Pectin – Candelilla Wax: An Alternative Mixture for Edible Films

Olga B. Álvarez-Pérez1, Julio Montañez1, Cristóbal N. Aguilar2 and Romeo Rojas2,*

Addresses: Dr. Romeo Rojas,
1Universidad Autónoma de Coahuila, School of Chemistry, Food Research Department, Boulevard Venustiano Carranza S/N, 25280, Saltillo, Coahuila, México, Tel.: 01 844 416 1238.
2Universidad Autónoma de Nuevo León, School of Agronomy, Agricultural Sciences Campus, Research Center and Development for Food Industries – CIDIA, Francisco Villa S/N, Col. Ex-Hacienda El Canadá, 66050, Escobedo, Nuevo León, México, Tel.: 01 811 340 4399.

*Corresponding author: romeo.rojasmln@uanl.edu.mx

ARTICLE INFO
Received 1. 7. 2013
Revised 11.2. 2015
Accepted 16.7. 2015
Published 1. 10. 2015

ABSTRACT
Edible films and coatings have received special attention in recent years due to the advantages that represent their use as edible packaging over synthetic plastics. This contributes in high degree to reduce the environmental pollution with non-biodegradable materials. By functioning as barriers, such edible films and coatings can improve the recycling and/or substitute some synthetic packaging materials. New packaging materials have been developed and characterized by some scientists from natural sources (biomaterials); however, it is necessary the manufacture tailor-made to every food. The main objective of this review is to provide basic and applied information and benefits that can be generate the use of two products with low cost (candelilla wax and pectin), but with great importance in the food industry and that can be used to manufacture edible films and coatings.

Keywords: Pectin, candelilla wax, glycerol, edible films, foods

INTRODUCTION
Two of the major problems in the food industry are the waste disposal from fruit industry and the short shelf life of fresh products. However, at present there are few but important alternative, like eco-solutions, for these problems, such as composts, the use as supports for solid-state fermentation, recovery of bioactive compounds, etc. Among these, we can find the recovery of pectin for use as an additive in the food industry (jams, preserves, jams, jellies, cheeses, ice creams, sauces, etc.). The main sources of pectin are apples, citrus, pineapple, guava, tomato, passion fruit and beetroot. It is worth mentioning that the quality of pectin depends on the source and the extraction process (physico-chemical or enzymatic). Also used in other industries such as pharmaceuticals, to modify the viscosity of their products and in the plastics industry and in the production of sparkling wines, as fining agent and binders (Gomez, 1998). However, there are some studies that point to the possibility of generating biomaterials (biofilms, biodegradable) to coat and extend the shelf life of these products fruits.

PECTIN
Pectin is a complex hetero-polysaccharide, which is present in nature (fruits and vegetables in particular) as a structural element of the cellular system of the plants (cell wall) with important roles in their physiology (Contreras-Esquível et al., 2006; Voragen et al., 2009; Qiu et al., 2009; Jamsazzadeh-Kermani et al., 2015). Chemically are linear chains of D-galacturonic acid joined by α-1,4-glycosidic linkages, which is partially esterified with methanol (Albertsheim et al., 1996; Berardini et al., 2005; Lazar, 2005; Xie et al., 2008; Fishman et al., 2015) (Fig 1.).

The amount of esterified units influences the properties and functional classification. Commercially are divided into pectin with a degree of methylation above 50% called high methoxyl (HMP), which gels very easily after heating in sugar solutions at a concentration above 55% and a pH of less than 3.5. Furthermore, the gel formation with low methoxyl pectin (LMP; DM <50%) requires the presence of calcium ions, this can be used as a gelling agent in low-sugar products such as jams and jellies low calorie (Oakenful and Scott, 1984; Pszczola, 1991; Thakur et al., 1997; Contreras-Esquível et al., 2006; Jamsazzadeh-Kermani et al., 2014). Usually, low methoxyl pectins are produced by high methoxyl pectins demethylation methods in which various agents can be used: acid, alkali, enzymes, and ammonia in alcohol (Iglesias and Lozano, 2004). Traditionally, the pectin is obtained from raw materials at acidic conditions with elevated temperatures (Koubala et al., 2008; Wang et al., 2014), followed by precipitation using alcohols such as isopropylalcohol (IPA), methanol or ethanol. (May, 1998; Fishman and Cooke, 2009; Zhang et al., 2013; Xu et al., 2014).

Figure 1 Chemical structure of pectin
Chemical Composition

Chemically, pectin’s are macromolecules composed of a complex group of heteropolysaccharides. Pectin molecules consist of three different sequences known as homogalacturonan (HGA), rhamnogalacturonan I (RG-I) and rhamnogalacturonan-II (RG-II), which constitute the two main regions of pectin, i.e. the linear region (HGA) and branched region (RG-I,II). Homogalacturonan consists α acid residues D-galacturonic α -4 linked together with partially methylated substitutions and / or acetylated, which are interrupted by L-rhamnose residues in adjacent positions and/or staggared. RG-I consists of a disaccharide repeat units [2] - α-L-rhamnose-acid-α-1,4-D-galacturonan-1], plus units also contain L-arabinose and D- mainly galactose, while the RG-II is a low molecular weight region, which is composed of a backbone of units of D-galacturonic acid α -4 linked together and some other rare sugars such as apo, 2 -O-methyl-fucose, 2 -O-methyl-xyllose, 2-keto-3-deoxy-D-mannan- octululonic (KDO), 3-C-carboxy-S-deoxy-L-xylolyl, among others; in both cases the content of such sugars vary depending upon the source, location, extraction method and other environmental factors (Berardini et al., 2005; Contreras-Esquivel et al., 2006; Yuliarti et al., 2015)

CANDELILLA

The plant (Euphorbia antisyphilitica Zucc) is a perennial shrub with densely compact, erect, cylindrical stems coated in wax (serves as protection for moisture retention), with the appearance of small candles, leafless and that becomes full of small flowers in the rainy season (Scora et al., 1995; Saucedo-Pompa, 2007). It belongs to the Euphorbiaceae family (Steinmann, 2002) and is considered an endemic species of the semiarid regions of the states of Chihuahua, Coahuila, Durango, Hidalgo, Nuevo Leon, Oaxaca, Puebla, Queretaro, San Luis Potosi, Tamaulipas and Zacatecas, Mexico. In the United States of America, is distributed in the states of New Mexico and Texas. This plant promotes the growth of some other plants such as Lechuguilla and Sotol. Its uses date back to the Indians of northern Mexico that used for ornamental or plant used as candles, to bend a bow, tanning hides and traditional medicine (Romahn, 1992; Kowalczek and Baraniak, 2014).

Candelilla wax

Candelilla wax is a complex material, hard, shiny and easy spray that is derived from plant with the same name through a "traditional" extraction of candelilla wax using a boiling solution of sulfuric acid (scrap fertilizer industry) in which the plant is submerged and the wax is recovered as a foam on the boiling water surface. However, this process is highly polluting, generates low quality wax and high health damage. Its color varies from light brown to yellow depending on the degree of refining. This material serum is used to harden other waxes, manufacturing synthetic polishes, polishes, for transport and storage of products as well as in various industries such as food, cosmetics, electrical, mechanical and plastic production (Cervantes-Ramírez, 2005; Canales-Gutiérrez et al., 2005; Rojas-Molina et al., 2011; Rojas-Molina et al., 2013).

Chemical Composition

Chemically, are esters of fatty acids and long chain fatty acids. Characterized by a high content of hydrocarbons (about 50%) and a relatively low amount of volatile esters. Its resin content can reach 40% of its weight, which gives it a sticky consistency. Insoluble in water, but soluble in acetone, chloroform, benzene and other organic solvents. (CENAMEX, 2006; Ochoa et al., 2011; Rojas-Molina et al., 2013). The following tables describe the composition and physicochemical properties of candelilla wax and because make it one of the most versatile products for industry (Tables 1 and 2).

Table 1 Typical composition of refined candelilla wax

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbons</td>
<td>50-57</td>
</tr>
<tr>
<td>Nonacosenne</td>
<td>2.5</td>
</tr>
<tr>
<td>Hentriacontane</td>
<td>46-46.5</td>
</tr>
<tr>
<td>Tritriacontane</td>
<td>2.5</td>
</tr>
<tr>
<td>Esters</td>
<td>28-29</td>
</tr>
<tr>
<td>Simple esters and lactones</td>
<td>20-21</td>
</tr>
<tr>
<td>Hydroxilated esters</td>
<td>6-8%</td>
</tr>
<tr>
<td>Alcohols, Esterols y Resines</td>
<td>12-14</td>
</tr>
<tr>
<td>Miricilic alcohol</td>
<td>ND</td>
</tr>
</tbody>
</table>

Table 2 Physico-chemical composition of candelilla wax

<table>
<thead>
<tr>
<th>Properties</th>
<th>Refined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity value</td>
<td>12-22</td>
</tr>
<tr>
<td>Iodine index</td>
<td>14-27</td>
</tr>
<tr>
<td>Saponification number</td>
<td>35-87</td>
</tr>
<tr>
<td>Melting point</td>
<td>67-79 °C</td>
</tr>
<tr>
<td>Refraction index</td>
<td>1.4545-1.462 @ 85 °C</td>
</tr>
<tr>
<td>Unsaponificable material</td>
<td>67-77</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.885</td>
</tr>
<tr>
<td>Flame point</td>
<td>-----</td>
</tr>
</tbody>
</table>


EDIBLE FILMS

Conservation through coatings is an ancient practice that was developed to mimic natural edible covers of vegetable products. There are reports dating from the twelfth and thirteenth centuries in which it is mentioned that in China, oranges and limes were dipping in wax to retard water loss (Kaplan, 1986; Greenner and Fenemna, 1994). During the sixteenth century in England was practiced the “buttered”, that is the fat use as a coating of food products to prevent moisture loss also of these. In the nineteenth century were used films based on gelatin for preservation of meats and other foods, around the 30s, paraffin waxes were already commercially available, that melted with heat, was used for coating citrus (Nussinovich and Lurie, 1995; Park et al., 2014), and in the early 50s were developed oil-water emulsions of carnauba wax for coating fresh fruits and vegetables (Kaplan, 1986; Kester and Fenemna, 1986). From the mid 50s to mid 80% a lot of work was focused on the use of films and coatings to extend shelf life and improve the quality of fresh, frozen and processed foods, which has been reported in both the scientific literature as patent. Unfortunately, most of this work is of limited value because of the lack of quantitative data on the characteristics of barrier coatings. It has been reported that the waxes were first used in edible coatings on fruits like apples and pears. In recent years, it has been reported that it is possible to achieve similar effects barrier to water vapor and gases in diverse products using different mixtures of oils (Shojaee-Allabadi et al., 2014; Wang et al., 2014a; Sanchez-Aldana et al., 2015), waxes (Fagundes et al., 2014; Pérez-Gago and Rhim, 2014; Rodrigues et al., 2014; De Leon-Zapata et al., 2015), proteins (Vonasek et al., 2014; Khanzadi et al., 2015; Hopkins et al., 2015) and polysaccharides (Costa et al., 2015; Wan et al., 2015; Razavi et al., 2015; Gutiérrez et al., 2015; Dang and Yoksan, 2015) The growing demand for food maintain maximum organoleptic properties, has fostered the continuous improvement of the processes used in the food industry in order to ensure its preservation and without affecting the quality and shelf life (Soliva-Fortuny and Martin-Bellosio, 2001; Ochoa et al., 2011; De Leon Zapata et al., 2015). The development of edible films and coatings and biodegradable coatings has received the most attention because it leads to the extension of the shelf life of food. Edible films are defined as one or more thin layers of a material that can be consumed by living organisms and which in turn can act as a barrier to the transfer of water, solutes and gases of food (Guilbert et al., 2006). Krotcha et al. (1994) defined edible films as thin continuous layers of edible material formed on (as a cover) or placed between the food components, and provide a means to carry food ingredients or additives and improve the handling of the thereof.

Interest in the edible films have grown considerably, because have several advantages, they can be ingested by the consumer, the cost is usually low, their use reduces waste and pollution, can improve the organoleptic, mechanical and nutritional properties in food, provide personal protection to small pieces or portions of food and can be used in heterogeneous foods as barriers between components. Edible films should be good moisture barrier to protect the food completely coated, have good barrier properties against oxygen, and have good mechanical and organoleptic properties (Guilbert et al., 2006; Sánchez-Aldana et al., 2014). However, for the development of these films is necessary to consider the mechanical factors involved in chemical and physical storage of the fruit. They can provide nutritional and organoleptic properties to foods when...
added antioxidants (Saucedo-Pompa et al., 2009; Ochoa et al., 2013; Ferreira et al., 2014; De León Zapata et al., 2015), artificial colors or flavors (Perez and Gaonkar, 2014; Kim et al., 2014) and other additives (Arrieta et al., 2014; Chiumarelli et al., 2014; Jouki et al., 2014; Kulkarni et al., 2015).

Lipid-polysaccharide Interactions

The feasibility of the formulation of edible coatings based on candelilla wax and pectin is based on pectin-lipid interaction. Due to candelilla wax are long chain fatty acids, the presence of certain interactions may occur between the polyols and the carboxylic moisties of pectin. An example is the occurrence of hydrogen bonds between methoxycarbonyl groups with oleic acid as the main bonding force. This was demonstrated by Falk and Nøgyvary, (1982) in their study exploratory of pectin-lipid interactions by using C13 NMR. However, the galacturonan seconuronic acid sequence is able to form hydrogen bonds with cholesterol or linoleic acid molecules probably due to the difference of conformation of the two molecules (Pau-Rohlot et al., 2010). This is because the long-chain lipid (in this case, candelilla wax) may interact with most of the carbons in a “pocket apolar” in the galacturonic and with the helix structure of glucuronic that provides only external carbon to interact with the lipid. Furthermore it is known that pectin under optimal conditions (in a physiological system) can bind four times its weight in lipids (Falk and Nøgyvary, 1982).

Films based on lipid-polysaccharides emulsions

In the formulation of films and coatings, it is necessary to use at least one component capable of forming a structural matrix with sufficient cohesiveness. Edible films made by combining several compounds, have been refined to take additional functional properties of each component, thus minimizing their disadvantages. Film forming substances create a continuous structure through interactions between molecules under the action of a physical or chemical treatment (Bureau and Multan, 1995; Guillbert et al., 1996; Debeaufort et al., 1998; Soliva-Fortuny and Martin-Belloso, 2001). Film forming polysaccharide frequently involves the formation of a gel and/or solvent evaporation. The polysaccharides can be used in the preparation of edible films. Generally produce films with good mechanical properties and are effective barriers against non-polar compounds. However, its hydrophilic nature makes present a low resistance to water loss (Parra et al., 2004). Its selectivity regarding permeability to oxygen and carbon dioxide conditions creating modified atmosphere inside the food, resulting in an increased product life.

Polymeric films, in general, have been studied as edible film forming materials (Diab et al., 2001; Lizardoiu and Billaderos, 2002; Marianello et al., 2003, Lee et al., 2004, Parra et al., 2004, Thomas et al., 2004; Turhan and Sahbaz, 2004; Tapia Blácido et al., 2005; de Brito et al., 2013; Arancibia et al., 2014; Lucenius et al., 2014; Mohan et al., 2015; Yang et al., 2015). These compounds have the characteristics of being long-chain polymers, soluble in water and produce a strong increase in viscosity when dispersed in it. So the use of a polysaccharide such as pectin for the manufacture of biomaterials for fresh fruit conservation is not a good alternative for its high hydrophilicity and water vapor permeability. For this reason, it is necessary the use of a lipid component in the formulation to improve the properties of the laminate. Edible films made from combinations of materials, like candelilla wax. These materials are typically used with the purpose of providing hydrophobicity to a certain surface and make an effective barrier against moisture (Soliva-Fortuny and Martin-Belloso, 2001). However, their use individually, not mixed with other substances, is limited because most lack sufficient structural integrity and stability. Therefore, generally requires the presence of a matrix serving as support. In this regard, studies on edible films and coatings using mixtures of lipid compounds and proteins or carbohydrates (support material) were made in order to exploit the characteristics of each material, improving the final properties of the films (Aguilar-Mendez, 2005). For this purpose, is considering the use of a polysaccharide and a lipid component, for the preparation of edible films. Saucedo Pompa et al. (2009) studied the effect of the addition of elagic acid in a matrix of Candelilla wax on quality and shelf life of avocados. According to their results using elagic acid as part of an edible film that significantly minimizes changes in appearance, solid content, pH, aw, lightness and weight loss, maintaining the quality of avocados, prolonging its shelf life. Furthermore, films were able to significantly reduce the damage caused by C. glomerata (Paudel et al.) major fungi which attack these fruits. It is found that using this new protection system, the negative effects by this fungus can be reduced satisfactorily.

视角的创新，使用低脂肪的水性系统，作为物理或化学处理。然而，硫酸软骨素硫酸序列能够形成氢键与胆固醇或亚油酸分子可能由于其碳的差异的两分子（Pau-Rohlot et al., 2010）。这是因为长链脂肪（在这种情况下，卡丹利蜡）可能与大多数碳在一个“pocket apolar”在硫酸软骨素和与螺旋结构的硫酸根，提供了只外部碳与介面的脂质。此外，已经知道pectin在最优条件下（在一个生理系统）可以与水结合四倍其重量的脂质（Falk和Nøgyvary, 1982）。

基于脂-多糖的食用薄膜

在薄膜和涂层的制备中，需要至少一个成分能够形成一个结构化的矩阵，具有足够的粘附性。由几种化合物组成的食用薄膜，已经得到一定程度的改良，通过每个成分的额外功能，从而最小化它们的缺点。形成薄膜的物质通常涉及形成一个凝胶以及/或溶剂蒸发。这些多糖化合物可用于食用薄膜的制备。通常产生具有良好机械性能且是有效的非极性化合物的障碍。然而，其亲水性自然使其具有较低的水分蒸发，导致水分损失（Parra et al., 2004）。就其选择性而言，对氧气和二氧化碳条件产生变化，形成调理气氛在食品内，导致产品生活延长。

聚meric薄膜，在一般情况下，已经研究使用可作为可食用薄膜形成材料的材料（Diab et al., 2001; Lizardoiu and Billaderos, 2002; Marianello et al., 2003, Lee et al., 2004, Parra et al., 2004, Thomas et al., 2004; Turhan and Sahbaz, 2004; Tapia Blácido et al., 2005; de Brito et al., 2013; Arancibia et al., 2014; Lucenius et al., 2014; Mohan et al., 2015; Yang et al., 2015）。这些化合物具有长链的特性，可溶于水且可产生强烈的增加在分散于其中的粘度。因此，使用一分子可食用多糖，如pectin制造生物材料的薄膜对新鲜水果的保鲜并不是一个很好的选择，对于其高的亲水性和水分蒸汽的渗透性。因此，这就需要使用一种脂质成分在配方中改善膜的性质，以改善其对水分的抵抗力。用此方法，可使用制造薄膜以达到表面的特定表面且做出有效防潮的障碍（Soliva-Fortuny and Martin-Belloso, 2001）。然而，单独使用的使用，不与其他物质混合，是有限的因为大多数缺乏足够的结构完整性及稳定性。因此，通常需要一个矩阵作为支持。在这种关系中，对可食用薄膜和涂层使用混合脂质成分和蛋白质或碳水化合物（支撑材料）进行了研究，以充分利用每个材料的特性，改进其最终薄膜的性能（Aguilar-Mendez, 2005）。为此目的，正在考虑使用一种多糖和一脂质成分，用于食用薄膜成分的制备。Saucedo Pompa et al. (2009)研究了添加亚利基酸在卡丹利蜡基质上的效果，以及对牛油果质量及货架期的影响。根据其结果，使用亚利基酸作为可食用薄膜的一部分可以显著改变外观，固体含量，pH，aw，光泽度和重量损失，保持牛油果的质量，延长其货架期。此外，薄膜能够显著地减少由C. glomerata（Paudel et al.）主要真菌对其作物的损害。它被发现使用这种新的保护系统，这种真菌的负面影响可以被显著地减少。
Euphorbia antisyphilitica. Influence of cassava starch and delilla wax on alligatory find uses in fat transmission in some blends of cassava starch edible films. Journal of Food Engineering, 61, 61-63.


