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# CRYSTALLINE CHARACTERISTICS OF BIODEGRADABLE COMPOSITE MATERIALS BASED ON MODIFIED CELLULOSE AND POLYLACTIDE

**Abstract.** This paper presents the results of studies on the production of biodegradable composite materials based on polylactide/modified cellulose. Modification of microcrystalline cellulose obtained from plant stems was carried out using lactic acid oligomers. Compared to pure microcrystalline cellulose, the polymer treated with OLA-g-MCC was found to be better dispersed with PLA. The obtained materials were studied by X-ray phase analysis. The incorporation of OLA-g-MCC has been shown to improve the crystalline properties of the materials.

**Keywords:** polylactide; biodegradation; modified cellulose; degree of crystallinity; mechanical properties; biodegradable materials.

**Introduction**. Biodegradable composite materials based on natural or synthesized polymers are increasingly being used with deteriorating environmental conditions around the world. Among such natural polymers, the most used are cellulose, starch and their composite materials with polyhydroxyalkanoates, especially with polylactide, polybutyrolactam and others. The physicochemical and mechanical properties of the resulting composite materials largely depend on their composition, their processing methods, and chemical modifications, which can be studied using various physical methods, such as X-ray phase analysis, thermal methods, IR spectroscopy, etc. [1].

Biodegradable composite materials based on poly(lactic acid) filled with various substances have been extensively researched in recent years. One of their main disadvantages is the low degree of crystallinity, which greatly affects the mechanical properties and strength of products based on them.

The literature provides many ways to improve the mechanical strength of composite materials. For example, thermal methods can be used to study materials well for their strength and stability [2]. The physicochemical and mechanical properties of composites can be improved using various methods. For example, additives of different copolymers [3], creation of stereocomplexes [4], Isothermal Crystallization [5], treatment with different physical and mechanical forces [6], and others. Biodegradable composite materials based on cellulose and polylactide have been studied and great results have been obtained in their implementation in everyday practice [7–10]. But, despite the huge amount of work, some aspects of such composites still remain unexplored. For example, modifiers used to improve the properties of materials are still not well understood. This paper presents the results of studying the influence of the type of modifier and the study of the physicochemical and mechanical properties of composite materials based on modified cellulose and polylactide.

**Experimental**

**Synthesis of polylactide**

A common method of obtaining polylactide is ring-opening polymerization. The synthesis of polylactide was carried out in three steps according to the method presented in [11]. Zinc oxide, zinc chloride, aluminum chloride and their mixtures in different proportions were used as catalysts, and good results were obtained on the basis of zinc oxide.

**Extraction of cellulose from the stem of cereal crops (wheat).**

In the next experiments, experiments were carried out on the extraction of cellulose from cereal crops, mainly from the stem of the wheat plant. To do this, first, the material was crushed, poured over it with a 10% solution of sodium alkali and boiled for 4 hours. After cooling, the liquid was poured into a plastic container. The product was washed with water. Waste water contains lignin and alkali. The remaining product was mixed with water 1:10 and mixed well with a blender. For disposal, lignin in the waste was mixed with water in a ratio of 1:10, sprinkled on the garden soil 1-2 times a week and treated with a biodegrader. The liquid (lignin) poured into the compost mixture loses its toxicity in 5-6 months.

**Modification of wheat straw cellulose with oligomeric lactide.**

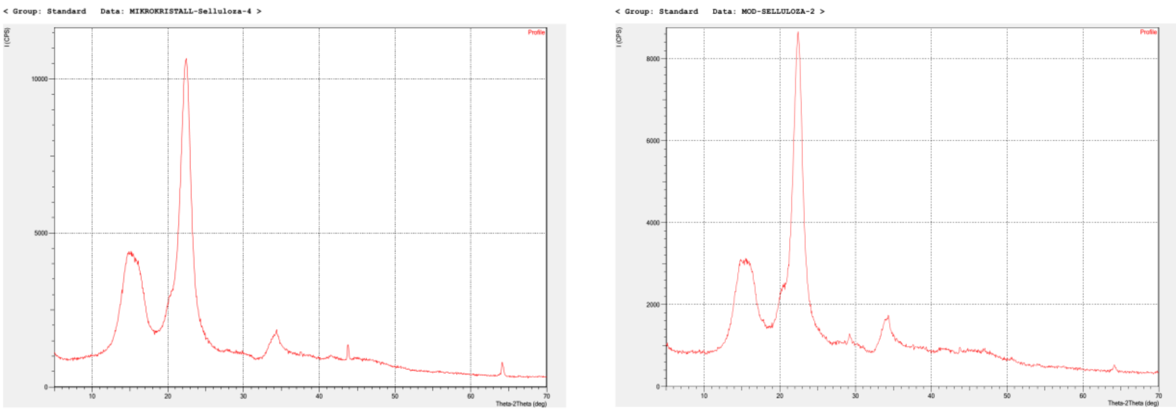
The yield of the reaction in polylactide synthesis is between 80-90%, and in each cycle 10-20% of the raw material is released in the form of oligomers. Since the degree of polymerization (molecular weight) of the oligomer is not so high, it is mainly in the form of a viscous liquid. As one of the ways to increase the interaction of wheat straw cellulose with polylactide, it was proposed to modify it with oligomeric lactide. In this case, 3-5% of the oligomer by weight of the resulting cellulose was mixed and heated at 60 °C for 2 hours with stirring. As a result, oligomer-conjugated microcrystalline cellulose (OLA-γ-MCC) was obtained [12].

After that, pure polylactide and modified OLA-g-MCC were made composite for 30 min under constant intensive stirring by liquidizing polylactide at 170 °C.

**Study of crystalline properties of PLA/OLA-g-MCC composite materials.**

Crystalline properties of polylactide and filler-modified cellulose (OLA-g-MCC) composite materials directly affect their strength and mechanical properties. Therefore, their crystalline properties were investigated in further studies. The crystalline properties of the PLA/OLA-g-MCC composite materials obtained in the experiments were studied with a powder X-ray diffractometer (XRD-6100, Shimadzu, Japan).

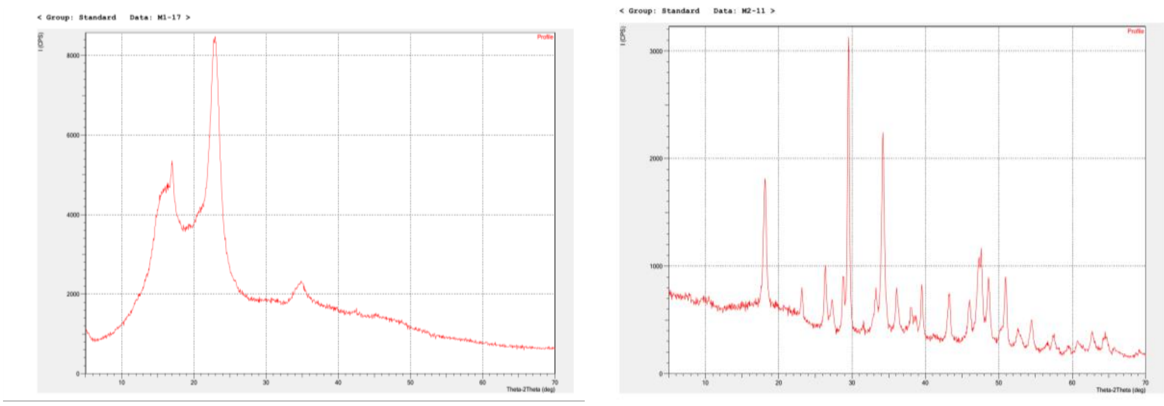
During the experiments, the crystallinity was comparatively studied by X-ray diffraction of the microcrystalline cellulose itself (Figure-1A), after its modification (Figure-1B), a composite of polylactide with unmodified (Figure-2A) and modified with oligolactide (Figure-2B) cellulose.




A) B)

Figure-1. X-ray phase analysis of pure microcrystalline (A) and modified (B) cellulose.

From the data obtained, it can be stated that with the introduction of the modifier, the degree of cellulose crystallinity will decrease (from 10500 to 8600) according to the highest peaks. After that, composites with unmodified and modified cellulose were obtained.



A) B)

Figure-2. X-ray diffraction analysis of the obtained composite materials of polylactide with unmodified (A) and modified (B) cellulose. (PLA/Cellulose - 60:40).

From the data obtained, it can be seen that the degree of crystallinity of the composite materials of polylactide with unmodified cellulose (2A) is not noticeably reduced, but the resulting material does not show sufficient strength. Adhesion between components is not good, since polylactide has a moderate polarity in the macromolecule, while cellulose has a high polarity in the macromolecule. They cannot directly form composite materials with improved properties. Therefore, in Figure-2B we can see that the degree of crystallinity generally decreases, but the total area of crystallinity increases. This is explained by the fact that the introduction of a modifier into the cellulose macromolecule promotes adhesion of two incompatible macromolecules.

The obtained results showed that the level of crystallinity of the PLA/OLA-g-MCC composite was higher than that of the original materials and other samples, and its crystalline properties were improved. Schematically it can be represented as follows (figure-3):

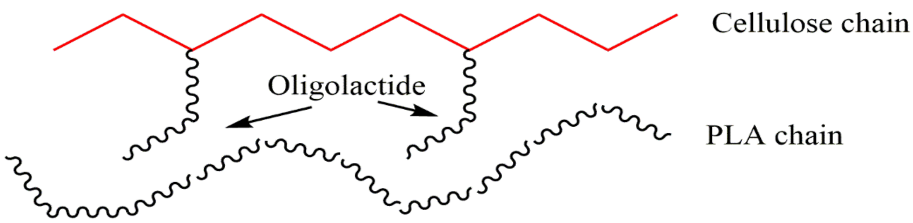



Figure-3. Interaction between the polar chain of cellulose and the non-polar chain of polylactide

As a result, the bond between the polar microcrystalline cellulose and the less polar polylactide is strengthened and the crystalline properties of the materials are improved.

**Conclusions.**

Polylactide was synthesized from lactic acid under ZnO, $ZnCl_2$, $AlCl_3$ catalyst by ring-opening polymerization method. Microcrystalline cellulose obtained from wheat straw was modified in the presence of oligomers formed as waste (about 10-20%) in the polymerization reaction. Compared to pure microcrystalline cellulose, OLA-g-MCC-treated polymer was found to disperse better with PLA. After modification of polar cellulose macromolecules with oligomers, it was found that interaction with PLA macromolecules of low polarity is improved, crystallites are formed on growth surfaces, and as a result, the degree of crystallization is high. It was observed that the properties of the materials improved after heat treatment due to the introduction of OLA-g-MCC and its synergistic effect.

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