

Karolina Gzyra-Jagięła

Abstract

## **„The development of modified polylactide fibres by melt spinning process”**

The global plastics market is rapidly evolving. In Europe, research and industry trends are focusing on recycling, closed-cycle systems, and biopolymers. This shift has been driven by European Union policies and a growing emphasis on environmental considerations. The green economy and sustainable development are frequently cited as essential aspects of Europe's policies. These concepts aim to promote a shift toward more sustainable production and consumption models, while also considering social justice and environmental balance. Therefore, biopolymers have garnered interest for their potential as renewable and biodegradable materials. They have the ability to replace petrochemical plastics in certain sectors due to their similar properties and reduced impact on the environment and human health. This is attributed to biopolymers ability to biodegrade, their non-toxic nature, biocompatibility, and lower carbon footprint.

The development of new solutions, including modifying biopolymers to change their mechanical, physico-chemical, thermal or functional properties, is an important activity that aligns with current trends. These modifications allow materials to be customized for specific applications and provide the ability to control important properties, making them particularly desirable. The research involved physically modifying polylactide using low-molecular-weight ester compounds and a biodegradable aliphatic-aromatic copolyester patented by the Lukaszewicz Research Network- Lodz Institute of Technology. In this study, the synthesis process to produce two types of polymer with different average molar masses was modified.

The modifiers were incorporated into the polylactide structure using an extruder by mixing it in a plastic state. Optimal extrusion conditions, such as the temperature gradient in the heating zone of the extruder, the extrusion rate, and the collection rate, were developed during the process. Subsequently, the modified biogranulate was utilized as a raw material for forming fibers, and optimal spinning conditions were established. The modified polymer allowed the spinning process in the extruder zone and on the spinning head to be carried out at a temperature 40°C lower than for the unmodified material. It was possible to produce modified fibers with low-molecular weight compounds up to 7% wt.. However, for higher concentrations, due to the strong plasticizing effect, it was impossible to pump the bioregranulate through the extruder of the spinning device. Modified polylactide fibers with aliphatic-aromatic polyester with a higher molar mass of only 5% wt. were obtained, for polyester with a lower molar mass it was possible to introduce 10% wt. of modifier. After the modification, the primary crystallization process produced a material with a higher degree of crystallinity. As a result, the drawing process required a lower draw ratio compared to the unmodified polymer. Despite using lower draw ratios, the modified fibers exhibited improved mechanical performance and a higher degree of crystallinity.

The use of triethyl citrate and bis(2-ethylhexyl) adipate has been found to impact the characteristics of hydrolytic degradation processes in Ringer's solution and biodegradation in compost. The research shows that these modifiers led to faster hydrolysis of polylactide. This was due to the presence of low-molecular weight modifiers in the amorphous phase of the polymer and their promotion of fine-crystalline structure formation during crystallization. Triethyl citrate, being a smaller molecule, was released more rapidly from the amorphous phase, resulting in accelerated degradation compared to bis(2-ethylhexyl) adipate. During both modifications, there was a significant degradation of chemical bonds. This was verified through analysis of the molar mass distribution. Similar effects were observed for the aliphatic-aromatic polyester. The lower molar mass variant experienced even faster degradation. When using aliphatic-aromatic polyester for modification, the synthesized polyester degraded more rapidly than the polylactide. The study found that hydrolysis followed a first-order reaction. The rate of biodegradation in the compost varied depending on the type of modifier. The material modified with bis(2-ethylhexyl) adipate degraded the fastest, followed by triethyl citrate, aliphatic-aromatic polyester of higher molar mass, and aliphatic-aromatic polyester of lower molar mass. The results suggest that modification significantly accelerated biodegradation in the initial stages of the process. Unmodified fibers biodegraded according to a first-order reaction, while after modification, they followed a second-order reaction.