The Role of Water On Structure Formation to Extrusion of Corn Starch Based Plastic Foams

Elena Mihaela NAGY¹, Maria TOMOAIA-COTIȘEL ², Maria FENEȘAN², Constantin COȚA¹, Gabriel FODOREAN³, Nicolae CIOICA¹

¹INMA Bucharest, Branch Cluj-Napoca, 59 Al. Vaida Voievod Str., Cluj Napoca, Romania, inmacj@click.net
²Babeș-Bolyai University of Cluj-Napoca, Faculty of Chemistry and Chemical Engineering, Department of Physical Chemistry, 11 Arany Janos Str., Cluj-Napoca, Romania, mcotisel@chem.ubbcluj.ro
³Technical University of Cluj-Napoca, Facuty of Mechanics, Department of Automotive and Agricultural Engineering, 103-105 Muncii Blvd., Cluj-Napoca, Romania, gabriel.fodorean@arma.utcluj.ro

Abstract. Foaming extrusion has been used to produce loose-fill starch-based packaging materials, in a similar way to the production of extruded expanded snack foods. Native starches are non-plastic due to the intra- and intermolecular hydrogen bonds between the hydroxyl groups in starch molecules, which represent their crystallinity. Thermal processing is used to disrupt and transform the semi-crystalline structure of starch granules to form a homogeneous and amorphous material. This transformation is usually accomplished using small amounts of molecular substances commonly known as gelatinization agents or plasticizers. This paper presents some results obtained during researches conducted in order to obtain a biodegradable starch-based loose-fill by thermoplastic extrusion, when using in different ratios between starch and plasticizers in the formula. Increasing the levels of water in the formula leads to lower viscosity value of the mixture and changing structure of the finished product.

Key words: corn starch, water, extrusion, plastic foams.

INTRODUCTION

During the last two decades a considerable amount of investment and R&D has been conducted worldwide to identify alternative raw materials that can be used to ensure the environmentally-friendly nature of plastic materials. Plastic foams represent an area where biodegradability would be a tremendous asset to a variety of insulation and packaging products, as most foams ultimately end their service lives in landfills. Starch, as a key component of these renewable raw materials, is becoming an increasingly important input to activities outside the food industry due to the variety of ways in which it can be modified to find applications such as destructured starch. The destructuring agent is usually water. Gelatinization is the disruption of the granule organization. The starch swells forming a viscous paste with destruction of most of inter-macromolecule hydrogen links. Gelatinization is particularly important because it is closely related to the other changes, and it is an irreversible process that includes granular swelling, native crystalline melting, loss of birefringence and starch solubilization. Under shearless conditions (the combination of water and heat) full gelatinization of starch requires more that 63% water content (Wang SS., 2010),
while gelatinization under shear conditions requires much less Wang SS water as shear stress enhances processing. The combination of thermal and mechanical inputs can be obtained by extrusion, a common plastic processing technique. Water acts as a plasticizer but it is a volatile plasticizer. By decreasing the moisture content (<20 wt%), the melting temperature tends to be close to the degradation temperature. (Shogren R. L., 1992). To overcome this last issue, is added a non-volatile (at the process temperature) plasticizer to decrease melting temperature Tm, such as glycerol or other polyols (Poutanen K., Forssell P., 1996).

This paper presents some results obtained during researches conducted in order to obtain a biodegradable starch-based loose-fill by thermoplastic extrusion, when using in different reports between water and glycerol in the formula.

MATERIALS AND METHODS

The normal corn starch used in this study was obtained from SC Amylon SA Sibiu, Romania. The initial water content of starch on dry wet was 12%. The other characteristics of this starch, supplied by the manufacturer are shown in Tab.1.

<table>
<thead>
<tr>
<th>Ash</th>
<th>Protein</th>
<th>Density</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>max. 0,1%</td>
<td>max. 0,5%</td>
<td>0.561 g/cm³</td>
<td>700 UB (10 min la 95 °C)</td>
</tr>
</tbody>
</table>

Structure of utilised starch granules was determined (M. Tomoaia-Cotisile, et al. 2010). The glycerol used in formula was purchased from SC Nordic Invest SRL Cluj Napoca. The glycerol had a concentration of 99.5% and a density of 1.262 g/cm³.

The water used was from the water supply system.

The Tab.2 indicate the ratio of the two components in the formula, based on which have been established the starch and plasticizer flow rate.

<table>
<thead>
<tr>
<th>Formula abbreviation</th>
<th>Water [% wet basis]</th>
<th>Glycerol [% wet basis]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATN 411</td>
<td>16.66</td>
<td>16.66</td>
</tr>
<tr>
<td>ATN 412</td>
<td>14.29</td>
<td>28.57</td>
</tr>
</tbody>
</table>

Fig. 1 shows a schematic representation of a utilized foaming extrusion system.

A laboratory twin-screw extruder with co-rotating intermeshing, self-wiping screws (Model ZK 25, Collin) was used to conduct the extrusions. The extruder has a maximum productivity of 15 kg/h, 25 mm screw diameter, 30:1 length to diameter ratio, max. 400 rpm screw speed and six independent electric heating and cooling areas. The first area of the extruder, which is the supply area, is not heated, but can be cooled with water. The two to five areas are provided with electric heaters and cooling fans. Each of these five areas is equipped with one temperature sensor that measures temperatures and control starting or stopping of the heaters or fans to maintain temperatures set in each area. The six area of the extruder is the die area - it has its own heater, and no cooling. Its temperature is measured and maintained at the value initially established by the temperature sensor. Also in the die area there are another two sensors that are in direct contact with the material that is processed and measuring its
temperature and pressure. These two parameters are very important, for them relying largely the quality and cross size of the extruded product.

Temperature values in these six areas of the extruder are initially set, achieved and maintained during extrusion plant operation with a program whose interface is the control panel of the extruder.

The starch was feed into the extruder hopper with a single screw volumetric feeder. The feeder can achieves starch flow rates ranging from 0.481 kg/h to 5.220 kg/h.

The dosing pump used to feed the plasticizers from the plasticizers tank was a low capacity and high dosing precision peristaltic pump (Model PERIPUMP D’5187, MTA KUTESZ, Hungary), with max. 42 ml/min flow rate. In order to use a single dosing pump both plasticizers (glycerol and water) being miscible, were mixed in the proportion of the formula and placed in the plasticizers tank.

Preliminary study indicated that the premixing starch powder and plasticizers tended to cause bridging in the feeding hopper. Therefore the plasticizers were added into the working area through a pipe connection located at 170 mm from axis of the supply hopper (Fig. 1).

The screw speed was set at 220 rpm and the barrel temperatures were maintained during the experiment at 30, 50, 100, 130, 150 and 150°C, respectively, from the feeding port to the die section. For the used formulas, the glass transition temperature was 73 °C for ATN411 mixture and 71 °C for ATN412 mixture.

A circular die plate with one hole was use. The diameter of the hole in the die is 3 mm.

The extruding product was collected and cooled to room temperature. At each experiment samples were taken after the extruder had reached steady state.

Fig. 1. Schematic representation of a foaming extrusion system
1 – Extruder; 2 - Starch tank; 3 – Starch feeder; 4 – Starch feeding hopper; 5 – Plasticizer tank; 6 – Plasticizer feeding pump
RESULTS AND DISCUSSIONS

The determined parameter for flours and starches of different provenience and which gives clues about their quality in terms of resistance to a force applied at a given temperature is the "falling index".

The device used for this analysis was Falling Time System (Sadkiewicz Instruments, Poland).

The gelatinization of starch suspension took place in a test pipe located in a water bath at 100°C. The estimating of the gelling degree of a suspension is making by measuring and recording, by the device, of the falling time of the agitator in the gel formed. The influence of formula on the falling time of the two samples is shown in Tab. 2.

The falling time is both an index of deformability and of baking properties of starch.

Tab. 3

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Mass ratio in sample preparation</th>
<th>Falling time [sec]</th>
<th>The macroscopic appearance of the sample after gelatinization</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATN 422</td>
<td>Starch 4, Water 2, Glycerol 2</td>
<td>250</td>
<td>The gel has many air bubbles embedded.</td>
</tr>
<tr>
<td>ATN 421</td>
<td>Starch 4, Water 2, Glycerol 1</td>
<td>362</td>
<td>The gel has aspect hollow.</td>
</tr>
</tbody>
</table>

The increase of water/glycerol ratio in sample leads to increase of falling time. The sample with higher water/glycerol ratio will have slower baking properties and a greater viscosity, having a greater falling time.

Fig. 2 shown the scanning electron micrographs of the finished products obtained by thermoplastic extrusion, for the two formulas used.

Fig. 2. Scanning electron micrographs of extruded starch foam

a – Sample ATN 421 (enlarged x200); b - Sample ATN 422 (enlarged x500).
For the finished product made from mixture ATN 421 we observe a fibrous structure, while for the finished product made from mixture ATN 422 we observe a deformed rods structure, which are in contact (compact packed).

These differences are explained by different deformability and baking properties of the samples after gelatinization.

CONCLUSIONS

Both plasticizers, glycerol and water, protect starch polymers against degradation during thermoplastic extrusion of starch. Tests results carried out show that the glycerol plasticizer effect, both from point of view of viscosity of the water-glycerol-starch mixture, and from point of view of extruded finished product structure, is stronger than that of water. The percentage of glycerol and the water/glycerol ratio in the recipe are limited by the requirements imposed finished product.

REFERENCES