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New green coatings made from fatty acid dispersions: improvement in barrier properties of biodegradable thermoplasticized-starch substrate

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This work was aimed at developing new coatings on biodegradable substrates for possible use in food packaging. In order to study barrier properties of these coatings made from fatty acid dispersions, oxygen permeability, water vapor permeability and also contact angle measurements were carried out. The coatings made from a fatty acid exhibited good barrier properties towards oxygen gas. Moreover, these coatings presented a higher contact angle value than the one obtained directly for the substrate without coating; this can be likely due to the hydrophobic nature of fatty acid and the recrystallization of fatty acid during the drying process.

Keywords: environmental friendly coatings; fatty acid; barrier properties; biodegradable thermoplasticized starch; food packaging.

Introduction

Important improvements have been made over the past few years in the field of bio-resources for the chemical industry. This is due to the introduction of new raw materials produced from plants; these materials are called agro-resources. The use of these natural resources is motivated by their huge abundance and their renewable nature. These polymers are biodegradable and as a result present an answer to many environmental issues in many areas including the biomedical and packaging fields.

The food industry is one of the main users of plastic for packaging. The primary role of packaging is to protect its contents. The preservation of food products requires specific packaging with very efficient barrier properties, especially toward oxygen gas and/or water. It is well known that some biodegradable polymers have barrier properties against gas and water vapor. For example, many studies have been devoted to poly-L-lactide (PLA) [1] This aliphatic polyester presents a medium-level water and oxygen permeability similar to polystyrene [2,3]. These properties limit its use to packaging very fresh products that have a short lifetime. Furthermore, packaging made from natural polymers is not always efficient in preserving food. This problem can be overcome by structuring the bio-packaging in different ways such as multi-layers, surface modifications, or coatings. In these cases, the layers or coatings have a specific property.

In order to produce barrier properties to water and oxygen gas, we have chosen to develop the use of fatty acids as green coatings. Indeed, thanks to their hydrophobic feature, fatty acids can act as a barrier toward water and oxygen. This idea was motivated by the fact that barrier property toward water and gas is common in nature. For example fruit skins that contain cutin, have surface barriers properties [4,5]. Cutin can be described as a polymeric network of esterified hydroxyl and dicarboxylic fatty acid with 16 and 18 atoms of carbon.

The polymorphism of lipids in aqueous solution has been widely studied. They are generally added in formulations based on proteins or polysaccharides as edible food coatings in order to improve barrier properties to water [6,7]. The idea of replacing coatings made from synthetic polymers by green environmental-friendly coatings has been developed over the past few years in many areas including the biomedical [8] and corrosion protection fields [9–11]. Nevertheless, the use of fatty acid as hydrophobic coatings has not been well researched. Recent works [12,13] have reported the use of stearic acid as a coating on magnesium substrates for biomedical applications. The authors only studied the corrosion resistance of these coatings and did not report on other properties or other substrates. No study has been reported in the literature on using lipids or fatty acid in the packaging field. One reason for this is that very few works on fatty acid dispersions in solution have been reported. Fatty acids have been used in the industrial field, and a few studies have approached the problem from a physicochemical point of view of their properties in solution. However, their very low solubility in water limits their applicability. Nevertheless, recently great progress was made in this area, and it was shown that mixtures of fatty acid can form stable dispersions under controlled experimental conditions [14–17]. For instance, it is possible to disperse fatty acids water in using soluble organic counterions. The counterions can be tetrabutyl ammonium hydroxide, choline, ethanolamine, or lysine [18].

The present work involves the development of new green coatings made from palmitic acid dispersions on a biodegradable thermoplasticized-starch substrate, with the coating acting as a barrier toward oxygen gas and water vapor. Contact angle measurements and scanning electronic microscopic images were used to characterize the coatings. The barrier properties found for the biodegradable substrate with and without coatings were compared with those of commercial plastics.

Materials and methods

Preparation of the fatty acid dispersions

Palmitic acid (Sigma–Aldrich, 98% purity) was weighed exactly in a tube, and ultrapure water was added so that the concentration was 10 mg/mL. Then, the desired volume of a 1 M stock solution of ethanolamine (Sigma–Aldrich, 99% purity) was prepared in ultrapure water and added to the solution in the tube to produce three solutions with the fatty acid to ethanolamine molar ratios of 0.5, 1 and 1.6. The mixture was melted at 80 °C for 15 min until all components were dispersed and then vigorously stirred. Then, all mixtures were stored at −20 °C. Prior to using, each sample was heated at 80 °C for 15 min and cooled at room temperature [15].

Substrate

A French company, Vegeplast (Bazet, France), expert in the field of transformation of renewable resources into 100% biodegradable plastic by injection molding, had developed a new green material in order to substitute petrochemical plastics. In this study, a substrate of a biodegradable thermoplasticized polymer made from maize starch [19] was coated with an environmental-friendly coating. In order to evaluate the properties of the coating, measurements

on commercial plastic (expanded polystyrene) were also made. This type of plastic has been chosen by our industrial partners because it represented one of the plastic materials used in food packaging.

Coatings elaboration

The coating was made just after the preparation of the fatty acid dispersions in order to keep the dispersion stable without risking the recrystallization of the fatty acid. This ensured that the fatty acid was homogenously laid down and not in the form of crystals. Moreover, fatty acid dispersions were rehomogenized prior to the coating process.

The fatty acid layer was prepared by a dip-coating technique using an NIMA DC Mono 160 (NIMA Technology, Coventry, England) instrument. This technique involved immersing the substrates in the dispersion at a controlled rate of withdrawal (250 mm/min). The immersion was done twice and each time, the substrate was maintained in the dispersion for 60 s. After the deposition process, the samples were dried at 20 °C for 2 h. The coatings were replicated in order to verify the reproducibility of the experiments. The thickness of the biodegradable substrate without a coating was 0.865 ± 0.003, mm whereas that of the substrate with a coating was 0.876 ± 0.003 mm. The thickness of the commercial plastic (expanded polystyrene) was 0.585 ± 0.018. For all cases the area of the substrate on which the oxygen permeability was measured was 78.5 cm^2; the substrate samples had a diameter of 10 cm.

Contact angle measurements

To evaluate the surface hydrophobicity of biodegradable thermoplastic starch with and without coatings, contact angles were determined by a calibrated drop technique, using a DGD Fast 60 goniometer (GBX Scientific Instruments, Bourg de Peage, France) coupled with software (Windrop++) to capture and analyze the images. Four microliters of an aqueous solution was deposited onto the substrate which was placed on an X–Y stage. The reported contact angle results were the average values of at least five measurements,with each at different positions on the substrate surface.

The contact angle measurements on the biodegradable substrate with coatings were made at three different times— 1 day, 12 days, and finally 21 days after the coating elaboration— in order to follow the evolution of the surface hydrophobicity of the coating with the aging of the coatings. These times have been chosen because they were representative of the food industry: For example, 21 days corresponded to the best-before date of a fresh product such as cheese or yoghurt.

Optical microscopic images

In order to characterize the samples, a surface optical microscope (VHX-1000 Keyence, Osaka, Japan) was used with a VH-Z100 W objective.

Water vapor permeability (WVP)

The water vapor permeability (WVP) was determined according to the ASTM E96-95. The materials were firmly fixed onto the test cells containing anhydrous $CaCl_2$. The system was weighed using an analytical balance (0.0001 g accuracy) and then maintained at 25 °C and 60% relative humidity (RH). Inside the cell, anhydrous $CaCl_2$ absorbed the water vapor and maintained a partial pressure close to 0. The difference in partial vapor pressure between the

inside and the outside of the cell was 1875 Pa. The water vapor permeated through the material to reach equilibrium and was controlled by the anhydrous $CaCl_2$, leading to an increase in weight of the cell, which was verified at regular times. According to the method, the measurements were stopped when the weight gain passed 10% of the initial weight in $CaCl_2$. All tests were made in triplicate. The WVP was calculated using the following expression: $\mathrm{WVP} = \frac{\Delta m \times e}{A \times t \times \Delta P}$, where Δm is the weight difference (g); e, the thickness of the material (m); A, the material area (m^2); t, the time (s); and ΔP, the difference in partial vapor pressure; the unit for the WVP was g.m/m^2 s Pa.

Oxygen gas permeability

Oxygen permeability measurements were carried out with a Systech Model 8001 Oxygen Permeation Analyser (GRUTER&MARCHAND, Nanterre, France.). The equipment involved two measurement cells in order to perform reproducibility tests. The measurement cell was divided in two chambers. All gases passing from one chamber to another had to pass through the sample. Pure oxygen (99.9%) was then introduced into the upper chamber, while an oxygen-free (99.999% zero grade N_2) carrier gas flows through the lower chamber. Molecules of oxygen diffusing through the sample into the lower chamber were carried to the sensor by the carrier gas.

Results and discussion

As soon as the substrate was removed from the fatty acid dispersion, it was transparent. However, after 2 h at room temperature, the coatings turned white, as shown in Figure 1. In all cases, at the macroscopic scale, the photographs illustrate that the coatings were homogeneous irrespective of the fatty acid to ethanolamine molar ratio (0.5, 1, and 1.6). For the rest of this paper, all measurements concerning the fatty acid coatings were made from the dispersion, with the fatty acid to ethanolamine molar ratio being equal to one. The reason why this ratio has been chosen is that these are preliminary results aimed at demonstrating the feasibility of adding green coatings made from fatty acid dispersions onto a biodegradable substrate. As a result, the influence of the quantity of fatty acid has not been studied.

The white color of coatings (see Figure 1) is, due to the recrystallization of fatty acid at room temperature. The coating was observed using an optical microscope (Figure 2). The Figure 2(A) shows the biodegradable substrate with fatty acid coatings,with the dotted line representing the start of the coating. The presence of crystals of various sizes (from few thousand to hundred thousand μm^2) was illustrated on the optical microscopic images of the Figure 2(A) and 2(C), which is a focus on one crystal.

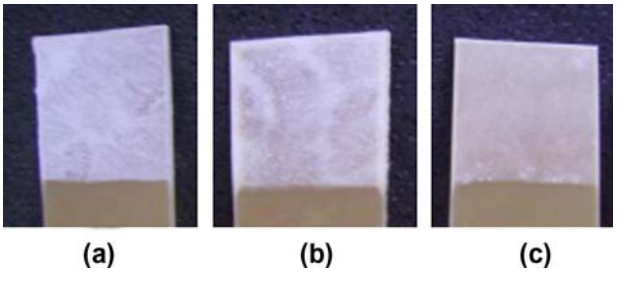

Figure 1. Photographs taken from fatty acid coatings after drying for 2 h at room temperature. A, B and C correspond to a fatty acid to ethanolamine molar ratio of 0.5, 1 and 1.6,.respectively

Figure 2. Optical microscopic images of substrate with fatty acid coatings. (A) Limit of the coating represented by the dotted white line: in the left of this line is the biodegradable substrate without coating whereas in the right is the fatty acid coating, (B) Fatty acid coating, and (C) Focus on a crystal. (fatty acids to ethanolamine molar ratio equal to 1).
Note: The scale bar represents 200 μm.

In order to determine the surface hydrophobicity of the coatings, contact angle measurements were carried out. In Table 1 the initial contact angles as control values are reported. Measurements on the fatty acid coating were made just after drying for 2 h. Moreover, the time evolution of the contact angle for biodegradable substrate with or without coatings is shown in Figure 3. For all samples, the figure shows that the contact angle decreases with the time after the contact. This is partly due to the water evaporation of the drop and the porosity of the substrate, both of which have a tendency to absorb water. The values obtained for a commercial plastic (expanded polystyrene) are also reported in this figure. At the initial time, the values are similar to those reported in Table 1 the contact angle obtained for the biodegradable substrate made from maize starch without coating was $(75 \pm 3)°$, whereas that for the one with a fatty acid coating one day after the coating elaboration was $(121 \pm 5)°$, indicating a much more hydrophobic surface. This increase is due to the intrinsic hydrophobic nature of fatty acid. The value found for the substrate without a coating correlated well with the hydrophilic nature of starch. The contact angle for a commercial plastic was (92 ± 3). These results were also illustrated by the photographs of water droplets deposited on different surfaces (surface without coatings, surface with fatty acid coatings, and commercial plastic) reported in Figure 3, which significantly show the lower wettability of the surface with fatty acid coatings compared with biodegradable surface without a coating.

An interesting point shown in the Figure 3 is the time stability of coating. Concerning the fatty acid coatings after many days (12 and 21 days), the initial contact angle values are still higher than those of biodegradable uncoated substrate: $(120 \pm 3)°$ and $(103 \pm 5)°$. Even 21 days after the coating was added, the fatty acid coating was still more hydrophobic than biodegradable substrate without a coating. The contact angle values of fatty acid coating after 21 days were still equivalent to those of the plastic substrate.

The fatty acid coatings led to a significant improvement in water resistance of the materials as shown by the initial value of the contact angle. We could expect that the values of

Table 1. Initial contact angle values as control. Measurements on the fatty acid coating were made just after drying for 2 h.

	Contact angle (°)
Biodegradable substrate	76 ± 3
Commercial plastic	125 ± 2
Fatty acid coating after drying for 2 h	92 ± 1

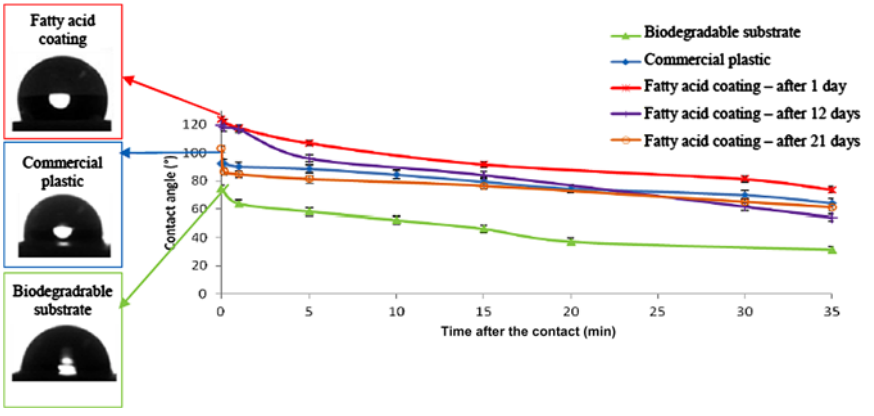

Figure 3. Contact angle values as function of time after the contact between the drop and the surface for the substrate with fatty acids coatings (fatty acids to ethanolamine molar ratio equal to 1). Measurements were made 1, 12, and 21 days after the elaboration of the coatings, as explained on the experimental section of contact angle measurements.
Note: On the side are shown the images of drops taken just after the deposition of the drop on the surface.

WVP confirm this tendency, but it was not the case. Indeed, the values are similar: the WVP of biodegradable substrate was $(1.7 \pm 0.3) \times 10^{-11}$ g m/m² s Pa, whereas the one obtained for fatty acid coatings was $(1.4 \pm 0.1) \times 10^{-11}$ g m/m² s Pa. This result can be explained for the biodegradable substrate by the presence of components others than starch ,which would have affected the WVP. Having said that, in the literature, Garcia et al. [20] have shown that the d presence of lipid decreased the WVP of a starch-based film. As a result, it appears as though the presence of fatty acid assemblies has an influence on the WVP.

Concerning the barrier properties toward the oxygen, the oxygen permeability as a function of temperature and RH is shown in Figure 4. The RH chosen for the study was 80% in order to be representative of the storage conditions of a refridgerator during food packaging. In all cases, the oxygen permeability increased with the temperature. It is well known that the temperature reduces the cohesion of material and facilitates the transport of oxygen molecules [20]. When the temperature increases, the polymer chains are more mobile and the oxygen molecules are more easily diffused. The oxygen permeability found for the biodegradable substrate made from maize starch without a coating varied from (3.0 ± 0.5) cc/m² /day at 5 °C

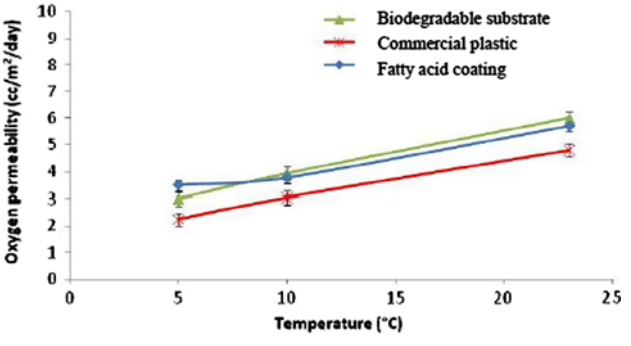

Figure 4. Oxygen permeability as function of temperature at a RH of 80%, for substrate without coating and with fatty acids coating (fatty acids to ethanolamine molar ratio equal to 1).

to (6.0 ± 0.2) cc/m^2/day at 23 °C. The values obtained for plastic substrate are equivalent to those of biodegradable substrate. The oxygen permeability value of fatty acid coatings was lower than the value of the initial substrate without a coating. The values were in the range of (2.3 ± 0.1) cc/m^2/day at 5 °C to (4.8 ± 0.2) cc/m^2/day at 23 °C. This result showed that the coating made from fatty acid decreased the oxygen permeability, showing that the coating improved the barrier properties of the substrate toward oxygen. It has been well discussed that the crystallization resulted in a decrease in the oxygen permeability. Indeed, the crystalline structures are relatively tightly packed and tend to reduce the permeability. It appears that the imposed tortuous path of the gas molecules reduced the diffusion of gas molecules and enhanced the barrier properties of the material [21,22].

Conclusions

The new biodegradable thermoplasticized-starch substrates were shown to have weak barrier properties against oxygen and a low surface hydrophobicity, mainly due to the hydrophilic nature of starch. This paper shows that it was possible to add coatings made from fatty acid dispersions to create efficient barrier properties in biodegradable substrates. This improvement was attributed to the hydrophobic nature of the fatty acid, resulting in a higher surface hydrophobicity, and also to the recrystallization of the fatty acid during the drying of coating, leading to lower oxygen permeability.

Further research should focus on the mechanisms of organization of these types of fatty acid assemblies on a solid surface. Based on the fact that fatty acids are environmental-friendly molecules, the use of these coatings could be extended to other fields such as biomedical or corrosion protection fields.

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