Agricultural materials based on eco-friendly polymers

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Abstract. The present article is concerned with materials based on polyhydroxybutyrate and polylactide as new materials for seed carriers, producing a stimulating effect on their germinating ability as well as the growth and development of plants. It has been established that the growth of wheat is fundamentally affected by the structure of these materials. The composition and chemistry of polymers determine a mechanism of its biodegradation in a biological environment. At the same time, the structure of polymers and polymer of composites determines the speed and affects the kinetics of processes. Thus, the use of the biodegradable polymers has a positive impact on both the growth of plants and the environment.

1. Introduction
These days, it is difficult to imagine the agricultural sector without polymers. In crop production, for instance, they serve for improvement of the micro-climate of indoor structures; they are used for mulching of soils, coverage of grains, packaging of fruit and vegetables, fertilizers and toxic chemicals. Recently, the following technologies have gained wide use: planting of crops and vegetables seeds into capsules, pellets, mini-pots, made of clay, peat, mixtures of natural substances, biological and synthetic polymers. The advantage of using the method is that capsules reliably protect seeds from the bright sun, drying, vermin (mice and birds), and blowing-off with wind blasts.

There are also those seed carriers that create environmentally-safe conditions for seed growing, protect them against impact of pathogenic systems, and provide for micro-climatic conditions, favorable to germination of seeds and development of plants. To ensure the proper germinating ability of seeds, growth and development of plants, it is required to simulate a structure of bio-degradable polymers in such a way that they could provide for a high rate of directed diffusion flows of water, mineral matters and oxygen.

Over recent years, growing interest in bio-degradable materials has been observed, which are used in packaging, farming, medicine and in other areas\cite{1, 2}. The field of application of bio-degradable polymer materials is ever expanding, with the result that researchers focused their attention on modifications of conventional materials to make them user-friendlier, for which, among other things, they also develop new polymer composites with use of natural materials. To this date, the most popular bio-degradable polymers are polyhydroxybutyrate (PHB) and polylactide (PLA). Despite their high price, they demonstrate good bio-degradation results\cite{3-8}.
The purpose of the present article is to establish the mechanism of effect of the environment, which is a carrier material, on the germination stage (ontogenesis), and select a material, contributing to faster germination of seeds, but at a more reasonable price and exhibiting more acceptable physical and chemical properties, as compared to those of materials, based on pure PHB.

2. Experimental
Polyhydroxybutyrate (PHB) from Biomer (Germany) and polylactide (PLA) 4032D from Nature Works (USA) were used. A solution of polymers in chloroform or a mixture of chloroform and dichlorethane, ratio 80:20 mass %, is mixed in a rotary-pulsed apparatus. As a solvent of PHB and PLA, chloroform was used, with a refraction index of 1.44858 at an ambient temperature of 15°C, and a crystallization temperature of -63.55°C, and a boiling point of 61.152 °C. To achieve a higher electric conductivity of the forming solution, formic acid was used. 7% PHB-solutions in chloroform were made upon the application of heat within 0.5 – 1.0 min. and mixing with use of an ultrasound mixer. To prepare samples of small-size fibrous materials and study electrospinning processes, one used a laboratory facility, equipped with capillary tubes. The structure was studied under an optical microscope Axio Imager Z2m (Carl Zeiss, Germany) in transmitted light.

Experiments for “Tanya” wheat growing were carried out on the surface of samples, placed into Petri dishes. As a reference sample made of filter paper was used. Seeds were germinated at temperatures varying between 20 and 22°C, with moisture content, maintained at the same level. At that daily, within 7 days, one measured a few germinated seeds. During the research one compared parameters of the germinating ability on surfaces of samples of PHB film, PHB non-woven fiber, and PLA non-woven fibers.

3. Results and discussion
Search for innovative technologies became one of those crucial tasks, which the modern agricultural production of cereal and vegetable crops now faces. These technologies are aimed at increase in productivity, use of non-conventional methods of their planting, storage, and manufacture of environmentally sound products. One of the ways to manufacture environmentally sound products is planting into a carrier, located in soil, for which a non-woven material is used, based on a bio-degradable polymer. The data obtained enabled to prove that on a pressed film wheat germ develop slower than within films made of non-woven materials (Figure 1).

![Figure 1](image_url)

**Figure 1.** Samples with germinated wheat seeds (5 days) on the carrier, made of PHB film (a) and PHB non-woven fibers (b).
At that, the comparison of the germinating ability of wheat seeds on non-woven material samples of a different composition revealed that maximum acceleration of seed germination is observed on non-woven materials made of PHB and its mixtures. Obviously, this is due both to different chemical compositions, structural features, and thickness of fibers, the non-woven material consists of. It is worth noting that differences in samples’ structures are due to differing electrospinning conditions, related to the type of solvents and polymer concentration in solutions.

It should be noted that wheat seeds grow more intensively on composite samples. Thus, in [9] it was shown that the addition of synthetic nitrile rubber increases the seed germination index. This indicator is 0.58 for pure PHB, and 0.78 for the composition of PHB/SNR. The degradation of the polymer matrix depends on polymer structure, the process of germination of seeds and their root system. Creating composite materials will reduce the cost of the final material while maintaining its functional properties. The data are confirmed by the method of differential scanning calorimetry: the melting point of PHB non-woven fiber after germination, the seed decreases slightly, only by 2 °C, but the degree of crystallinity decreases by 12 %. DSC data indicates the degradation of the material.

Microphotographs (Figure 2) show that: first, films exhibit a denser structure, as opposed to a non-woven material; second, non-woven material samples are characterized by free spaces between single fibers, which, apparently, enable to provide for a water diffusion velocity, required for development of plants. It means that most suitable for seed sprouting is a material that has free spaces, ensuring a required velocity of water diffusion to seed surfaces.

**Figure 2.** Microphotographs of initial PHB film (a), PHB non-woven fiber (b) and PLA non-woven fibers (c and d).
Stresses arising in PHB polymer chains under the action of a mechanical force cause both breakdown of bonds and radically initiate chain oxidation processes [10].

Fibers made of PLA were used as a material for wheat seed planting. The purpose of the agricultural fibers for seed planting is to create environmentally sound conditions for germination, protect the seeds from the impact of pathogenic systems and form micro-climate conditions, favorable to germination and development of plants.

It has been established that the non-woven material, based on PLA, under review, is subject to degradation during growth and development of plants planted into it. The degradation process carries under the action of plants ferments and in progress of hydrolysis [9, 11]. Molecular weight the polymer is reduced during hydrolysis and the critical value of degradation is reached when oligomers begin to diffuse from the polymer.

4. Conclusion
1. Non-woven materials based on biodegradable polymers are suitable for an agricultural complex.
2. The structure of a polymer-carrier affects both the root growth rate and polymer degradation intensity.
3. Degradation of polymers results from breakdown of their crystalline structures.
4. The use of PHB-based mixtures will enable to balance their high price and improve mean physical and mechanical properties of PHB.

References
[1] Ramot Y, Haim-Zada M, Domb A J and Nyska A 2016 Adv. Drug Deliv. Rev. 107 pp 153-162
[2] Carrasco F, Pagés P, Gámez-Pérez J, Santana O O and Maspolch M L 2010 Polym. Degrad. Stab. 95 pp 116-125
[3] Arrieta M P, López J, López D, Kenny J M and Peponi L 2016 Ind Crops Prod. 93 290–301.
[4] Tertyshnaya Yu V and Podzorova M V 2018 Rus J Appl Chem. 91(3) 417–423.
[5] Bittmann B, Bouza R, Barral L, Diez J and Ramírez C 2013 Polym Compos. 34(7) 1033–1040.
[6] Peponi L, Sessinia V, Arrieta M P, Navarro-Baena I, Sonseca A, Dominici F, Gimenez E, Torre L, Tereják A, López D and Kenny J M 2018 Polym Degrad Stab. 151 36–51.
[7] Arrieta Í P, Lopez J, Hernández A and Rayon E 2014 Eur. Polym. J. 50 p 255
[8] Lasprilla A J R, Martinez G A R, Lunelli B H, Jardini A L and Filho R M 2012 Biotechnol. Adv. 30 pp 321-328
[9] Shibryaeva L S, Tertyshnaya Yu V, Pal’mina D D and Levina N S 2015 Selkhoz. Mach. and Technol. 6 14-18
[10] Tertyshnaya Yu V and Shibryaeva L S 2013 Polym Sci. Ser. B. 55 (3-4) p 164
[11] Rapacz-Kmita A, Stodolak-Zych E, Szaraniec B, Gajek M and Dudek P 2015 Mater. Lett. 146 73-76