1. Introduction

Microfluidics is a quite new technology platform that classically requires a multidisciplinary approach for building effective systems through the interface of physics, chemistry, engineering and biochemistry. These devices usually consist of macro-structures that are fabricated in the micrometer-scale and can be designed to produce diagnostically useful systems for potential point-of-care measurements. Systems based upon microfluidics operation possess a unique set of potential advantages, such as reduction in reagent cost, enhancement of assay speed, potential for mass production of devices at low cost and the ability to integrate several processing steps into a single system (i.e., size control) [Situma et al., 2006; Wu & Nguyen, 2005].

Cellulose, the most abundant organic polymer in the biosphere, is a polydisperse linear homopolymer consisting of β-1,4 glucopyranose units. The properties of cellulose including good mechanical properties, low density, biodegradability, and availability from renewable resources have become increasingly important and have contributed to a rising interest in this material [S. Y. Lee et al., 2009]. Native cellulose is generally known to be fibrillar and crystalline and the cellulose fibrils play a significant role in contributing to the high strength of plant cell walls [Lu & Hsieh, 2010; Zuluaga et al., 2009].

Cellulose derivatives have been widely studied, and there are numerous industrial applications in fiber, film and gel based materials. Cellulose ethers are strongly studied in barrier packaging. As they are often water-soluble [Moura et al., 2008], they are mostly used as coating [Coma et al., 2001] or in the preparation of edible films with efficient oxygen barrier properties [Kamper & Fennema, 1984]. Hydroxypropyl methylcellulose (HPMC) is a
Advances in Microfluidics

most commonly used cellulose ether. It is approved for food applications by FDA (21 CFR 172.874) and the EU (EC, 1995). The films obtained from HPMC are resistant to oils and fats, flexible, transparent, odorless, and tasteless but tend to have moderate strength [Bilbao-Sainz et al., 2011]. Other cellulose ether most utilized for edible films is carboxymethylcellulose (CMC), a sodium salt of carboxymethyl ether cellulose. It is synthesized by swelling cellulose with sodium hydroxide and alkali-catalyzed reaction of cellulose with chloroacetic acid [Sudhakar et al., 2006]. CMC has a high water bonding capacity, good compatibility with skin and mucous membrane, is widely available and cheap [Ramli & Wong, 2011].

Natural cellulose fibers have been used as a reinforcement material. One disadvantage is the lack of strength of interfacial bonding. Natural fibers include those of vegetable origin constituted of cellulose, a polymer of glucose bound to lignin with varying amounts of other natural materials. The interest of using cellulose fibers for polymer matrix reinforcing has rapidly grown in the last decade because of the above mentioned advantages and because the natural fibers are obtained from annually renewable resources [Azeredo, 2009].

Edible coatings such as those formed by wax on various fruit surfaces have been used for centuries to prevent moisture loss and to create a shiny fruit surface. Several edible materials have had their film-forming properties studied to produce edible films and coatings to be used in food packaging, not completely replacing petroleum-derived plastics, but rather improving their efficiency, thus reducing the amount of synthetic polymers required for each application. Since edible biopolymers do not have satisfactory barrier and mechanical properties to packaging application, the addition of reinforcement material is helpful to make these materials more adequate to industrial application.

Polymer-based composite materials reinforced with organic-based fillers have received significant interest. Especially, many synthetic polymeric materials have been substituted by biopolymers combined with natural reinforcing fillers to improve their mechanical and barrier properties. In this chapter, the principal idea is to analyze the importance of microfluidics technic in produce cellulose microfibers for composite materials.

2. Microfluidic technology

2.1 Principles and advantages

Microfluidic technologies are indicated to manipulate small quantities of liquids or fluids usually through channels with at least one dimension smaller than 1 mm, for emulsion formation, mixing and dispersion [Skurtys & Aguilera, 2008]. This leads to greatly reduced reagent consumption and exhibits intrinsically efficient heat and mass transfer due to high surface area-to-volume ratios [Hung & Lee, 2007; Il Park et al., 2010].

Microfluidizer high shear fluid processors are unique in their ability to achieve uniform particle size reduction, bottom-up crystallization and efficient cell disruption - enabling innovative companies to develop nano-enabled medicines, chemicals and consumer products that change the world. Product enters the system via the inlet reservoir and is powered by a high-pressure pump into the interaction chamber at speeds up to 400 m/s. It is then effectively cooled, if required, and collected in the output reservoir. The exclusive fixed-geometry interaction chambers are the heart of our technology, and combines with a
constant pressure pumping system to produce unparalleled results. By reducing particles to
the nano-level more efficiently, customers use less energy to achieve particle size results that
are, on average, half the size of even the most effective homogenizer outputs.

Lee et al., 2011 defined the aim of microfluidic mixing schemes as a device to enhance the
mixing efficiency and to achieve a thorough and rapid mixing of multiple samples in
microscale devices, being the sample mixing essentially achieved by enhancing the diffusion
effect between the different species flows. Also, the diminutive scale of the flow channels in
microfluidic systems increases the contact area between the species to be mixed, and this
factor is one of the most efficient means of enhancing the diffusive mixing effect. Other
important alternative to increase the contact area between the mixing species into the
microfluidic devices is designing the microchannel configurations allowing that the species
are folded multiple times as they flow along the mixing channel.

Microfluidic process has become an attractive technology for numerous applications [Atalay
et al., 2011; Cho et al., 2011; Napoli et al., 2011; Schirhagl et al., 2010; Thompson et al., 2010;
Zhang et al., 2011] due to unique characteristics, such as: i) efficient and rapid mix leading to
rapid chemical reaction; ii) homogeneous reaction environments; iii) continuously varied
reaction conditions and iv) precise time intervals to add reagents during reaction [deMello,
2006; DeMello & DeMello, 2004]. Therefore, the application of the microfluidic devices
improves the control of the synthesis parameters and thus the nanoparticle sizes and
properties [Il Park et al., 2010] and optimizes the miniaturization of the microstructures.

2.2 Utilization of microfluidizer systems for different applications

Microfluidizer system belongs to microfluidic process which has been extensive proposed as
a green alternative technology in miniaturization from macro to micro/nano structure
dimensions.

Some recent applications using microfluidizer technology are discussed as following. Nik et
al., 2010 applied the microfluidics technology to obtain oil-in-water emulsions stabilized
with whey protein isolate or with β-lactoglobulin or α-lactalbumin (individually or
combined). The experimental set consisted of the mixture pre-homogenized with Ultra-
Turax mixer for 2 min followed by homogenization with four passes through a
microfluidizer (M-110EH Microfluidizer Processor, Microfluidics, Newton, MA, USA) at 350
kPa. In these experiments, bleached soybean oil was used as oil source.

In the work described by Cavender & Kerr, 2011, they investigated how microfluidization
affects the physical and sensory properties of ice cream made from mixes which contain
either xanthan gum or locust bean gum (LBG). The mixes were stirred for 1 min and
processed at 220–250 MPa using a high pressure processing system (Model M140-K,
Microfluidics) fitted with a diamond interaction chamber (Model G10Z, Microfluidics). They
showed that by treating full-fat ice cream mix with microfluidization, one can affect both
sensory and physical properties of the finished product, and further, those changes differ
based on the gum used. The authors also concluded that consumers preferred the firmness
and creaminess of ice cream made from microfluidized mixes with LBG.

Liu et al., 2011 investigated the aggregation changes of whey protein induced by high-
pressure microfluidization (HPM) treatment by using M-7125 Microfluidizer with pressure
range of 400,000 psi. The whey protein concentrate (WPC) at 1 mg/mL was treated under pressures of 40, 80, 120 and 160 MPa, being each solution repeated 3 times at each pressure. The average particle size of whey protein decreased as the pressure increased from 407 nm (untreated whey - 0 MPa) to 196 nm when the Microfluidizer pressure was increased to 160 MPa. Functional properties (solubility, foaming, and emulsifying properties) of WPC ultrafiltered from fluid whey were evaluated. As main results, they showed significant modifications in the solubility (30% to 59%) and foaming properties (20% to 65%) of WPC with increasing pressure, suggesting that HPM treatment of WPC is appropriate for applications in selected dairy products.

Chen et al., 2011 studied the effect of the sonolysis, microfluidization and shearing treatments on the degradation kinetics of chitosan solutions prepared by dissolving chitosan in an acetic acid buffer (0.2 mol L\(^{-1}\) acetic acid/0.1 mol L\(^{-1}\) sodium acetate, pH = 4.3). In the microfluidization treatment, 300 mL of chitosan solution was placed in a water bath at controlled temperature of 0 ± 1, 30 ± 1 and 50 ± 1ºC and treated with a microfluidizer (M-100Y Cell Disruption, Microfluidics) at pressures of 82.7 and 117.2 MPa for 5, 10, 15, 20 and 25 passes. SEC-HPLC method was used to determine the molecular weight of chitosan and from this technique to accompany the chitosan degradation. The results showed that among three physical methods studied, the microfluidization treatment results in the highest efficiency when higher chitosan solution concentrations were utilized. Also, the degradation mechanism of the chitosan is different for each of the physical methods; in the microfluidization method, the mechanism is entanglement and stretch plus cavitation.

Rao and McClements, 2011 established experimental conditions to prepare food-grade stable microemulsions, nanoemulsions or emulsions using sucrose monopalmitate (SMP) as a surfactant and lemon oil as an oil phase. After a prehomogenization using a high-speed blender for 2 min at ambient temperature, the oil and aqueous phases were passed through a high pressure homogenizer for 3 passes at 9,000 psi (Model M-110L Microfluidizer Processor, Microfluidics). According to the authors, emulsions (r > 100 nm) or nanoemulsions (r < 100 nm) were formed at low surfactant-to-oil ratios depending of homogenization conditions; and microemulsions were formed at higher ratios. In other work, Rao and McClements, 2012 prepared a nanoemulsion with mean droplet diameters of 105±15 nm (pH = 7) from stock emulsion formed by lemon oil (10 wt%), SMP (1wt%) and buffer solution (89 wt%) by using of the same microfluidization way.

Bonilla et al., 2012 reported the influence of homogenization treatment of the essential oil type (basil and thyme) on the physical properties of chitosan-based film-forming dispersions. Two different homogenization treatments were used. In the first one, the film-forming dispersions were prepared by using an Ultraturrax rotor-stator homogenizer at 21,500 rpm for 4 min. The second treatment consisted of the association of the first treatment and microfluidization at 165 MPa in a single pass by means of a Microfluidizer® M110-P processor. The authors concluded that microfluidization at 165 MPa affected the properties of the emulsions and films based on chitosan and basil/thyme essential oils. Also, a reduction was observed in oil droplet size and viscosity, which promoted the adsorption of chitosan on the oil-water interface.

2.3 Our contribution to microfluidics technology

Our contribution to microfluidics technology focuses specifically on the miniaturization of the cellulose microfibers to obtain nanofibers to be incorporated into polymeric matrices for application as nano-reinforcement to edible films and polysaccharide hydrogels.
2.3.1 Miniaturization of cellulose microfibers for application in polymeric matrices

2.3.1.1 HPMC films

Recently, our research group [Moura et al., 2011] employed the microfluidics technology to decrease the size of cellulose microfibers and to study the effect of addition of such fibers on the properties of hydroxypropyl methylcellulose (HPMC) films with desired properties to be applied in food packaging. The particle size of fibers and mechanical properties, water vapor and oxygen permeabilities, total pore volume, and light and electron microscopy micrographs of films were analyzed. Data were analyzed by 2-sample t-Student tests, and one-way ANOVA with Tukey’s multiple comparison tests at 95% confidence level using Minitab version 14.12.0 statistical software (Minitab Inc., State College, PA, USA).

To deagglomerate the commercial cellulose fibers (trade name CF1), and to reduce their median particle size, a Microfluidizer® processor model M-110EH-30 was used, with a pressure of 20,000 psi. The most important results of this research will be now discussed. Fig. 1 shows the influence of the amount of passes through the Microfluidizer® on the size values of cellulose fibers. A Partica LA-910 laser scattering particle size distribution analyzer was used to obtain the particle size distribution, assuming particles shaped as spheres. A gradual decrease in the fiber size was observed with an increase in the number of passes of the fiber suspension through the Microfluidizer®. This trend may be explained by the fact that the processor equipment maximizes the energy-per-unit fluid volume, resulting in uniform submicron particle and droplet sizes. The CF1 fibers originally had an average size of 37.5 ± 2.5 µm. When 7, 10, and 20 passes of the fiber solution were done in the Microfluidizer® equipment the size values decreased to 6.8 ± 0.6, 5.2 ± 0.5 and 1.6 ± 0.9 µm, respectively.

![Fig. 1. Particle size of hydroxypropyl methylcellulose/cellulose fiber film-forming solutions affected by increasing number of passes in a Microfluidizer®. a,b,c Different letters indicated significant difference at P < 0.05 [Moura et al., 2011].](www.intechopen.com)
Fig. 2 shows that the size of the crystalline cellulose fibers, by birefringence under crossed polarizers, diminishes in size considerably following 7 passes in the Microfluidizer®. The fibers appear to continue to reduce in size following subsequent passes through the Microfluidizer®.

Fig. 3 shows the scanning electron microscopy micrographs of cross sections of HPMC films with crystalline cellulose fibers added. In Fig. 3a, the white spots throughout the HPMC film and on the surface are thought to be pores. In Fig. 3b HPMC film are viewed with the back-scattered electron detector to provide a slightly different view of the pores. The dark appearance of the pores indicates that they have less density than the surrounding material, thus they are likely to be voids or empty spaces. Fig. 3c and d shows HPMC with 1% cellulose fiber (CF1) with zero passes through the microfluidizer®. The CF1 are embedded in a smooth matrix of HPMC. Close examination of a fiber (Fig. 3d) shows that the fiber is made up of many smaller fibers. Fig. 3e and f shows the HPMC with CF1 films made with solutions after 7 passes through the microfluidizer®. The film has rough areas where small fibers have been incorporated as well as very smooth areas of HPMC. Some of the fibers are still in clumps. Fig. 3g and h shows the HPMC with CF1 films made with solutions after 10 passes while Fig. 3i and j correspond to films made with solutions after 20 passes. The fibers might be smaller and better-dispersed with increased numbers of passes through the Microfluidizer®.

Transparent, flexible, homogeneous, surface smooth films without pores and cracks were obtained after drying the film-forming solutions containing fibers and HPMC. Incorporation of cellulose fibers in the films improved their mechanical and barrier properties significantly. The percentage of elongation of the HPMC films changed when particle size was decreased as shown in Table 1. The increase of the elongation improved the tenacity of the films. The elastic modulus of the HPMC films increases with addition of the fibers and did not present significant variation with different sizes of fibers. In addition, the elasticity of the films was preserved with addition of microfibers. The suitable use of packaging is also strongly dependent on its favorable mechanical and barrier properties. The addition of microfibers to HPMC films results in significant improvements in film mechanical properties. Table 1 also shows the effects of size on tensile strength of microfibers/HPMC films. When CF1 fibers with 37.5 µm were included in the HPMC films, the tensile strength of the film was 18.4 ± 1.0 MPa. For films containing fibers with 6.8 µm, TS increased from 18.4 to 42.7 MPa. When the fiber size was decreased from 6.8 to 1.6 µm, TS increased to 70.0 MPa. This enhancement is attributed to the increased strength and bonding of smaller fibers with the HPMC matrix compared to HPMC matrix with CF1 without microfluidization. This reinforcing effect is attributed to the better dispersion into the HPMC matrix of the fibers with small size because of increased contact surface area between HPMC-microfluidized cellulose promoted by increased hydrogen bonding of cellulose fibers with the HPMC matrix.

The knowledge of gas permeability is essential for the application of polymers as oxygen barrier food packaging materials. The important factors that affect the permeability are its dependence on relative orientation of the fibers in the matrix and the state of aggregation and dispersion of these fibers in the film matrix [Bharadwaj, 2001]. Table 2 shows the values of water vapor permeability of HPMC film with fibers at different sizes at 25 °C. In general, it was observed that the presence of microfluidized fibers in the HPMC films decreased the values of WVP. For instance, the incorporation of fibers with around 1.6 µm decreased the WVP from 0.894 to 0.455 ± 0.010 g mm kPa⁻¹ h⁻¹ m⁻². So, the water vapor permeability
decreases with decreasing fiber sizes. The oxygen permeability of fibers/HPMC films (Table 2) were also analyzed, since they are important characteristics to be considered for a finished packaging material to increase the shelf life of foods [Miller & Krochta, 1997].

Fig. 2. Hydroxypropyl methylcellulose films incorporated with 1% cellulose fiber viewed through crossed polarizers to show the birefringence of the cellulose fibers in the matrix of the films. (a) zero passes; (b) after seven passes; (c) after ten passes and (d) after twenty passes through the Microfluidizer® [Moura et al., 2011].
Fig. 3. Cross sections of hydroxypropyl methylcellulose (HPMC) films viewed using scanning electron microscopy (SEM). (a) HPMC film; (b) HPMC film viewed with a backscattered electron detector; (c and d) HPMC with 1% cellulose fiber (CF1) with zero passes; (e and f) HPMC with CF1 after seven passes; (g and h) HPMC with CF1 after ten passes, and; (i and j) after twenty passes through the Microfluidizer® [Moura et al., 2011].
Microfluidizer Technique for Improving Microfiber Properties Incorporated Into Edible and Biodegradable Films

<table>
<thead>
<tr>
<th>Type of HPMC film</th>
<th>Thickness (µm)</th>
<th>Tensile strength (MPa)</th>
<th>Elastic modulus (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero passes (without CF1)</td>
<td>34 ± 2</td>
<td>28.3 ± 1.0</td>
<td>900 ± 34</td>
<td>8.1 ± 0.7</td>
</tr>
<tr>
<td>Zero passes (1% CF1)</td>
<td>57 ± 4</td>
<td>18.4 ± 1.5</td>
<td>783 ± 67</td>
<td>5.7 ± 1.1</td>
</tr>
<tr>
<td>After 7 passes (1% CF1)</td>
<td>36 ± 4</td>
<td>42.7 ± 1.9</td>
<td>1359 ± 110</td>
<td>13.6 ± 3.6</td>
</tr>
<tr>
<td>After 10 passes (1% CF1)</td>
<td>39 ± 2</td>
<td>52.3 ± 1.3</td>
<td>2273 ± 204</td>
<td>7.5 ± 1.7</td>
</tr>
<tr>
<td>After 20 passes (1% CF1)</td>
<td>39 ± 2</td>
<td>70.0 ± 3.2</td>
<td>1876 ± 162</td>
<td>10.6 ± 4.6</td>
</tr>
</tbody>
</table>

Different letters within a column indicated significant difference at P < 0.05.

Table 1. Effect of cellulose fibers (CF1) reduced in sizes after successive passes in a Microfluidizer® on thickness, elastic modulus, and elongation of hydroxypropyl methylcellulose (HPMC) films [Moura et al., 2011].

Our findings showed that the oxygen permeability (O₂P) of films containing fibers was markedly low, this feature being probably associated with the more compact structure of these materials determined by the dispersion of fibers in the HPMC matrix. The important result is that after the Microfluidizer® treatment of fibers, without chemical treatment, the O₂P values to the fibers/HPMC matrix decreased to 101.2 ± 0.1; 92.0 ± 0.2 and 85.0 ± 0.2 cm³ µm⁻² d⁻¹ kPa⁻¹ for fibers processed with 7 passes; 10 passes and 20 passes, respectively.

<table>
<thead>
<tr>
<th>Type of HPMC film</th>
<th>Water vapor permeability (g mm kPa⁻¹ h⁻¹ m⁻²)</th>
<th>Oxygen permeability (cm⁻³ µm⁻² d⁻¹ kPa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero passes (without CF1)</td>
<td>0.89 ± 0.03</td>
<td>182.4 ± 0.4</td>
</tr>
<tr>
<td>Zero passes (1% CF1)</td>
<td>0.95 ± 0.03</td>
<td>172.2 ± 0.3</td>
</tr>
<tr>
<td>After 7 passes (1% CF1)</td>
<td>0.49 ± 0.01</td>
<td>101.2 ± 0.1</td>
</tr>
<tr>
<td>After 10 passes (1% CF1)</td>
<td>0.46 ± 0.02</td>
<td>92.0 ± 0.2</td>
</tr>
<tr>
<td>After 20 passes (1% CF1)</td>
<td>0.46 ± 0.02</td>
<td>85.0 ± 0.2</td>
</tr>
</tbody>
</table>

Different letters within a column indicated significant difference at P < 0.05.

Table 2. Water vapor and oxygen permeability of hydroxypropyl methylcellulose (HPMC) film with cellulose fiber (CF1) reduced in sizes after successive passes in a Microfluidizer® [Moura et al., 2011].

In summary, our study demonstrated that the addition of fibers processed by microfluidics results in improvement of mechanical and barrier properties of the HPMC films. In special, the observed reductions in WVP and O₂P permeability are promising as a means to improve quality and shelf life of food or pharmaceutical products coated with these types of films.

2.3.1.2 Polysaccharide hydrogels

In other work developed by our group [Aouada et al., 2011], cellulose nanofibers (CNFibers) were extracted by acid hydrolysis from commercial fibrous cellulose powder (trade name CF11) and the effect of their incorporation on the mechanical, hydrophilic, thermal, morphological, microscopic and structural polyacrylamide-methyl cellulose (PAAm-MC) hydrogel properties was studied.

Firstly, CF11 was deagglomerated by using Microfluidizer processor (model M-110EH-30) at 20,000 psi, in order to facilitate the acid hydrolysis of the microfiber due to its better water
dispersion. After sulfuric acid hydrolysis, a highly stable suspension of hydrolyzed cellulose nanofibers was obtained from CF11. The opalescent suspension was the first indication of cellulose nanofiber extraction. The efficiency of the acid hydrolysis treatment was confirmed by the transmission electronic microscopy (TEM) technique (Figure 4) in which nanostructures with nanometer dimensions can be visualized. So, the network-structured cellulose nanocrystals were observed to exhibit micrometer-scale dimensions along both their length and width.

In this research, we can highlight that the Microfluidizer process is very efficient artifice to help obtain of the nanofibers with narrow size distribution. In general, the presence of the nanofibers improved mechanical and structural network properties without negatively impacting their thermal properties. For instance, the value of maximum compressive stress increased from 2.1 to 4.4 kPa when the cellulose nanofiber was incorporated into PAAm-MC hydrogel.

Here, we only show the effect of the nanofibers on the morphologic properties of the hydrogels and more results of the improvement of the PAAm-MC hydrogels by incorporation of the cellulosic specimens are showed in Aouada et al., 2011. Fig. 5a depicts the SEM micrograph of a PAAm-MC hydrogel swollen in water, whereby a highly porous structure with well-defined shapes exhibiting some spread in pore size was observed. The presence of cellulose specimens causes a significant decrease in pore size, and the formation of three-dimensional well-oriented pore structure can be observed (Fig. 5b). This trend is possibly related to the fact that the cellulose nanofibers are distributed around and inside the three-dimensional porous material. This effect is better demonstrated by an analysis of further enlarged SEM micrographs (Fig. 6).
3. Composite edible films

Nowadays, most materials used for food packaging are non-degradable, representing a serious environmental problem. Biopolymers materials have been increasingly exploited to develop edible and biodegradable films as an effort to extend shelf life and improve quality of food products while reducing packaging waste. However, the use of biopolymers has been limited because of problems related to performance, such as brittleness, poor gas and moisture vapor barrier, low degradation temperature, and cost.

Polymer composites are mixtures of polymers with inorganic or organic fillers with certain geometries (fibers, flakes, spheres, particulates). Several composites have been developed by adding reinforcing compounds to polymers to enhance their thermal, mechanical and barrier properties. Materials reinforced with macroscopic fillers usually contain defects and poor interactions at the filler-matrix interface, which become less important as the particles
of the reinforcing component are smaller [Ludueña et al., 2007]. The addition of reinforcements to biopolymers opens new possibilities for improving the properties and applicability of biopolymers as food packaging materials.

Edible films and coatings may be heterogeneous in nature, consisting of a blend of polysaccharides, protein, and/or lipids. The main objective of producing composite films is to improve the permeability or mechanical properties as dictated by the need of a specific application. These heterogeneous films are applied either in the form of an emulsion, suspension, or dispersion of the non-miscible constituents, or in successive layers (multilayer coatings or films), or in the form of a solution in a common solvent [Bourtoom, 2008]. Recently, many researchers have extensively explored the development of composite films based on the diverse works.

Composite edible films and coatings can enhance food quality, safety and stability. They can control mass transfer between components within a product, as well as between product and environment. They can improve performance of the product through the addition of antioxidants, antimicrobial agents, and other food additives. Composite films can be formulated to combine the advantages of each component. Biopolymers, such as proteins and polysaccharides, provide the supporting matrix for most composite films, and generally offer good barrier properties to gases, with hydrocolloid components providing a selective barrier to oxygen and carbon dioxide [Baldwin et al., 1997; Drake et al., 1991; Guilbert, 1986; Kester & Fennema, 1986; Wong et al., 1992]. Lipids provide a good barrier to water vapor [Nisperos-Carriedo, 1994], while plasticizers are necessary to enhance flexibility and improve mechanical properties. Monitoring the film formulation allows adapting the mechanical and barrier properties of these materials to the desired application, improving the efficacy of preservation for packaged foods.

### 3.1 Preparation and characterization

Composite films are prepared by using 2 or more hydrocolloids. This requires dissolution of biopolymer molecules. Some polysaccharides require solubilization at a higher temperature, while others require dissolution in a pH-regulated medium (e.g., chitosan).

Composite suspensions can be used to obtain either coatings or films. In the case of coatings, surface tension and rheological behavior of the suspension are important factors that will affect suspension spread ability and coating adhesion. In formulation of composite biopolymer films, it is important to characterize the miscibility of biopolymers and interactions that may occur between them, since these attributes ultimately influence film microstructure.

Films can be prepared by casting, extrusion or lamination, which are similar processes used in the synthetic polymer industry [Stepto & Tomka, 1987].

Casting is a common, small-scale production method used to obtain biodegradable films. In this technique, a portion of the film suspension is poured onto a surface (e.g., acrylic plates), and then dried in a ventilated oven or at room conditions. This simple technique produces films that can be easily removed from plates, and tolerates films of variable thickness to be obtained by varying the weight of film suspension applied and the area of the plate onto which films are cast (Fig. 7).
Fig. 7. Casting of polysaccharide films at room temperature.

The casting technique is frequently used in systems containing micro- and nanomaterials. In the study performed by Moura et al., 2009, the hydroxypropyl methylcellulose (HPMC) films with CS-TPP nanoparticles were obtained by addition of 3.0 g of HPMC in 100 mL of nanoparticle solution (recently synthesized) under magnetic stirring for 12 h. After the solutions were prepared, the flasks were kept closed during 6 h to prevent microbubble formation in the films. The solutions were then poured in a glass plate (30 x 30 cm) covered with Mylar (Polyester film, DuPont, Hopewell, Va., USA) for film casting preparation. The solutions were cast at a wet thickness of 0.5 mm onto plates using casting bars and the plates were placed on a leveled surface at room temperature and let dry for 24 h. After drying, the films were removed and conditioned in sealed plastic bags stored at room temperature.

Fig. 8 shows the effect of CS/TPP nanoparticles on tensile strength of HPMC films. There were significant differences in tensile strength, demonstrating that the incorporation of nanoparticles improved the resistance of the film.

Fig. 8. Effect of nanoparticles on tensile strength of HPMC films. Columns show the means and error bars indicate the standard deviations. Different letters within a column indicated significant difference at P < 0.05 [Moura et al., 2009].
The morphology of the composite HPMC films containing nanoparticles (221 nm) prepared by casting was analyzed through scanning electron microscopy (SEM). Control film prepared from a solution containing only 3% w/v of HPMC in water (Fig. 9a), exhibited a high degree of porosity evenly distributed throughout the film. Compaction of HPMC film was observed when chitosan nanoparticles were added as shown in Fig. 9b. This compacting further decreased WVP and increased tensile properties of films. This result confirms the efficiency of the method to prepare cast films with properties suitable for various applications.

![Fig. 9. Scanning electron microphotographs of (a) HPMC films and (b) HPMC films with CS-TPP nanoparticles of 221 nm [Moura et al., 2009].](image)

The main attributes involved in characterizing composite films are: optical properties, water-solubility, thickness, thermal behavior, barrier properties (water vapor and oxygen permeabilities) and mechanical properties.

All edible composite films should have the following properties as they are removed from the substrate drying: self-standing, peelable, colorless, flexible, easily handled, and with a homogenous, smooth surface. These characteristics should be the first analyzed after detached from casting substrate.

Solubility in water is an important property of edible films. Potential applications may require water insolubility to enhance product integrity and water resistance. However, in some cases, water solubility before consumption of the product might be beneficial [Pérez-Gago et al., 1999]. Film solubility in water was a very important characteristic of the polysaccharide films, because they must fully disintegrate upon immersion in aqueous solution. Turhan & Sahbaz, 2004 studied various aspects of methylcellulose (MC) films, including the solubility to evaluate the effects of film-forming solution composition and plasticizers on these properties.

The solubility of MC depends on its degree of substitution (DS), and MC used in this research (DS = 1.9) was reported as water-soluble. Films prepared only with water or water/ethanol dissolved slowly, whereas plasticized film pieces dissolved rapidly after coming into contact with water. The low dissolution rate indicated the high cohesion of MC matrix via numerous hydrogen bonds between MC chains.
It is important to know the behavior of any packaging material when exposed to changing temperatures during storage. The glass-rubber transition temperature ($T_g$) of a packaging material is an important parameter which controls mechanical properties, matrix chains dynamics, and swelling behavior. The glass transition is marked by a substantial change in molecular chain mobility. Below the $T_g$, the polymer chains show a minimum mobility and a low free volume resulting in great fragility and low diffusion properties; above $T_g$, the mobility sharply increases, and the mechanical and barrier properties of the polymer are impaired [S. L. Lee et al., 2008]. $T_g$ increasing effects of cellulose micro- or nanofibers on polymer films have been reported [Alemdar & Sain, 2008; Anglès & Dufresne, 2000], probably because of the restricted mobility of polymer chains in the vicinity of the interfacial area.

The barrier properties of a food packaging material are related to the transport of gases or vapors through the material, influencing the preservation of the food quality. Oxygen permeation through the package may cause oxidation in lipid foods that result in off-flavors (the so-called oxidative rancidity), color changes and nutrient losses.

All the properties that describe the reactions of a material to application of forces are named mechanical properties. The kind of force involved, its time of application, magnitude, direction etc. are important to define different properties. Particularly important for packaging materials are tensile properties. Zimmermann et al., 2004 reported that the addition of cellulose fibrils to polymer matrices increased their tensile strength and elastic modulus.

4. Microfibers reinforced films and edible films

In an overview study, Sanchez-Garcia et al., 2010a described some important works related to addition of cellulose fibers and nanowhiskers for mechanical, thermal stability and barrier performance improvements of different matrices [Fendler et al., 2007; Kvien et al., 2005; Orts et al., 2005; Petersson et al., 2007; Tserki et al., 2006].

Other authors have proposed the addition of microfibers from different sources as reinforcement agent for improvement of the final film properties. The study realized by Dogan and McHugh, 2007 was the first to investigate the use of different size fillers for the purpose of preparing edible composite films. In this pioneering work, the inclusion of MCC (microcrystalline cellulose) fillers in different sizes on water vapor permeability and mechanical properties of HPMC based films was investigated. Measurements of the light scattering particle size analyzer indicated that the mean particle sizes of MCC were 0.5, 1.5, and 3.0 μm and the images from scanning electronic microscopy indicated that these MCC had rod-like shape. According to the authors, a decrease in diffusion coefficient is expected with the addition of cellulose fibrils because the diffusion of water in the films depends on the available pathways for water molecules. However, there was no observed noticeable difference in water vapor permeability of these composite films when compared to neat HPMC films. On the other hand, by analyzing the elongation and tensile strength, it was possible to see clearly the reinforcing effect of MCC fillers. For instance, tensile strength of films increased around 10% with the addition of 1.5 - and 3.0-μm MCC fibers to over 100% with the addition of 0.5 μm MCC to HPMC films. The authors also relates the importance of the edible films and coatings in foods as materials that increase shelf-life and improve
sensory characteristics of foods by avoiding deterioration of food components and therefore promoting preservation of the final product. In addition, the composite materials with improved properties made from polymers reinforced with organic-based filler materials have received significant interest starting from the mid-1990s, when Favier et al., 1997 showed that the addition of 3% to 6% crystalline cellulose in a copolymer acrylate latex film increased dynamic modulus by more than 3-fold.

The addition of cellulose fibers to enhance the mechanical and moisture barrier properties of the starch films was reported by Muller et al., 2009. Composite films were prepared by casting technique from a suspension containing cassava starch, glycerol, water and cellulose fiber with 1.2 mm in length and 0.1 mm in diameter. The authors observed that the incorporation of cellulose fibers reduced the films moisture uptake due to the lower water affinity of cellulose fibers compared to starch. Also, films reinforced with fibers presented higher values of tensile strength and elasticity modulus, and lower values of elongation at break when compared to non-reinforced films. For example, the incorporation of 0.10 and 0.50 g fiber/g starch increased the tensile strength of reinforced films 6.7 and 18 times respectively, showing the reinforcement effect of the fibers addition. The addition of the fiber suspension also decreased the water vapor permeability of the starch films because of the low hygroscopicity of cellulose fibers. In fact, the water vapor permeability depends on both water diffusivity in the polymeric matrix and the solubility coefficient of water in the film [Larotonda et al., 2005; Muller et al., 2007].

Mango purees edible films reinforced by Azeredo et al., 2009 with cellulose nanofibers (CNF). CNF were effective in increasing tensile strength, and even more noticeable in enhancing elastic modulus, which increased more than 100% with a CNF loading of 10 g/100 g matrix. The remarkable effect of CNF on modulus was ascribed to the formation of a fibrillar network within the matrix, the fibers being probably linked through hydrogen bonds [Helbert et al., 1996]. The addition of CNF was also effective to improve water vapor barrier of the films.

Azeredo et al., 2010 reported effects of CNF in enhancing tensile strength, elastic modulus and water vapor barrier of chitosan films. CNF showed no specific orientation when observed by atomic force microscopy (AFM), which suggests an exfoliated nanocomposite, with good dispersion of CNF in the matrix, which explains the good performance of the nanocomposite films.

Sanchez-Garcia et al., 2010b reported enhanced water vapor barrier of carrageenan films due to incorporation of cellulose whiskers (CW), prepared by acid hydrolysis of highly purified cellulose microfibers. The nanobiocomposites containing 3 wt % of CW exhibited 71% reduction in water vapor permeability, which was mainly attributed to a filler-induced water solubility reduction. However, TEM and water vapor permeability data suggest that increasing the nanofiller loading in excess of 3 wt % leads to agglomeration of CW due to hydrogen-bonding-induced self-association.

By adding of the jute micro/nanofibrils (JNF) to starch/polyvinyl alcohol (PVA), Das et al., 2011 prepared and characterized different biocomposite films reinforced with 5, 10 and 15 wt.% JNF produced by solution casting method and using glycerol as plasticizer. Tensile properties results indicated that the tensile strength of the biocomposite films (5, 10 and 15 wt.% filler loaded) increased by 51%, 130% and 197% respectively in comparison to the
unreinforced one. The authors attributed this increase to very fine nature of JNF and due to effective stress transfer at the interface between the matrix and JNF. The uniform dispersion of the JNF in the matrix and effective intercomponent bonding significantly increased the thermal stability of these biocomposites. Another important result proceeding of the fiber incorporation is that the moisture uptake decreased in all the biocomposite films compared to the unreinforced one. Possibly, this decreasing is related to lowering in the amount of free hydroxyl groups of the matrix which took part in hydrogen bonding with the JNF and the incorporation of JNF provided a stabilization effect to the matrix by forming a three dimensional cellulosic network which strongly restricted the dissolution of the matrix in water. Finally, according to the authors, the 10 wt.% JNF loaded films exhibited the best combination of moisture uptake behaviour, mechanical, thermal, and morphologic properties.

5. Final remarks

Researches on biopolymer based edible and biodegradable films have been a tendency for food packaging in times of great concern about the huge waste accumulation derived from the extensive use of non-biodegradable packaging materials. However, biopolymers have limited barrier and mechanical properties, requiring reinforcements to improve their performance. Cellulose micro- and nanofibrils have been extensively studied as reinforcement materials for biopolymers, since their good mechanical properties, biodegradability and compatibility with most biopolymers favor such applications. This kind of improvement in biopolymer based materials is of utmost importance when trying to replace (at least partially) the conventional petroleum-based polymers by biodegradable materials in packaging sector. Microfluidization has been shown as a useful technology to improve the applicability of cellulose microfibers as reinforcements to biobased packagings, enhancing cellulose interactions with the matrices and the resulting performance of the resulting composite materials.

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7. References


Advances in Microfluidics


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Advances in Microfluidics provides a current snapshot of the field of microfluidics as it relates to a variety of sub-disciplines. The chapters have been divided into three sections: Fluid Dynamics, Technology, and Applications, although a number of the chapters contain aspects that make them applicable to more than one section. It is hoped that this book will serve as a useful resource for recent entrants to the field as well as for established practitioners.

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