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MANUFACTURING THE RYE STARCH-BASED BIOPLASTICS USING GLYCERINE AS A PLASTICIZER

BY

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Abstract. Bioplastic film based on rye starch and glycerine was experimentally produced. The starch extraction from rye grains was made after very fine grinding of rye grains together with distilled water, the powder filtration through cotton cloth, decanting, and slow drying at 60ºC. Different starch/glycerine weight ratios in the range of 2.5-3.7 constituted three versions of the mixture subjected to the stirring process and heated to 60ºC. The slurry-mixture was poured into a metal die and pressed forming 1-1.5 mm-sheet. After completing the drying, removal from the die, and keeping at room temperature for 2 days, the bioplastic was characterized. The results (density of 1.7 $g\cdot cm^{-3}$, tensile strength of 2.8 MPa, elongation at break of 6.3%, water contact angle of 53.4º) corresponding to the optimal version of the starch/glycerine ratio of 3.7, were almost similar to those obtained in making the bioplastic based on sweet potato starch.

Keywords: bioplastic, film, rye starch, glycerine, tensile strength.

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1. Introduction

The major impact on the environment of plastic waste resulting from the annual world production of over 380 million tons, with an annual growth rate of 4% (Rosenboom *et al*., 2022) justifies the concern of research towards the recycling of this waste and the search for new solutions for the manufacture of bioplastics. The role of plastics is essential in several areas of modern civilisation such as energy, road and air transport, health and food.

Traditional non-biodegradable plastic materials accumulated in large landfills, but also in the seas and oceans of our planet, constitute a major danger for the environment as well as for human and animal health. According to (Nanda *et al.*, 2022), the world production of plastics, mostly non-biodegradable, from 2020 increased compared to 2010 by 36%.

Bioplastics, that have recently become interesting for humanity, have several advantages compared to conventional plastics including biodegradability and a "low carbon footprint". Also, they have the ability to replace plastics based on petroleum fossils and the application field is wide from biomedical applications to the automotive industry.

Theoretically, plastics produced from polymers based on bio materials as well as from renewable or recycled feedstocks could be the solution to increase the life cycle of currently used plastics. Unlike plastics based on fossils (i.e. polyethylene, polypropylene, polyethylene terephthalate, polystyrene, etc.) (Walker and Rothman, 2020), those based on biomaterials have the advantage of low carbon dioxide (CO_2) emission in the atmosphere, which represents in fact the current trend worldwide.

In the case of manufacturing bioplastics, the monomers must be synthesized from biomass and then polymerized. Biomass extraction can provide natural non-synthetic polymers (e.g. starch, natural rubber, proteins) (Walker and Rothman, 2020).

With the beginning of producing bioplastics from natural resources (vegetable oils and starches), especially in Asia, Europe and USA, the fossil consumption is estimated to decrease by 15-20% until 2025 (Ashter, 2016). According to a work mentioned in Ashter, 2016, the proportion of recycled plastic waste in the world reaches only 3%, by comparison with the degree of recycling other major wastes (35% for metals, 30% for paper and cardboard, and 18 % for glass). The main companies working in the field of bioplastics have facilities in USA, Japan, South Korea, China, Germany, South Africa, etc.).

As mentioned above, starch represents one of the main natural sources for producing bioplastics. Starch-based biopolymers are considered the most promising biopolymers due to their wide availability and low cost. The mechanical properties of starch-based bioplastics are practically similar to conventional plastics (Nanda *et al*., 2022). Starch-based feedstocks include cereals (corn or wheat), and fibers (sweet potato, ordinary potato, and cassava), being in the form of long sugar molecule chains. Through relatively simple methods, the starch is converted into fermentable sugar and this into ethanol. The fibrous part of plants can be transformed into biofuels (Starch, 2018).

According to the same reference, several vegetable crops are adequate for recovering and using their starch content. Thus, wheat is recognized to have a starch content of about 70%. Although it is an important food plant, its starch can also be transformed into bioethanol. Corn has in his composition 70% starch and barley as a winter crop contains starch within the limits of 50-70%. Rye (Secale cereale), a cereal that grows on poorer soils, contains about 60% starch and millet that can be used in crop rotation soils as an ameliorant, contains 75% starch. Potato (*Solanum tuberosum*) has a lower content of starch of up to 19%, while sweet potato (*Ipomoea batatas*) reaches about 70%. Cassava, a major feed and food crop specific in tropical areas, can reach about 40% starch. According to the literature (Vu *et al.*, 2019), a research team from UK (York and Cambridge universities), France, and Denmark has found that lytic polysaccharide monooxygenase has the ability to convert starch to sugars.

Starch as a polysaccharide is produced by most plants to store the energy. Natural starch contains 75-80% amylopectin and the rest amylose (Brown and Poon, 2005). Amylopectin contains several branches of the sugar molecule chain, representing the main difference from the structure of amylose characterized by a linear chain. By mixing with hot water, the starch turns into a paste that can be used as a thickening or stiffening agent for the industrial process of manufacturing adhesives. The supplementary addition of a plasticizer such as glycerine can generate "thermoplastic starch" using extrusion, injection moulding or compression moulding techniques (Liu *et al*., 2009).

The paper (Ferreira Santana *et al.*, 2018) presented the results of research carried out on the starch extracted from jackfruit seeds plasticized with glycerine. Starch and glycerine were mixed in variable ratios between 20-60 g starch and 100 g glycerine. The bioplastics were prepared by the casting method. The microstructural analysis of bioplastic samples highlighted the presence of intact starch granules and the sample with the maximum proportion of starch (6%) was the most hydrophilic. The solubility of the bioplastic films was dependent on the starch concentration having values within the limits of 16.4-23.3%.

Considering the high starch content of the sweet potato (70%) (Starch, 2018), the solution of using this biomaterial together with glycerine as a plasticizer for the production of bioplastic was adopted (Abdullah *et al*., 2019). Different starch/glycerine weight ratios from 2.5:1 to 3.5:1 was tested. The physical-mechanical properties were identified by measuring the density, tensile strength, and elongation. The hydrophobicity was analysed by determining the water contact angle. Also, biodegradability was examined by enzymatic degradation by microbes. The incomplete gelatinization with increasing the starch/glycerine ratio highlighted by the microstructural investigation showed inhomogeneous granules. Under the conditions of using the 3.5:1 starch/glycerine ratio, the highest tensile strength of 2.57 MPa and the lowest elongation of 6.27% were revealed. The highest density of 1.66 g·cm^{-3} and the contact angle of 50.1º were the other characteristics of the bioplastic sample with the ratio 3.5:1 starch/glycerine. The physical-mechanical and biodegradability properties corresponding to the bioplastic produced from sweet potato starch were considered excellent.

Different experimental variants of composites or mixtures based on synthetic and natural polymeric materials as well as natural fillers were tested in (Chiellini *et al*., 2004). Due to its ability to be processed by both melt extrusion as well as solution or suspension, a synthetic polymer (polyvinyl alcohol) was adopted in this experiment. Starch and gelatine were chosen as polymers from renewable sources, while fillers were natural waste from the food industry and agriculture (sugar cane, wheat, orange and apple peels, corn and others). Bioplastics were made in the form of degradable films by compression and injection moulding.

Isolation and extraction of polysaccharides (in particular starch) is necessary to make bioplastics based on plant starch. According to the literature (Shi, 2016; Mello El Halal *et al*., 2019; Verwimp *et al*., 2004), several frequently used methods are known: (i) extraction method with hot water, (ii) dilute alkali-water solution, (iii) enzymolysis. The first of these methods is the most used, based on the property of polysaccharides to have higher solubility in hot water. In chemical terms, it is stable in hot water, so the extraction process does not influence the product quality. The usual technique consists in keeping the material in hot water for 2-6 hours. The low viscosity of the extract facilitates the separation of polysaccharide by filtration.

In the present work, the authors' concern was focused towards the experimental realization of bioplastic in the form of sheets (films) by extracting the starch from a cereal (rye) that contains this polymeric carbohydrate in about 60% proportion and using glycerine as a plasticizer.

2. Methods and Materials

The method of extracting starch from rye included the following steps. First, the rye granules combined with distilled water in a ratio of 1:2 (w/v) were ground in a blender. The resulting extremely fine powder was filtered through cotton cloth. The decantation of the starch suspension was done for 4-5 hours at room temperature, being collected in a wet state, which required subsequent drying in laboratory electric oven at maximum 60ºC for about 1 day.

The bioplastic preparation method involved mixing starch with glycerine (as a plasticizer) at three ratio values (2.5; 3.1; and 3.7). Separately, the three mixtures were heated in the electric oven at 60ºC for about 1.5-1.75 hours and intermittently, were stirred at a rate of 300 rpm. After thickening, the mixtures in form of slurry were poured into metal dies (12x12 cm) and pressed, so that the sheet thickness to be between 1-1.5 mm. The drying into the oven at 60ºC was carried out for 8 hours. After completing the drying, sheet bioplastics were removed from dies and were kept at room temperature and maximum humidity of 50% for 2 days before testing the sample characteristics.

The materials used in this experiment were: rye grains purchased from a private agricultural farm in France and 85% solution of glycerine ($C_3H_8O_3$), a trihydroxyalcohol commercially purchased from Romania. Commercial distilled water was used to apply the starch extraction method mentioned above.

The characterization methods of bioplastics were adapted to the type and shape of specimens, i.e. sheet (film) bioplastics. The density was determined according to the ASTM D792-20 standard, under the conditions of sheet (film) thickness of only 1-1.5 mm, using a pycnometer and water bath. Tensile strength was measured according to EN ISO 527-5:2009 and elongation at break of the bioplastic film was determined on a universal testing machine with crosshead rate of 50 mm·min^{-1} according to ASTM D882-12) (Yuniar *et al.*, 2019). Hydrophobicity by measuring the water contact angle was determined according to ISO 15989:2004 and the microstructural particularities of samples were identified with ASONA 100X Zoom Smartphone Digital Microscope.

3. Results and Discussion

As mentioned above, the weight proportion of rye starch reported to the proportion of glycerine varied between 2.5 and 3.7%. Percentage-wise, this means that starch represented between 71.4-78.7% and glycerine between 21.3-28.6%. Three experimental versions according to Table 1 were adopted, in which the percentage ratios of the two material components (starch/glycerine) varied as follows: 71.4/28.6 (version 1), 75.6/24.4 (version 2), and 78.7/21.3 (version 3).

Table 1
Characteristics of starch-based bioplastic specimens

Version	Starch/glycerine ratio	Density (g·cm^{-3})	Tensile strength (MPa)	Elongation at break (%)	Water contact angle (º)
1	2.5	1.45	0.9	17.32	45.2
2	3.1	1.61	2.1	16.82	49.8
3	3.7	1.70	2.8	6.30	53.4

The appearance of experimentally made starch bioplastic specimens is presented in Fig. 1.


a b

c

Fig. 1 – Experimentally made starch bioplastic specimens
a – version 1; b – version 2; c – version 3.

The characterization of bioplastic starch specimens carried out according to the adopted methods aimed at determining the density, tensile strength, elongation at break, and hydrophobicity by identification of the water contact angle. The results of these determinations were included in Table 1. According to the data in this table, the higher starch/glycerine ratio increased the density value of bioplastic from 1.45 to 1.70 g·cm^{-3}, the tensile strength value from 0.9 to 2.8 MPa, and the hydrophobicity by increasing the water contact angle from 45.2 to 53.4^{o}. Instead, the elongation at break sharply decreased from 17.32 to 6.30%, showing the favourable influence of the use of rye starch on the physical-mechanical characteristics of bioplastic.

Investigating the microstructural aspect of the three bioplastic specimens was carried out based on the images in Fig. 2.

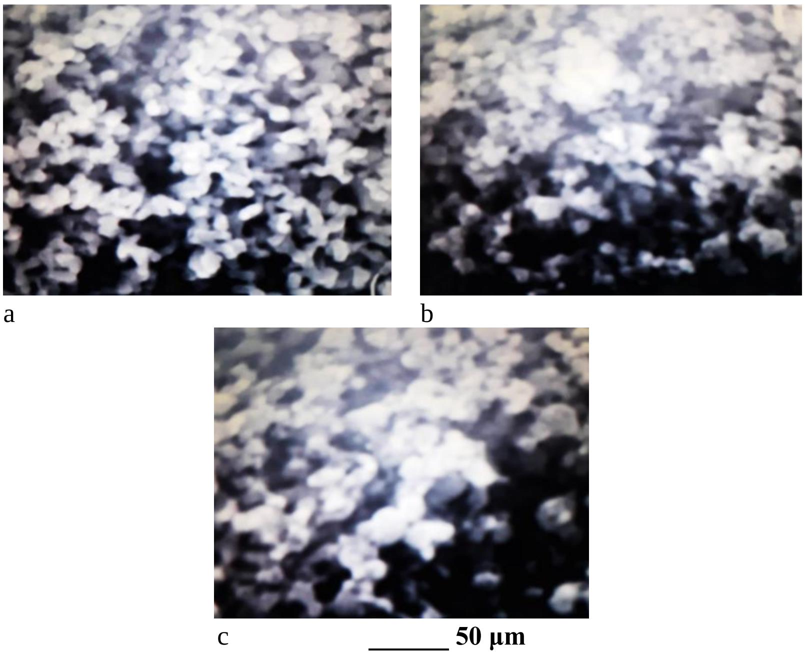

Fig. 2 – Microstructural aspect of starch bioplastic specimens
a – version 1; b – version 2; c – version 3.

The different starch/glycerine ratios influenced the roughness of analysed surfaces of bioplastic and this fact can be seen in images in Fig. 2. The relatively inhomogeneous starch granules as a result of the incomplete gelatinization process characterize the microstructural aspect of specimens. The action of glycerine molecules as plasticizer on starch molecules for reducing intermolecular hydrogen bonds in starch was more effective at lower proportions of starch (Fig. 2a), favouring the obtaining of low roughness and smoother bioplastic surfaces. The inhomogeneous aspect of spreading starch granules was accentuated through increasing the starch/glycerine ratio (Fig. 2b and c) leading to obtaining of rougher surfaces of bioplastic.

Analysing the results of the three tested versions, it was admitted that version 3, made with starch/glycerine ratio of 3.7, is the optimal. The rye starch-based bioplastic had tensile strength of 2.8 MPa, density of 1.70 $g\cdot cm^{-3}$, elongation at break of 6.30%, and water contact angle as a measure of hydrophobicity of 53.4º.

The analysis of the physical-mechanical and structural characteristics of the rye starch-based bioplastic showed that such a product can be obtained in ecological and economic conditions at a quality level close to that manufactured industrially in conventional conditions. In the world, concerns and partial results of the research teams in the field of testing the production of bioplastic using a wide range of plants (wheat, corn, barley, sweet potato, ordinary potato, cassava, sugar cane, jackfruit, etc.) as a cheap and environmentally friendly supplier of starch are already known.

Among the technical data provided by the literature regarding the production of starch bioplastics, few of them could be selected to be compared with the results of this article. The most complete information refers to the use of starch extracted from sweet potato combined with glycerine (as a plasticizer) to obtain bioplastic in the form of a film, compatible with the bioplastic obtained from rye starch in the experiment presented in this paper. According to (Abdullah *et al*., 2019), the sweet potato starch-based bioplastic reached the following optimal characteristics: density of 1.66 $g \cdot cm^{-3}$, tensile strength of 2.57 MPa, elongation at break of 6.27%, water contact angle of 50.1º, under conditions of starch/glycerine optimal ratio of 3.5:1, and the starch contain of sweet potato of about 70%. The comparison of results obtained in the current experiment and respectively, in the case of manufacturing the sweet potato starch-based bioplastic, shows remarkable similarity between them, although the starch proportion in the two plants is different (60% in rye respectively, 70% in sweet potato).

The main advantages of bioplastics made from bio-based polymers compared to fossil-based plastics is the low carbon footprint, influencing the level of greenhouse gas emissions, their biodegradability, and the low cost of manufacturing.

4. Conclusions

The objective of the paper was the experimental making of bioplastic based on rye starch. Rye grains have a starch content of about 60% according to the literature, but they are not a bio-vegetable material of interest for the research carried out so far in the world such as wheat, corn, cassava, sweet potato, ordinary potato and others. The choice of rye as a supplier of starch for the manufacture of bioplastic can be considered as the originality of this work. Among the known methods of extracting the starch from the finely ground grains of the plant, the most frequently used one was adopted, that of the addition of hot water at maximum 60ºC. Also, glycerine as a plasticizer was introduced into the formed mixture, which was then poured and pressed as a film into the metal die. The optimal starch/glycerine ratio was experimentally determined at 3.7. Main physical-mechanical characteristics of the bioplastic film were: density of 1.7 $g \cdot cm^{-3}$, tensile strength of 2.8 MPa, elongation at break of 6.3%, water contact angle of 53.4º, being almost similar to those of the bioplastic produced according to the literature from the starch extracted from sweet potato combined with glycerine. The main advantages of using bioplastic based on bio-vegetable materials compared to fossil-based plastic are the low carbon footprint, biodegradability, and the low cost of manufacturing.

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FABRICAREA BIOPLASTICELOR PE BAZĂ DE AMIDON DIN SECARĂ UTILIZÂND GLICERINĂ CA PLASTICIZANT

(Rezumat)

A fost produs experimental un film de bioplastic pe bază de amidon din secară și glicerină. Extracția amidonului din boabele de secară a fost realizată după măcinarea foarte fină a boabelor împreună cu apă distilată, filtrarea pulberii prin pânză de bumbac, decantarea și uscarea lentă la 60ºC. Amestecul sub formă de șlam a fost turnat într-o matriță metalică și presat formând o foaie de 1-1,5 mm. După finalizarea uscării, scoaterea din matriță și menținerea la temperatura camerei timp de 2 zile, bioplasticul a fost caracterizat. Rezultatele obținute (densitatea de 1,7 $g{\cdot}cm^{-3}$, rezistența la tracțiune de 2,8 MPa, alungirea la rupere de 6,3%, unghiul de contact al apei de 53,4º) corespunzând variantei optime a raportului amidon/glicerină de 3,7 au fost aproape similare cu acelea obținute la fabricarea bioplasticului pe bază de amidon din cartof dulce.