**Summary**

Starch foam trays were developed as an alternative to the single-use expanded polystyrene (EPS) trays used for food products. The foam trays were prepared by heating a mixture composed of cassava starch, cellulose fibres and calcium carbonate inside a metallic mould. Starch-based foam trays are brittle and sensitive to moisture and thus further treatments are necessary to improve their mechanical properties and water resistance. To minimize water absorption, the foam trays were impregnated with starch acetate dissolved in chloroform at concentrations of 1:3 (g.mL⁻¹), 1:5 (g.mL⁻¹) and 1:10 (g.mL⁻¹). The impregnation was carried out at atmospheric pressure and also by applying a vacuum pulse. The use of vacuum pulses decreased the water absorption of the impregnated foam trays by about 66%. On the other hand, there was no significant improvement in the mechanical properties of the impregnated trays. This work demonstrates that impregnation of porous samples with starch acetate is an alternative to decrease their water absorption.

**Key words:** Starch foam trays; Starch acetate; Impregnation; Biopolymer.

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**Resumo**

Bandejas à base de amido expandido foram desenvolvidas como uma alternativa às badejas de poliestireno expandido (EPS), normalmente utilizadas para acondicionar alimentos. Bandejas à base de amido expandido foram preparadas através do aquecimento de uma mistura de amido, fibras de celulose e carbonato de cálcio no interior de um molde metálico. Bandejas à base de amido são quebradiças e sensíveis à umidade. Para reduzir a absorção de água, as bandejas foram impregnadas com acetato de amido dissolvido em clorofórmio em concentrações de 1:3 (g.mL⁻¹), 1:5 (g.mL⁻¹) e 1:10 (g.mL⁻¹), com aplicação de um pulso de vácuo e totalmente à pressão atmosférica. O uso de um pulso de vácuo reduziu a absorção de água das amostras impregnadas em até 66%. Por outro lado, não houve melhora significativa nas propriedades mecânicas das amostras impregnadas. Este trabalho demonstra que a impregnação de materiais porosos com acetato de amido pode ser uma alternativa para a redução da absorção de água.

**Palavras-chave:** Bandejas de amido; Acetato de amido; Impregnação; Biopolímero.
1 Introduction

Foam trays were produced by heating starch-water mixtures (with or without the addition of fibres) under pressure in closed moulds (TIEFENBACHER, 1993; LAWTON et al., 1998; SHOGREN et al., 1998; GLENN et al., 2001; LAWTON et al., 2004; SOYKEABKAEN et al., 2004). However, starch-based materials are brittle and sensitive to moisture, thus further treatments are necessary to obtain the strength, flexibility and water resistance necessary for their commercial use (FANG and HANNA, 2000; SHOGREN et al., 2002).

An improvement in the properties of starch/water composite foams has been achieved by casting them with polyesters by adding polyvinyl alcohol (PVOH) to the starch-water mixture before the heat treatment (LAWTON et al., 1998; SHOGREN et al., 1998), or by impregnating them with a solution of starch acetate in chloroform (LAROTONDA et al., 2005; MATSUI, et al., 2004). The water affinity of starch materials can be reduced chemically by substituting the starch hydroxyl groups by a hydrophobic group (SAGAR and MERRIL, 1995; THIEBAUD et al., 1997; PAVLATH and ROBERTSON, 1999; DEMIRGOZ et al., 2000; KIATKAMJORNWONG et al., 2001). Starch acetate with a high degree of substitution (DS) is one of the most important starch esters for use in engineering materials (MULLET and PACSU, 1942; WHISTLER and HILBERT, 1944; WOLFF et al., 1951). Xu and Hanna (2005) and Larotonda et al. (2005) reported that starch hydrophobicity increased with the degree of substitution (DS), increasing its suitability as packaging material.

The objective of this work was to investigate the effect of impregnating starch-based foam trays with starch acetate, on the mechanical properties and water absorption of the resulting material.

2 Material and methods

Foam trays were produced from a mixture of cassava starch, cellulose fibres and calcium carbonate. Unmodified cassava starch was purchased from Yoki Alimentos S.A., Brazil. Calcium carbonate was purchased from a local retail store in Florianópolis, Brazil. Cellulose pulp fibres with 1.2 mm softwood short fibres were obtained from Klabin S.A., Brazil. The mixture was prepared in the proportions of 50% cassava starch, 39% calcium carbonate and 11% cellulose fibres by weight. The compounds were weighed and blended with water for 8 min, using a mechanical stirrer (Fisaton, mod 713D, Brazil). A thermopressing process was carried out in a mould using a hydraulic machine, where the temperature was set at 200-205 °C by two PID controllers. The size of the mould cavity was 159 mm in length, 109 mm in width and 1.12 mm in depth. The mixture was placed in the centre of the mould and covered by a lid. During the pressing process, the steam generated escaped from the sides of the hot plate, expanding the mixture. The mould was then maintained under a pressure of 0.36 MPa for a further 3 min. This heating time was necessary to reduce the moisture of the foam trays to 2-4%. The foam (expanded starch) trays were cooled to room temperature.

The density of the foam trays was determined from the mass/volume ratio. The samples (4 × 4 cm) were weighed on a balance with a precision of 0.001 g (Gehaka, BG 400, Brazil). The sample thickness was measured using a digital external micrometer (Mitutoyo Co., Japan) at four different points of the sample and the other dimensions were measured with a caliper. The density was expressed in g of dry matter/volume (g.cm⁻³).

2.1 Preparation of the starch acetate and impregnation of the trays

The starch acetate was prepared by the process described in US Patent nº 5,710,269 (FEUER, 1998), replacing the catalytic agent MSA (methane sulphonic acid) by concentrated sulphuric acid (LAROTONDA et al., 2004). The highest possible degree of substitution (DS) is 3, since there are three hydroxyl groups (OH) available for substitution on each anhydroglucose unit (LEPENIOTIS et al., 1998; SHOGREN et al., 1998; GLENN et al., 2001). The best mechanical properties and water resistance for use in food packing and for biodegradation have been reported for DS values between 1.2 and 1.7 (NARAYAN et al., 1999).

The starch acetate used in this work had a DS = 1.48.

The starch acetate used to impregnate the foam trays was prepared and diluted in chloroform at ratios of 1:3, 1:5 and 1:10 (g starch acetate: cm³ of chloroform). Foam tray samples with dimensions of 25 × 100 mm and 100 × 100 mm were impregnated by immersion in the starch acetate solutions. Foam tray samples were impregnated at atmospheric pressure and by the application of vacuum pulses in a desiccator containing the samples and the starch acetate solution. Impregnation at atmospheric pressure was performed by immersing the foam tray samples in the solutions for 5, 10 or 30 min. The procedures were all performed at room temperature. In the second case, pressures of 40 mmHg were applied to the desiccator containing the samples and solution for 3 min, followed by a period of 5, 10 or 30 min at atmospheric pressure. The vacuum was applied to remove most of the air present in the system and in the porous spaces of the samples, which facilitates the subsequent penetration of the solution (FITO, 1994). After impregnation, the samples were maintained at 100 °C for 3 h in a ventilated oven, to evaporate off the chloroform. The conditions used for sample impregnation are given in Table 1.
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2.2 Scanning electron microscopy (SEM)  
Micrographs of the foam tray samples were obtained using a model XL-30 (Philips, Holland) scanning electron microscope. Before obtaining the micrographs, the foam tray samples were coated with a thin gold layer using a model SCD 005 (BAL-TEC, Switzerland). All samples were examined using an accelerating voltage of 20 kV.

2.3 Tray water absorption  
A comparative water absorption study was performed using a modified procedure based on the ABNT NBR NM ISO 535 Standard (1999), which was derived from the Cobb method. It consisted of a gravimetrical analysis in which a sample (with a known dimension of 25 × 50 mm) was weighed before and after immersion in distilled water for 1 min. The water adhered to the sample surface was removed with absorbent paper.

2.4 Measurement of the mechanical properties  
The mechanical properties of the foam trays were determined using the tensile strength test in accordance with the ASTM D828-97 standard test method. Before the mechanical tests, the foam tray samples were conditioned for 5 days at ambient temperature (about 25 °C) and a relative humidity of 75% (obtained using a saturated solution of sodium chloride). The conditioning is important because the water absorbed by the materials acts as a plasticizing agent, modifying the material properties (SHOGEN et al., 1998; SOYKEABKAEW et al., 2004). The model TA.XT2i texture analyser (SMS, Surrey, UK) with the 25 N load cell was used to determine the mechanical properties of the foam tray samples. The tensile strength and elongation at break were determined from the tension tests. In the tension tests, foam tray samples with dimensions of 25 × 100 mm were fixed to the machine, and the tests performed at 2 mm/s.

The force at break and relative deformation were determined from the puncture tests. The puncture tests were performed using a spherical probe (21 mm diameter), previously fixed in an annular space with a diameter of 80 mm, as sketched in Figure 1. The spherical steel probe was built specially for these mechanical tests, to avoid sharp edges that could influence the material break. During the tests, the probe was moved through the sample, from top to bottom, with a speed of 1 mm/s, until 30 mm below the sample level. The load applied was 0.5 N and the tests were performed with 10 repetitions for each sample. For this test, the relative deformations at break were represented by Equation 1.

\[ \delta = \frac{\Delta L}{D} \]  

where \( \Delta L \) = the probe vertical shift, from the moment it touched the sample to the break point; \( D \) = diameter of sample under test and \( \delta \) = relative deformation of the samples at break.

2.5 Water sorption isotherms  
The foam tray samples were previously dried and conditioned in recipients with different relative humidities (RH = 7 to 90%), obtained using saturated salt solutions at constant temperature (25 °C). The samples were

Table 1. The conditions used for sample impregnation.

<table>
<thead>
<tr>
<th>Sample codes</th>
<th>Starch acetate/chloroform (g.mL⁻¹)</th>
<th>Impregnation time (min)</th>
<th>*Pressure condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A = non-impregnated sample</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AP, 1:3,05 min</td>
<td>1.3</td>
<td>5</td>
<td>AP</td>
</tr>
<tr>
<td>AP, 1:3,10 min</td>
<td>1.3</td>
<td>10</td>
<td>AP</td>
</tr>
<tr>
<td>AP, 1:3,30 min</td>
<td>1.3</td>
<td>30</td>
<td>AP</td>
</tr>
<tr>
<td>VP, 1:3,10 min</td>
<td>1.3</td>
<td>10</td>
<td>VP</td>
</tr>
<tr>
<td>AP, 1:5,05 min</td>
<td>1.5</td>
<td>5</td>
<td>AP</td>
</tr>
<tr>
<td>AP, 1:5,10 min</td>
<td>1.5</td>
<td>10</td>
<td>AP</td>
</tr>
<tr>
<td>AP, 1:5,30 min</td>
<td>1.5</td>
<td>30</td>
<td>AP</td>
</tr>
<tr>
<td>VP, 1:5,10 min</td>
<td>1.5</td>
<td>10</td>
<td>VP</td>
</tr>
<tr>
<td>AP, 1:10,05 min</td>
<td>1.10</td>
<td>5</td>
<td>AP</td>
</tr>
<tr>
<td>AP, 1:10,10 min</td>
<td>1.10</td>
<td>10</td>
<td>AP</td>
</tr>
<tr>
<td>AP, 1:10,30 min</td>
<td>1.10</td>
<td>30</td>
<td>AP</td>
</tr>
<tr>
<td>VP, 1:10,10 min</td>
<td>1.10</td>
<td>10</td>
<td>VP</td>
</tr>
</tbody>
</table>

* Pressure condition: AP = atmospheric pressure; and VP = vacuum pulses, followed by a period at atmospheric pressure.

Figure 1. Spherical probe and base used to fix the sample during the puncture tests.
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frequently weighed to constant weight and the equilibrium moistures determined. The water sorption isotherms were fitted using the GAB model (Guggenhein, Anderson, de Boer), Equation 2.

\[ X = \frac{X_0 k C a_w}{(1 - k a_w)(1 - k a_w + C k a_w)} \]  

where \( X \) = sample equilibrium moisture content on a dry weight basis; \( X_0 \) = monomolecular layer equilibrium moisture content on a dry weight basis; \( a_w \) = water activity (RH/100); \( C \) = Guggenheim constant, related to the first molecular layer heat sorption; \( k \) = constant related to the multilayer heat sorption.

## 3 Results and discussion

Figure 2 shows the micrographs of a regular starch foam tray obtained by thermopressing. Figures 2a, b represent the surface and cross section, respectively, of a foam tray sample. In both figures, interlacement of the compounds (starch, calcium carbonate and fibres) and voids formed by steam escaping can be visualized.

![Micrographs of the foam trays: a) Surface; b) Cross-section.](image)

Figure 3 shows the results for the specific mass (from triplicates) of the foam trays, before and after impregnation. Foam trays impregnated with the 1:3 (g.mL\(^{-1}\)) starch acetate solution (most concentrated solution) presented the greatest specific mass when compared to those impregnated with the 1:5 and 1:10 (g.mL\(^{-1}\)) concentrations. Increases of 24, 15 and 16% were observed in the specific mass for samples from VP, 1:3,10 min; VP, 1:5,10 min and VP, 1:10,10 min, respectively. The specific mass of samples from experiments AP, 1:10,05 min; AP, 1:10,10 min and AP, 1:10,30 min increased by 4.0, 5.0 and 5.5%, respectively, while those from AP, 1:5,05 min; AP, 1:5,10 min and AP, 1:5,30 min showed increases of 6.5, 7.0 and 10.0%, respectively. Finally, the specific mass of samples from AP, 1:3,05 min; AP, 1:3,10 min and AP, 1:3,30 min increased by 10, 13 and 18%, respectively. These values can be explained by the application of vacuum, which removed the air entrapped inside the material, facilitating penetration of the starch acetate solution (FITO, 1994; LAROTONDA et al., 2005).

Figure 4 shows the water absorption values obtained for foam trays impregnated with the different starch acetate solutions (1:3, 1:5 and 1:10 g.mL\(^{-1}\)) for the different immersion times (5, 10 and 30 min). In most cases, the sample water absorption decreased to about 70% of the value found for non-impregnated samples. The non-impregnated samples absorbed about 80 g.cm\(^{-2}\) more water than any of the impregnated samples. For samples impregnated under the conditions VP, 1:3,10 min and AP, 1:3,30 min, the water uptake decreased to about
40%, compared to the non-impregnated samples. This can be explained by the filling up of the porous spaces in the material by starch acetate solution and by the coating on the material surface. Figure 8 shows the more homogeneous starch acetate film formed at the material surface for VP, 1:3,10 min. Moreover, since starch acetate is hydrophobic (LAROTONDA et al., 2005), the impregnated material became less hygroscopic, contributing to a reduction in water uptake. Similar results were reported by Larotonda et al. (2003) and Matsui et al. (2004).

Matsui et al. (2004) reported data obtained with cassava bagasse-Kraft paper composites impregnated with starch acetate/chloroform solutions (concentrations of 1:5 and 1:10 (g.mL⁻¹), for 5 and 10 min). The impregnation decreased water absorption by the material by about 75%. The water uptake by commercial Kraft paper (75 g.m⁻²) impregnated with starch acetate/chloroform solution, decreased by 56.4% for the samples impregnated using vacuum pulses and 11.4% for the samples impregnated under atmospheric pressure (LAROTONDA et al., 2003).

Shogren et al. (2002) studied the preparation of starch foam trays with the addition of hydrophobic compounds to improve the water absorption resistance. Trays produced with the addition of paraffin wax, vegetable oil, silicone oil, resin, aryl acid ester, citric acid, butane-tetra-carboxylic acid, succinic acid and ethylene glycol resin failed to reduce the water absorption. Only monoester citrate presented a significant decrease in water absorption.

The values obtained for tensile strength and elongation at break of the impregnated and original foam trays are shown in Figures 5a and b. The results obtained with the impregnated foam trays were compared with non-impregnated samples and with commercial EPS (expanded polystyrene) trays. Impregnation had a small influence on the mechanical properties mentioned above. Similar results were reported by Matsui et al. (2004) for composites formed from cassava bagasse and Kraft paper, impregnated with starch acetate/chloroform solutions (concentrations of 1:5 and 1:10 (g.mL⁻¹) for 5 and 10 min). These authors reported that impregnation did not influence the tensile strength and elongation at break of the samples. Larotonda et al. (2003) reported that impregnation of Kraft paper with starch acetate/chloroform solutions (concentrations of 1:5 g.mL⁻¹) increased the material tensile strength 1.5 times.

Figure 4. Influence of impregnation on tray water absorption.

Figure 5. Foam trays impregnated with a starch acetate/chloroform solution: a) Tensile strength; and b) Elongation at break.
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The environmental aspects of using chloroform as the solvent must be carefully evaluated. For industrial use, it is important to evaluate the residual concentration of this solvent in the foam trays and also find ways to recover the chloroform evaporated during the vacuum pulses (impregnation) and foam tray drying procedures.

The puncture tests results for the impregnated and non-impregnated foam trays are presented in Figures 6a and b. In general, the samples impregnated with the more concentrated solutions (1:3 and 1:5 g.mL⁻¹) presented relatively less deformation than samples impregnated with the lower concentration (1:10 g.mL⁻¹). This behaviour can be explained by the greater starch acetate impregnation obtained with the more concentrated solutions.

Moisture sorption isotherms of the impregnated and non-impregnated foam trays are shown in Figure 7. The GAB model fitted the experimental sorption data for the impregnated and non-impregnated samples well. The values for the GAB constants are shown in Table 2. The moisture content of the monomolecular layer was higher for non-impregnated samples. A plausible explanation for this result is the coating of both the sample surface and part of its porous space by starch acetate, which is hydrophobic (LAROTONDA et al., 2005). Figure 8 shows the SEM micrographs of the surface of an impregnated foam tray, and some aspects of the thin acetate film that coat the sample surface can be observed. The film presented a dense structure, interspersed with cracks, due to the brittle characteristic of starch acetate (LAROTONDA et al., 2004, 2005). Similar film coatings were reported by Matsui et al. (2004) and Larotonda et al. (2005).

Figure 9 shows micrographs of cross-sections of the impregnated foam trays. It is impossible to identify the starch acetate film inside the structure, but details of the fibres and calcium carbonate distribution can be seen, as well as the voids formed by the arrangement of the materials formed during the heating process.

![Figure 6. Foam trays impregnated with a starch acetate/chloroform solution: a) Force at break, N; and b) Relative deformation at break, δ.](image)

![Figure 7. Sorption isotherms for the impregnated and non-impregnated foam trays.](image)

<table>
<thead>
<tr>
<th>Constants</th>
<th>Non-impregnated sample</th>
<th>Impregnated sample (1:10 g.mL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.9613</td>
<td>0.9989</td>
</tr>
<tr>
<td>X₀</td>
<td>0.0269</td>
<td>0.0168</td>
</tr>
<tr>
<td>C</td>
<td>17.981</td>
<td>11.574</td>
</tr>
<tr>
<td>R² (Adjusted) GAB</td>
<td>0.9941</td>
<td>0.9645</td>
</tr>
</tbody>
</table>
Water absorption and mechanical properties of starch foam trays impregnated with starch acetate

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Figure 8. SEM micrographs of foam tray surfaces: a) VP, 1:3, 10 min; b) AP, 1:3, 10 min; c) AP, 1:5, 10 min; and d) non-impregnated sample.

Figure 9. SEM micrographs of foam tray cross-sections: a) VP, 1:3, 10 min; b) AP, 1:3, 10 min; c) AP, 1:5, 10 min; and d) non-impregnated sample.
4 Conclusions

The impregnation of starch foam trays with starch acetate solutions did not significantly influence their mechanical properties, but decreased their water absorption, increasing the potential use of this material for food packaging. Moreover, starch acetate impregnation is a feasible procedure to reduce the water sensitivity of packaging. Moreover, starch acetate impregnation is a feasible procedure to reduce the water sensitivity of packaging. Furthermore, the use of the trays presented in this work should be evaluated with respect to the legislation for food packaging in Brazil.

References


SHOGREN, R. L.; LAWTON, J. W.; TIEFENBACHER, K. F. Baked starch foams: starch modifications and additives improve
Water absorption and mechanical properties of starch foam trays impregnated with starch acetate

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