Polylactide composite films with silver nanoparticles in the structure

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This article investigates the process of obtaining polylactide film composite materials with the simultaneous formation of silver nanoparticles. Impact of polylactide and its composition (amorphous and amorphous-crystalline), and glycerol plasticiser on the kinetics of solvent evaporation is determined. To impart fungi bactericidal properties to polylactide composites, a silver reduction reaction by the interaction of argentium salts with polyvinylpyrrolidone was utilized. The formation of silver nanoparticles was confirmed by an energy-dispersive analysis of the composite. A fundamental technological scheme for the preparation/production of polylactide-based films with silver nanoparticles is proposed/suggested, which proves their effective practical use as packaging materials for/during food and drugs.

Keywords - polylactide, film, silver nanoparticles, fungicidal properties, polyvinylpyrrolidone.

Introduction

The study aims to discuss the process of obtaining packaging polylactide film composite materials with a simultaneous formation of silver constituent nanoparticles to impart fungi bactericidal properties to the composites. Among the promising polymers, polylactide (PLA) is widely used in many industries, especially in the food, packaging, and paper lamination industries, agriculture, medicine, and biotechnology due to its performance property biodegradability. Polylactide materials, including films, are modified with various additives (nanoparticles, plasticisers, polymers) to ensure improved functional characteristics. In this context, nanoparticles of noble metals, especially silver, have been widely applied as antimicrobial agents during food and drug packaging. Their unique properties in many cases depend on the size and shape of silver nanoparticles.

Results and discussion

The solution casting method was applied to form a composite film with silver nanoparticles, which was modified by adding an ethanol solution of polyvinylpyrrolidone (PVP) with AgNO₃ and changing the preparation technique [1]. PVP, in addition to being a silver reducing agent, is used as a modifier to the properties of composite materials for medical purposes [2].

The method of forming films based on PLA from solutions makes it possible to combine film formation process with the modification of polymer properties. Glycerol-plasticised PLA films without nanoparticles remain relatively smooth, strong, and homogeneous. Films with silver nanoparticles retain a dark brown colour, and white specks are visible on the polymer surface when viewed under a microscope. The formation of silver nanoparticles was confirmed by energy dispersive analysis of the composite using DRON-4-07.

The kinetics of solvent evaporation and the degree of the films’ swelling at different temperatures, and pH environment are under analysis. The findings are presented in Table 1.

All samples are characterised by a low swelling degree at/under room temperature, whereas at T 313 K the swelling degree almost doubles.
### Table 1.

Swelling degree of composites due to composition and pH environment

<table>
<thead>
<tr>
<th>№</th>
<th>Composition, w/w/w</th>
<th>Swelling degree α, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T=291 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH=4</td>
</tr>
<tr>
<td>1</td>
<td>PLA:Ag⁺:PVP = 90:0:10</td>
<td>0,3</td>
</tr>
<tr>
<td>2</td>
<td>PLA:Ag⁺:PVP = 90:1:9 *(293 K)</td>
<td>0,4</td>
</tr>
<tr>
<td>3</td>
<td>PLA:Ag⁺:PVP = 90:1:9 *(373 K)</td>
<td>0,9</td>
</tr>
<tr>
<td>4</td>
<td>PLA:Ag⁺:PVP = 89:2:9</td>
<td>0,4</td>
</tr>
<tr>
<td>5</td>
<td>PLA:Ag⁺:PVP = 82:1:17</td>
<td>0,1</td>
</tr>
</tbody>
</table>

* washed away

It was also found that the PLA:Ag⁺:PVP composites = 70:15:15 w/w/w demonstrate bactericidal activity, caused by the evolution of inhibition zone within 10...12 mm (60...100%) regarding the bacteria Escherichia coli HB 101 (E. coli), Staphylococcus aureus (S. aureus), and 7.5 mm (80%) for the fungus Aspergillus niger (A. niger). The composites with non-silver nanoparticles proved not to exhibit fungi bactericidal properties. Their comparative analysis revealed the interdependence between their composition and properties. It means that the composites without silver nanoparticles did not exhibit fungi bactericidal capacities, whereas the composites containing silver nanoparticles block the bacteria and fungi growth.

For this reason, the pivotal technological scheme for producing polylactide films with silver nanoparticle production has been suggested.

Presumably, composites based on PLA with silver nanoparticles will be highly efficient in developing composites during food and and drug packaging and tend to increase their shelf life.

### Conclusion

The fungi bactericidal PLA:Ag⁺:PVP nanocomposite films are created by solution spin-coating. Studies on the solvent evaporation kinetics, degree of films swelling at different temperatures and pH environments have shown a low degree of swelling. The obtained polylactide composite materials demonstrate strong fungicidal and bactericidal properties when compared to various groups of bacteria and fungi. A fundamental technological scheme for the formation of polylactide films with silver nanoparticles was suggested. Based on the findings, technological and fungi bactericidal characteristics of films based on mixtures of PLA with glycerol and silver nanoparticles, can be recommended as useable materials for food and drug packaging.

### References
