic wastes and disposal of these become serious concern as well as strong regulations and criteria for cleaner and safer environment, have directed the search for eco-friendly materials [5]. Biopolymers like starch, cellulose, PHA, PLA etc, obtained from renewable sources are alternative to synthetic nonbiodegradable polymers. Another way to increase the biodegradability is to incorporate biopolymers like starch, cellulose, or lignocellulosic material into the synthetic polymer matrix. Even though, starch is an abundant biopolymer; it has no physico-mechanical characteristics and processing properties good enough to allow the whole replacement of the composite materials based on synthetic polymers.
products from starch are mostly water soluble and brittle. Some properties of starch can be improved by blending with synthetic polymers [6–8]. Cellulose is another abundant biopolymer used in packaging industry, but unfortunately common paper made from lignocelluloses does not provide sufficient barrier for water, oxygen or oil [1]. Therefore, biopolymer films have disabilities to obtain wide commercial applications. Moreover, the barrier properties of the biopolymers are not as good as conventional packaging materials derived from petroleum based polymers like PP, PE etc [9].

Since PVA has excellent chemical resistance, optical, physical properties and film forming ability, they find use in a number of fields. To enhance the barrier and performance, PVA is usually reinforced with polymer or fillers. Incorporation of naturally occurring polymers or fillers like cellulose or starch improves the eco-friendliness [6,10]. Even though, PVA has good oxygen barrier properties and mechanical properties in dry state; due to moisture sensitivity its applications are limited in this field. High moisture uptake and fast moisture transmission due to hydroxyl groups restricts its potential use in many applications. In order to widen the application of PVA, improvement in the water resistance properties of PVA is necessary and fillers have been incorporated to improve the water resistance properties [11].

The ability of a film to form a barrier is critical in the packaging industry and the most important properties are the oxygen transmission rate (OTR) and the water vapour transmission rate (WVTR). Water vapour and oxygen are two main permeates studied extensively in packaging applications, because they get transferred through the packaging material from internal or external environment, changing the quality of the product and shelf-life [12]. The factors which affect the barrier properties are nature of the permeant molecule like size, shape, polarity etc., temperature,
concentration of the permeate in the polymer and the nature of the polymer chain like flexibility, crystallinity, polarity etc [13].

Choi and Simonsen 2006 isolated cellulose nanocrystals (CNXLs) from Whatman 1 filter paper, used as filler in carboxymethyl cellulose (CMC) containing glycerine as plasticizer and compared the properties to that containing MCC. The results showed that the composites containing CNXLs improved the strength and stiffness than MCC. Moreover, nanocomposite become water resistant after heat treatment [14].

Cellulose nanocrystals (CNXL) isolated from Whatman 1 filter paper was studied as reinforcement in PVA along with Poly (acrylic acid) (PAA) as the cross linking agent by Paralikar et al. in 2008. Moisture transport gets reduced by the presence of CNXLs and PAA. The improvements in barrier performance were minimum for composites containing modified CNXL [15]. Fukuzumi et al. in 2008 prepared cellulose nano fibres by TEMPO mediated oxidation (TOCN). The results indicates that a thin layer of TOCN on the PLA film drastically decreased oxygen permeability of PLA film [16].

Avella et al. in 2012 prepared PVA based foams containing pulp cellulose fibres and microfibrillated cellulose (MFC). Foams containing pulp cellulose fibres showed reduction in water vapour absorption. Different swelling behaviour was observed for foams containing pulp cellulose and MFC fibres [17]. Fortunati et al. 2012 isolated cellulose nanocrystals from MCC, modified by using surfactant (s-CNC) and used as reinforcement in PLA. Water permeability showed a reductions of 34% for films containing 1 wt.% of s-CNC, while composites containing 1 wt.% and 5 wt.% of modified and unmodified cellulose nanocrystals showed good oxygen barrier properties [18]. Chen et al. 2012 isolated cellulose nanocrystals from potato peel and used as reinforcement in PVA along with thermoplastic starch.
Water vapour transmission measurements showed a marginal reduction in water permeability for the PVA composite, but starch composites showed no effect [19].

Abraham et al. 2013 isolated nanocellulose from banana fibre by the steam explosion and used as the reinforcing filler in natural rubber (NR) latex. The transport of nonpolar organic solvents through composites decreased and the resistance increased with increasing the nanofibre content. Diffusion coefficient and the equilibrium solvent absorption was also found to be decreased with the addition of nanocellulose [20]. Lani et al. 2014 isolated nanocellulose from oil palm empty fruit bunch fibre and studied their reinforcing effect in PVA/starch blend films. Good properties were shown by composites containing 5% (v/v) of nanocellulose. Water absorption of nanocellulose reinforced films was found to be lower than starch-PVA blend films [21]. Liu et al. 2014 prepared foams of PVA reinforced with cellulose nanofibrils (CNF) through unidirectional freeze drying technology. Results showed that the incorporation of CNF at a weight ratio of 30 wt.% greatly enhanced the mechanical strength, modulus, water resistance, and dimensional stability of the composites [22]. Pereira et al. 2014 isolated CNC from banana pseudostems fibres, and studied their effect as fillers in PVA. The Water vapour permeability (WVP) results showed that the incorporation of 5 wt.% CNCs decreased the WVP of pure PVA films from 0.61 ± 0.04 g.mm/kPa.h.m² to 0.44 ± 0.01 g.mm/kPa.h.m² [23].

Lim et al. 2015 prepared PVA blend films by cross linking with boric acid (BA). As BA content increase up to 5% the oxygen transmission rate (OTR) of pure PVA decreased from 5.96 to 0.15 cc/m² day but water resistant pressure and tensile strength increased [11]. Lim et al. 2016 also prepared poly (acrylic acid) cross linked PVA blend films. The oxygen transmission
rate of pure PVA decreased from 5.91 to 1.59 cc m$^{-1}$ day$^{-1}$ with increasing PAA ratio and water resistance also increased [24].

Since no known pure polymer exhibits all the desired mechanical and barrier properties, they are often modified by using plasticizers, cross-linking agents, fillers and compatibilizers [25]. Nano clays have also been used in polymeric materials to improve the barrier properties [2]. No systematic studies have been reported on the barrier properties of bio-nanocomposites, especially on PVA containing CNCs without any cross linking agent. Therefore, the main objective of the present chapter is to study the barrier properties of PVA containing CNC with special emphasis on packaging application.

8.2 RESULTS AND DISCUSSION

8.2.1 Fabrication of barrier membranes

Solution casting technique was used for the fabrication of bio-nanocomposites as barrier membrane. Barrier membranes fabricated are listed in Table 8.1. The detailed method of fabrication has already been given in Chapter 3.2.6. The prepared membranes were labelled as 5PVA-0.5CNC, 5PVA-0.75CNC, 5PVA-1CNC, which contains 0.5, 0.75 and 1 wt.% of CNC respectively.

<table>
<thead>
<tr>
<th>Wt. of PVA (g)</th>
<th>Volume of solution used (mL)</th>
<th>Wt. % of CNC relative to PVA (g)</th>
<th>Barrier membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>25</td>
<td>0</td>
<td>5PVA</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.5</td>
<td>5PVA-0.5CNC</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.75</td>
<td>5PVA-0.75CNC</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>1</td>
<td>5PVA-1CNC</td>
</tr>
</tbody>
</table>
8.2.2 Water vapour transmission rate (WVTR)

Table 8.2 shows the WVTR of bio-nanocomposites. The amount of the mass exchange between the packaged material and the external environment determines the permeability of packaging material. The weight loss when water molecule transferred is plotted against time, dividing the slope of this graph with area in m² gives WVTR of bio-nanocomposites in g h⁻¹ m⁻² [Chapter 3.3.9.1]. The transport of permeate molecules through polymeric materials is determined by the potential capacity of a polymer matrix to sorb the permeate molecules and the ability of those molecules to diffuse through the polymeric material [26]. WVTR is the measure of ability of moistures to cross the film. The values of WVTR are given in Table 8.2.

**Table 8.2** WVTR values of 5PVA and bio-nanocomposite membranes

<table>
<thead>
<tr>
<th>Polymer/ bio-nanocomposite membranes</th>
<th>WVTR (g h⁻¹ m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5PVA</td>
<td>16.5±0.5</td>
</tr>
<tr>
<td>5PVA-0.5CNC</td>
<td>16±0.2</td>
</tr>
<tr>
<td>5PVA-0.75CNC</td>
<td>15.7±0.2</td>
</tr>
<tr>
<td>5PVA-1CNC</td>
<td>15.4±0.3</td>
</tr>
</tbody>
</table>

As shown in Table 8.2 all composite films exhibited slightly lower WVTR values compared to neat PVA film. When the CNC content increases, due to interaction between CNC and PVA, segmental motion and hence porosity in the polymer surface are reduced leading to low water vapour transmission. High degree of crystallinity of cellulose nanocrystals supplemented with composite structure formed due to rigid hydrogen bonded network were responsible for the slight reduction in WVTR by decreasing the effective diffusion and to increase tortuosity of the permeation path for water molecules [15,27]. The barrier properties get improved due to interactions
between water and CNCs, resulting in rearrangements of water molecules in the matrix, leading to lowering of plasticizing effect and improving the barrier properties of the material [19,28].

8.2.3 Moisture uptake (MU)

Figure 8.3 Illustrates the percentages of the MU for 5PVA and bio-nanocomposites at different periods of time calculated using the Equation 3.1. Eventhough, PVA is one of the important biodegradable polymers its poor resistance to water absorption limits its wide applications. Addition of fillers is an effective way of decreasing its moisture uptake [29].

![Figure 8.2 Moisture uptakes of (a) 5PVA, (b) 5PVA-0.5CNC (c) 5PVA-0.75CNC and (d) 5PVA-1CNC.](image)

From Figure 8.2 it can be clearly observed that initially moisture uptake is rapid, then slowly increases and almost reach equilibrium in 48 hours. As the CNCs content increases MU % decreases. The hydroxyl group of cellulose nanocrystals with a compact chemical structure and having high
crystallinity are less accessible, therefore it would be expected to show only lower water uptake compared to PVA, leading to reduced moisture uptake [21,22,30,31]. Absorbed water molecules can accumulate in cellulose nanocrystals and at the polymer/cellulose nanocrystals interface. Since crystalline cellulose does not absorb significant amounts of water leaving only the CNC/polymer interface to accommodate most part of absorbed water molecules at equilibrium [32]. The formation of the network structure between the cellulose nanocrystals and PVA can also prevent the water molecules leading to improvement in the water resistance of the film [21].

8.2.4 Oxygen transmission rate (OTR)

Table 8.3 shows the OTR values of 5PVA and bio-nanocomposites. Hydrophobic polyolefin like polypropylene and polyethylene are characterised by low WVTR but high OTR, but cellophane, nanocellulose like cellulosic films have low OTR but have a very high WVTR [33].

Table 8.3 OTR values of 5PVA and bio-nanocomposite.

<table>
<thead>
<tr>
<th>Polymer/bio-nanocomposite membranes</th>
<th>OTR (cm³/m².24 hrs at 0.1 Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5PVA</td>
<td>10.729</td>
</tr>
<tr>
<td>5PVA-0.5CNC</td>
<td>11.849</td>
</tr>
<tr>
<td>5PVA-0.75CNC</td>
<td>12.125</td>
</tr>
<tr>
<td>5PVA-1CNC</td>
<td>14.065</td>
</tr>
</tbody>
</table>

From the Table 8.3 it can be observed that the bio-nanocomposites shown slight increase in OTR values on the addition of CNCs. Contrary, CNC addition is not affected the oxygen transmission rate of bio-nanocomposites. For hydrophilic polymer like PVA, increasing the humidity
from 0 up to 100%, increases the oxygen permeability by a factor 2500 [34]. The barrier properties of hydrophilic polymers can be seriously affected by the presence of organic vapours and liquids that penetrate and plasticize the polymer. Moreover, polymers that contain hydroxyl groups like cellophane and amide groups like nylon 6, nylon 6,6, etc., show large increase in permeability as they absorb water [26]. The deterioration of oxygen barrier under humid conditions is therefore the main drawback, limiting the use of these polymers and composites in food packaging, especially for packaging high moisture foods or food which will lose quality when in contact with moisture or oxygen [34]. But for packaging fresh fruits and vegetables, high barriers to migration or gas diffusion are undesirable because shelf life is dependent on the availability of continued supply of oxygen for sustained cellular respiration. OTR values lower than 20 mL m\(^{-2}\) day\(^{-1}\) has been recommended for packaging applications. Since there are differences in the morphology of prepared cellulose nanocrystals the slight increase in the OTR values reveals the poor connectivity of the pores in the composite film [35]. Polymers such as polyethylene and polyethylene terephthalate do not change their barrier resistance when allowed to come into contact with moisture because the hydrophobic polymers do not absorb enough water to plasticize the polymer chains to cause an increase in gas permeability.

Nanocomposite containing bentonite has shown reduction in the permeability of the PLA while the MCC nanocomposite drastically increased the oxygen permeability of the PLA [36]. But there are reports on reduction in oxygen transmission rate on PLA by addition of cellulose nanocrystal [18]. The transport properties of gases through polymer films are governed by the tortuosity of their path, shape and aspect ratio of the filler, degree of exfoliation or dispersion, filler loading, orientation, adhesion to the matrix, moisture activity, filler induced crystallinity, polymer chain immobilization,
filler induced solvent retention and porosity [37]. However, to the best of our knowledge there are no prior literatures related to OTR values of the bio-nanocomposites of PVA reinforced with CNCs. The newly developed bio-nanocomposite materials, could find application in packaging industry in fields such as consumer and agriculture, like carriers for chemicals, fertilizers, pesticides etc. Many packaging applications demand certain barrier properties as well as mechanical resistance, therefore 5PVA-0.75CNC found to be better.

8.3 CONCLUSION

Bio-nanocomposite has been developed as barrier membrane with a view to using them for packaging application. The barrier properties of the membrane like, water vapour transmission rate, moisture uptake and oxygen transmission rate of these membranes were therefore examined. Water vapour transmission rate and moisture uptake were found to be decreased as the CNC concentration increases, which show resistance to moisture. However bio-nanocomposite films exhibit a slight increase in oxygen transmission rate. Since many packaging applications demand certain barrier properties as well as mechanical resistance, the bio-nanocomposites developed 5PVA-0.75CNC can be effectively used in place of PVA for better packaging application in consumer and agricultural fields.
REFERENCES


11. Lim, M.; Kwon, H.; Kim, D.; Seo, J.; Han, H.; Khan, S. B. Highly-enhanced water resistant and oxygen barrier properties of cross-linked


