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Novel biodegradable potato starch-based compositions as candidates in packaging industry, safe for marine environment

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Abstract

About 70% of our planet's surface is covered by seas and oceans to which even 10 million tons of waste go every year. It makes these places the largest global landfills, containing up to 90% of plastic waste. In this article we present the results of research on novel starch-based compositions expected to be more safe for the marine environment. For these purpose biopolymers such as, thermoplastic starch (TPS), polylactide (PLA) and poly(vinyl alcohol) (PVA) were reactive extruded and formed into films by high-pressure compressing. Their physical, thermal and mechanical properties were examined. Compositions were tested in seawater collected from the Gulf of Gdansk Baltic Sea. The obtained samples were completely disintegrated after 3 weeks. BOD test in the presence of bacteria pseudomonas augerinosa confirmed biodegradation of prepared compositions. The impact assessment of received materials on the marine environment was also evaluated by degradation tests in the presence of Phaeodactylum tricornutum diatom. Cells growth of Phaeodactylum tricornutum diatoms was only slightly inhibited in the presence of TPS/PLA/PVA compositions.

Keywords*: Packaging bio-polymers, Biodegradation, Marine environment, Microorganisms, Plastic pollution*

1. Introduction

For a considerable amount of time synthetic polymers have been very common packaging materials, because they present several desired features like softness, lightness and transparency. The most popular packaging materials are conventional petrochemical-based plastics (so called 1-st generation polymers), such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyamide (PA). The aforementioned polymers are widely available at relatively low cost and they have good mechanical performance, such as tensile and tear strength, good barrier to oxygen and possibility to make very thin films [1]. Such a packaging often performs an important and yet positive role in protecting the environment. They are useful in transport of toxic and corrosive products; protect the environment from contamination. However, the increased use of synthetic polymer packaging films leads to serious ecological problems due to their non-biodegradability. Those packing polymer materials are difficult to dispose after using them, so they occupy a lot of space on the Earth. It is a known fact that there are islands on the surface of the oceans made from rubbish (marine litter) where 90% are found to be plastics [2,3]. Those disposed plastics pose a threat not only to the society and economy, but in particular to marine animals. Large amounts of wastes threaten the bottom benthos which wrongly recognize miniscule waste as a nourishment source. Each year about 100,000 marine mammals die because of swallowing plastic non-biodegradable bags [4].

Insert Figure no. 1 here

Therefore, polymeric biomaterials have come to be treated as an alternative to dangerous conventional polymers . “Bio-plastics” (2nd generation of polymers) is a

wide family of resource efficient materials derived from biomass or petroleum. Division and examples of polymers belonging to the bio-plastics group is presented in Fig. 1. European Bioplastic describes these material group as biodegradable, bio-based or both [5]. The global production capacity of bio-plastics in 2015 was estimated at 4 Mt (according to research conducted by European Bioplastic [5]), and 7,8 Mt (according to research conducted by nova-Institute [6]). It is incomparably less than the value of production of petroleum plastic materials amounting to 322 Mt [7]. The prognosis for 2020 provides for an increase of global bio-plastics production capacity to the level of even 12 Mt [6] (Fig. 2). Study conducted by Plastic Europe in 2016 proves that nearly 40 % of total plastic demand is covered by the packaging sector [7]. This overlaps with the amount of packaging waste, which accounts for over 90% of all plastic debris [8].

Insert Figure no. 2 here

Thus there is a strong demand for overworking new polymer compositions, especially those quickly biodegradable in many environments. The paper is sought to be one of solutions leading to those demands. The experimental part concentrates on potato starch, polylactide (PLA) and poly(vinyl alcohol) (PVA) biodegradable polymers. The first two, are already widely described in the literature as biodegradable and compostable packaging materials [9–12]. Furthermore, the potential of starch-based biopolymers as marine safe materials have already been reported [13–15]. Studies confirm the disintegration of these materials both in laboratory and *in situ* marine conditions, but do not confirm their biodegradation. The exception is MaterBi® (a biodegradable polymer blend based on corn starch) which in tests in marine coastal sediments showed 90% biodegradation after about one

year [16]. In turn, PVA has been successfully used as a modifier to increase the water susceptibility and decrease time of biodegradation [17–19]. PVA biodegradability proceeds first by dissolution of the polymer in water, followed by decomposition to carbon dioxide and water under the influence of the relevant bacterial strains [20]. The period of biodegradation for this substance is about 30 days [21]. However, it should be noted that, biodegradation process of the polymers occurs under specified conditions. It requires the presence of micro-organisms and mineral nutrients, oxygen access and moisture, as well predetermined temperature depending on the type of bacteria and pH (for the 5-8) [22–24]. Marine environment is a highly complex milieu; its components and properties change with area, depth, season, or degree of pollution [25] . Thus, biodegradable polymer waste present in the oceans are exposed to the completely different conditions than those occurring on land. This can lead to disruption or even inhibition of the biodegradation process of biopolymers [26]. Therefore, the problem of the formulation of marine waste may deepen. Research on new bio-plastics should take into account biodegradation in the terrestrial as well as in marine environment.

In the literature, many papers can be found regarding the study of changes in polymer properties after incubation in the marine environment [27–32]. These reports are most of all focused on molecular structures, weight loss, tensile strength changes or description of the type of plastics degradation pathways. However, there are limited studies analysing the desired final biodegradation (conversion into CO2 or CH4, H2O and biomass) products after incubation of polymeric materials in marine environment or studies considering the impact of the biodegradation process and products on marine flora. Therefore, it seems important to supplement this type of research with: (1) laboratory tests measuring O_2 consumption or CO_2 evolution under

optimized conditions, (2) exposure of living marine flora to the material or its components.

Taking all together, the article is devoted to the study of novel biodegradable potato starch-based compositions modified by PLA and PVA ingredients with the idea to prepare safer for marine environment and more economic packaging materials. Therefore, we obtained TPS/PLA/PVA compositions, determined their physico-chemical and mechanical properties, carried out the biochemical oxygen demand (BDO) test to estimate the biodegradability of obtained polymer composition in marine environment . Finally, analyzed the impact of the obtained composition on the marine flora population with using *Phaeodactylum tricornutum* diatoms.

2. Experimental

2.1 Materials

The following materials were used to prepare the compositions: potato starch (Castello-Lidl Poland, humidity max. 10%), vegetable glycerol (99.8% purity) originated from the POCH S.A., PL, served as a native starch plasticizer. Polylactide (PLA) (ZHEJIANH ESUN CHEMICAL C, China) and polyvinyl alcohol (PVA) (Sigma-Aldrich) used to enhance and modify thermoplastic starch (TPS) properties.

2.2. Blends preparation

Native potato starch and glycerol at a weigh proportion of (33,4/66,6 w/w) were pre-mixed until homogeneous consistency was obtained. Then, prepared mixture was extruded using Brabender Plastti-Corder, Duisburg (80 rpm, 160 ºC), thus obtaining a thermoplastic starch (TPS), which was subsequently again extruded (50rpm, 160 ºC) with various amount of PLA and PVA. The TPS/PLA/PVA compositions with the ratio of the components equal to 2/1/1, 1/1/1, 2/3/1, w/w, were obtained. They were formed

into film sheets using hydraulic compression moulding machine (ZUP Nysa). The moulding process was carried out under a mould pressure from 5 to 20 MPa for 5-10 min, at 160 – 190ºC. Prepared TPS/PLA/PVA films (the thickness around 0,5 mm) were used for further characterization. Immediately, after processing they were kept under airtight conditions.

2.3 Material characterization

2.3.1 Infrared analysis (FTIR)

Chemical structure of TPS/PLA/PVA samples were examined using a Fourier transform infrared spectroscopy (Nexus Thermo – Nicolet, Technical University of Lisbona), over the wave-numbers in the range of 500 – 4000 cm^{-1}, at the ambient temperature (25°C). The FTIR equipment consisted of ZnSe mirror cap; diamond optical device; heated plate.

2.3.2 Thermal properties

The thermal analysis was performed using a differential scanning calorimeter DSC 204 (Netzsh) and thermal analyzer TG 2090 (Netzsh). About 5 mg of sample was used in each trial. Firstly, the samples were conditioned at 30ºC for 2 min. Then, they were heated at 10°C/min, from 25 to 220°C, under nitrogen atmosphere.

2.3.3 Physico-mechanical properties

Hydrostatic balance (RADWAG WPS 510/C/2) was used to measure the density of TPS/PLA/PVA films, according to PN-EN ISO 1183-1:2004 standard. The measurement was performed at room temperature (22°C). As a reference medium *n*-heptane was used (0,682 g/cm^3). Five tests were carried out for a particular

compositions and the results were averaged. Hardness was measured by using Shore method (type A) according to PN-EN ISO 868:2004 standard (Zwick/Roell B7206:200, 1008.105 Shore Digital, and pressure 12,5 N). Five measurements of each sample were taken and the results averaged. Melt flow rate (MFR) was performed by using plastometer (Monney), according to the PN-EN ISO 1133:2005 standard (160ºC, load of 2,16 kg). The value of MFR is expressed as a 10 g of material extruded through the standard capillary (diameter 2,095mm) placed in a heating nozzle during 10 min [g/10min]. Three measurements were taken and the results averaged.

2.3.4 SEM analysis

The microstructures of film surfaces were examined using Philips-FEI XL 30 ESEM. The surface was sputter coated with gold prior to observation (Quorum, Q150T). Pictures were made at randomly selected places of the sample at 200x and 1000x magnification. Electron micrographs were taken on samples collected just after compression moulding, one year after compression moulding and in the presence of selectively etching agents: water and dichloromethane, respectively.

2.4 Degradation tests of prepared compositions

2.4.1 Marine environment (static system, laboratory conditions)

Evaluation of susceptibility to degradation in seawater was conducted at room temperature. Five rectangular samples (150x20x0.5 mm) of each film were placed in Erlenmeyer vessel filled with Baltic seawater. The vessels were placed in a sunny location. After the required incubation time, the samples were taken out and dried at

30°C to the constant weight. The weight loss (Δm) of films were estimated based on the formula (1):

$$\Delta m = \frac{(m_p - m_k)}{m_p} x100 \qquad (1)$$

Δm –the weight loss of film [%]
m_p– the weight of film before degradation [g]
m_k – the weight of film after degradation and drying [g]

2.4.2 Biochemical oxygen demand (BOD) test

Prepared samples were sealed in containers equipped with snap-ons for monitoring pressure changes (OxiTop system, LNEG, Portugal), caused by bacterial activity. Incubation was conducted on agar culture medium with *Pseudomonas aeruginosa,* for 21 days at 37°C. Respirometric and weight loss measurements were carried out in accordance with ATCC13388 standard. The study was conducted under sterile conditions. The value of BDO was calculated according to the formula (2):

$$BOD = \frac{M(O_2)}{R \times T_m} \times \left(\frac{V_t - V_1}{V_1} + \frac{\alpha \times T_m}{T_0} \right) \times \Delta p(O_2) \qquad (2)$$

$M(O_2)$ - molecular weight of oxygen molecule (32000 mg/mol)
R – gas constant (83,1441 mbar/mol*K)
T_0 – reference temperature (237,15 K)
T_m – measurement temperature [K]
V_t – volume of measuring cylinder [ml]
V_1 – sample volume [ml]
α – Bunsen absorption coefficient (0,03103)
$\Delta p(O_2)$ – Difference in molecular pressure of oxygen [mbar]

2.5 Impact assessment of the obtained composition on the marine flora population.

In the experiment *Phaeodactylum tricornutum* (Bohlin SAG 1090-la) was cultured in Falcons with Baltic seawater in the presence of the selected polymer composition. The measurement was performed in 3 replications. The incubation period was equal to 14 weeks at 37°C. Before each survey, water was subjected to filtration (glass

filters, GF/C, Wathman, pore diameter 0,7 μm) – in order to remove phytoplancton. As a result of the study, measurements of cell number were determined using coulter counter instrument (Z series, Beckman, IO PAN). The cells number were presented as percentage value relative to the control sample.

3. Results and discussions

3.1 Film preparation

Table 1 shows the description of obtained TPS/PLA/PVA compositions, parameters of compression moulding process and visual assessment of the obtained samples. Observations allowed to select samples for further investigation. Temperature below 190°C caused insufficient homogenization, which indicates that not all of components have been plasticized. This resulted in fragile and highly heterogeneous structure. The most optimal processing parameters are for the temperature of 190°C and a mould pressure equal to 10MPa. Consequently, a highly homogeneous and flexible TPS/PLA/PVA films with different content of components were obtained.

Table 1 The composition of obtained TPS/PLA/PVA films, processing parameters and observations.

	TPS/PLA/PVA		
Composition (w/w)	2/1/1	1/1/1	2/3/1
Processing parameters [T(°C) / p (MPa)]	Observations		
170/ 10	-	-	-
180/ 5	-	X	-
180/ 10	-	X	-
190/ 5	-	X	-
190/ 10	**+**	**+**	**+**

x yellow, flexible, heterogenous
+ white, flexible, homogeneus and durable
- yellow, fragile, heterogenous

3.2 Infrared analysis (FTIR)

Figure 3 shows FTIR spectra of obtained TPS/PLA/PVA films. The wave numbers and important bands identification of compositions are shown in Table 2. In the spectrum, a broad PVA absorption peak is seen at 3200 – 3500 cm^{-1} (O – H

stretching vibration). Observed intensity fluctuations of this peak within the compositions may be the result of formation of intramolecular hydrogen bonding between starch or PLA carbonyl groups. The PLA characteristic peaks are seen at 1750 cm^{-1} (C = O stretching vibration) derived from a carbonyl group and at, 1184, cm^{1} coming from the ester group (C − O) of PLA chain, which is in accordance with Wu and Liao [33] results. A fission of carbonyl peak (at 1750 cm^{-1}) may indicate a high proportion of hydrogen bonds in TPS/PLA/PVA (2/1/1) sample. The peaks appearing at 750 – 930 cm^{-1} are characteristic for (−C – C−) stretching vibration bonds present in the starch molecules [34] .All films display absorption at approx. 1260 and 1360 cm^{-1}, as a result of -CH_2 deformation vibration of CH_2OH groups at the amylose and amylopectin molecules [34].

Insert Figure no. 3 here

The peak at 1453 – 1456 cm^{-1} (C – H) comes from -CH_2 group at PVA chain. Appearing changes of this peak intensity may indicate the varying number of hydrogen bonds between starch and PVA particles. Furthermore, in all samples there is a distinctive absorption peak at 2947 cm^{-1} corresponding to − C – H stretching vibration of PVAs methylene group. The most intense peak (at 1087 cm^{-1}) is assigned to stretching vibration C – OH bond representing secondary alcohol (PVA). Moreover, weak absorption peak at 1650 cm^{-1}, probably comes from absorbed water (water bound) by PVA molecules.

Table 2. Bands assignments of the selected TPS/PLA/PVA compositions.

Wave number range [cm^{-1}]	**Assignments**	**Origin**

3200-3500	strong and a broad absorption peak of O–H stretching vibration	PVA
2947	C–H stretching vibration of methylene group -CH_2	PVA
1750	C=O stretching vibration of carbonyl group >C=O	PLA
1650	water molecules adsorbed by the PVA particles	H_2O
1453-1456	-C–H binding vibration of -CH_2 linkage	PVA
Approx. 1360	deformation vibration of -CH_2 group from – CH_2OH linkage	amylose and amylopectin molecules
1087, 1184, 1260,	Asymmetrical and symmetrical valence vibration of -C–O- ester bond	PLA
750-930	vibration of -C−O−C- group	TPS

The FTIR spectra of TPS/PLA/PVA blend indicates that there are some molecular interactions between components. Presumed partial miscibility of components may be attributed to the possible hydrogen bonding that occurs between the starch molecules, PLA and PVA molecules. Varying content of the components in the TPS/PLA/PVA mixture results in a shift of mentioned bonds which implies a varying proportion of hydrogen bonds between the molecules thereby affecting the degree of miscibility.

3.3 Thermal properties

Table 3 presents the thermal properties of the selected composition TPS/PLA/PVA(1/1/1) and its components. Thermal analysis revealed as follows; glass transition temperature (T_g) for TPS was 51.9°C and a melting temperature (T_m) around 155°C; TPS/PLA exhibited a T_g at 64.2°C and a T_m around 170°C; T_g of TPS/PLA/PVA(1/1/1) composition was equal to 61.4°C (T_m ~ 165 – 189°C). Glass transition temperature of TPS/PLA/PVA compositions is above room temperature, so the material is stiff at these conditions. The incorporation of PVA caused slight

decrease of T_m value compared to TPS/PLA composition, as well as led to increase of T_m value up to 179°C. According to the results of the thermal analysis, pressure moulding (shaping out of the particular product) of the obtained composition should be carried out at following temperatures; TPS – above 155°C, TPS/PLA – above 170°C, TPS/PLA/PVA – up to 190°C, respectively.

Table 3. Thermal properties of TPS/PLA/PVA components.

Sample	Tg	Tm	Forming temperature
TPS	51.9	155	>160
TPS/PLA (1/1)	64.2	170	>170
TPS/PLA/PVA (1/1/1)	61.4	143-179	~190

3.4 Physico-mechanical properties

The results of the density, hardness and MFR survey of the TPS/PLA/PVA films are presented in Table 4. There is a density downward trend with increasing quantity of PLA in the obtained compositions. For all samples studied the density is higher than 1g/cm^3. Thus the films will not occupy the surface of ocean or sea for a long time in case they will be found there. Therefore, TPS/PLA/PVA compositions can be friendlier for marine birds and limiting to some extent the choking during swallowing the plastic rubbish by mammals.

Table 4. The density, hardness and MFR values for chosen TPS/PLA/PVA films.

Sample – temp./pressure	Density [g/cm^3]	Hardness [° Sh A]	MFR [g/10min]
TPS/PLA/PVA(2/1/1) – 190/100	1.30±0.00	67.31±1.72	25.50±3.50
TPS/PLA/PVA(1/1/1) – 190/100	1.25±0.00	49.69±5.26	7.34±1.25
TPS/PLA/PVA(2/3/1) – 190/100	1.24±0.00	84.81±4.32	6.80±1.55

Furthermore, obtained samples have a wide hardness range (49-85° Shore A). The more PLA is used in the composition the higher hardness of the material is observed,

which can be explained by PLA crystallinity. A wide range of hardness could be used to design a variety of packaging, according to their destination.

MFR as an important parameter of the polymer processing was also investigated. It was observed that increase in TPS content was leading to significant increase of MFR, up to 25.50 g/10min value (TPS/PLA/PVA(2/1/1)-190/100). The lowest value exhibited TPS/PLA/PVA(2/3/1)-190/100 composition (6.80 g/10min), what is closely related to higher PLA presence.

3.5 SEM analysis

After the preliminary assessment of the films the following sample was selected for further analysis: TPS/PLA/PVA(1/1/1)-190/100.

Insert Figure no. 4 here

Figure 4 presents scanning electron micrographs of this film. The pictures were taken the day after compression process (Fig. 4a) and after a year of storage under room conditions (Fig. 4b). The surface of the TPS/PLA/PVA(1/1/1)-190/100 film was not changed noticeably as a result of annual storage, which may suggest films stability during storage.

For further morphology characterizations, the films were subjected to selective etching. The samples were treated with dichloromethane and water, which are good solvents for the relevant components (Fig. 5). PLA particles in TPS/PLA/PVA (1/1/1)-190/100 samples were etched by dichloromethane and holes in the images are related to the extraction of these particles. From the images presented it was clear that PLA particles were satisfactory dispersed in the matrix, only some agglomerates were detected (Fig. 5b,d). The treatment with water resulted in an intensive

dissolution of PVA from the polymer matrix. In the presented SEM micrographs interpenetrating phases were visible that give us the information about high partial miscibility and compatibility of the components.

Insert Figure no. 5 here

3.6 Degradation test (marine environment)

Insert Figure no. 6 here

Degradation test in seawater environment was estimated as percentage weight loss of the samples (Fig. 6). Two selected compositions were tested: TPS/PLA/PVA(1/1/1)-190/100; TPS/PLA/PVA(2/3/1)-190/100.

At the beginning (up to 1 week) of incubation in seawater of TPS/PLA/PVA(1/1/1)-190/100 and TPS/PLA/PVA(2/3/1)-190/100 films, the weight loss of both samples was similar and it was about 50%. After 3 weeks of study the weight loss of the TPS/PLA/PVA(1/1/1)-190/100 composition increased by 81% while for TPS/PLA/PVA(2/3/1)-190/100 it was almost 60%. After a period of 3 months from the start of the test, the samples were significantly swollen and disintegrated. Therefore, the samples were not suitable for further weight measurements. According to Heimowska et. al, [35] which conducted the incubation of different packaging materials in the Baltic Sea (*in situ* and laboratory studies), samples of PE, PE/starch, and PET were completely insensitive to marine environment even up to 12 months. The changes in weight lost and properties were not observed at all. From the extrapolation of the results presented in Fig. 6, it can be assumed that after a period of seven weeks incubation in seawater, the TPS/PLA/PVA(1/1/1)-190/100

composition should be completely degraded (films disintegrated into micropieces). In turn, TPS/PLA/PVA(2/3/1)-190/100 composition showed a higher resistance to degradation in seawater. The forecast shows that a period of 3 months may not be enough to completely degrade the sample. From the analysis of the data for the TPS/PLA/PVA films it can be concluded that for a quick dissipation process of samples in seawater it is better to prepare the composition with a lower content of PLA in the composition. It is known that the presence of thermoplastic starch (TPS) in polymer composites promote the wettability, mineralization and consequently increases the decomposed rate [1,36,37]. Consequently TPS/PLA/PVA(1/1/1) sample was used for further degradation analysis.

3.7 Biochemical oxygen demand (BOD) test

In BDO test, after the first 24 hours of incubation, it was observed that TPS/PLA/PVA(1/1/1) sample was adherent to the vaccinated with *Pseudomonas aeruginosa* bacteria agar medium. Initial degradation was noticeable – turbidity of agar medium in the immediate vicinity of the samples (Fig. 7a). After 21 days of incubation, the sample was completely dispersed - only a streak remained on the agar base (Fig. 7b). The TPS/PLA/PVA(1/1/1) composition was completely decomposed by incubation with *Pseudomonas aeruginosa bacteria.* Thus, 100% of the initial mass of the sample was taken as the result of the weight loss.

Insert Figure no. 7 here

The biochemical oxygen demand (BOD) study included measurement of pressure change during incubation process. The results are shown in Fig. 8. It was observed that, with the duration of test the pressure drops. After 21 days of incubation, the

lowest value was recorded for the TPS/PLA/PVA(1/1/1) sample (-77 hPa). The control test for this sample reached -56 hPa. Increase in the PLA content in compositions (TPS/PLA/PVA 2/3/1) led to an increase of pressure, up to -42 hPa. For the test carried out without the presence of the polymer composition the pressure value was -14 hPa.

Insert Figure no. 8 here

The pressure drop in the system is related to the higher consumption of O_2, which in turn is closely associated to the activity of microorganisms. For the TPS/PLA/PVA(1/1/1) sample, pressure drop to value -77 hPa which correspond to BOD equal 6110 mg/l. This result is more than 1/3 higher than for TPS/PLA/PVA(2/3/1) sample (Table. 5). As expected, the susceptibility to biodegradation of the polymeric compositions decrease with the increase of the PLA content. A similar relationship was observed by Moura et al. [38]. In this paper, biodegradability (expressed in BOD measurements) of the blends increased with the increasing amount of thermoplastic starch (TPS). Among the factors facilitating penetration of microorganisms into the polymer composition are amorphous structure and hydrophilic nature of TPS [39,40].

Table 5. Biochemical oxygen demand of TPS/PLA/PVA(1/1/1) and TPS/PLA/PVA(2/3/1) in the presence of *Pseudomonas aeruginosa* bacteria.

Microorganism type	Sample	BOD [mg/l]
-	Control	-
P.a.	TPS/PLA/PVA(1/1/1)	6110
P.a.	TPS/PLA/PVA(2/3/1)	4029

P.a. - Pseudomonas aeruginosa

3.8 Impact assessment of the obtained composition on the marine flora population.

The results from the experiment with using *Phaeodactylum tricornutum* are purpose to evaluate the growth of diatom populations in the presence of TPS/PLA/PVA(1/1/1) compositions and their components.

Insert Figure no. 9 here

Insertion to the system the polymer composition led to decrease of diatom cell number up to a value 68% (Fig. 9) of the control sample (100%c refer to value 11,40 x 10^6 cell per 1 cm^3 - control test). Thus, the presence of degradation products affected cell division of algae, limiting to some extent their growth. An ingredient that could cause inhibition of *Phaeodactylum tricornutum* cell growth are PLA and PVA. In both cases the cell number decreased by 24%, relative to control test. From the other hand, pure TPS acted as a culture medium for diatom growth. At week 14, the pure TPS sample reached cell numbers in the diatom population equal 105% of the control sample. The influence of the TPS-based polymer on *Phaeodactylum tricornutum* marine diatom growth was previously reported [13] . Guzman et al., investigated the impact of commercial packaging based on thermoplastic starch (TPS over 85%) on marine life. It was proved that high content of TPS in polymer sample favours the growth of diatoms, acting as an energy source for *Phaeodactylum tricornutum* microorganisms.

4. Conclusions

Three new starch-based TPS/PLA/PVA compositions have been obtained, with the following properties:

- The density is in the range of 1,24 – 1,30 g/cm^3, what is much higher in comparison to so far used PE bags (LDPE ~0,94 g/cm^3). Therefore,

TPS/PLA/PVA compositions will not occupy the surfaces of seawater for a long time what is positive fact for seabirds.

- The samples have wide range of physico-mechanical and rheological properties (hardness 49-84 ºShA, MFR (160ºC, 2,16kg) 6,8 – 25,5 g/10min), what can be useful to obtain different type of packaging materials by various technological process
- SEM analysis has shown that the obtained polymer compositions are stable during 1 year storage.
- The obtained samples disintegrate in seawater (laboratory test) within 3 weeks what is very positive in comparison to conventional petrochemical polymers (PET, PE) which are very stable in seawater for a huge amount of time.
- Complete biodegradation in the presence of *Phaeodactylum tricornutum* was confirmed for the obtained samples by BOD test,
- The presence of PLA or PVA in the composition leads to a slight inhibition of diatom cells population, while TPS acts as a diatom growth medium.

Taking into account the described and summarized test results we can assumed that our new TPS/PLA/PVA compositions are safer alternative to conventional packaging materials, especially if there is a probability of getting these waste into marine environment. They are fully-biodegradable in marine environment. Our future studies will concentrate on the impact assessment of obtained compositions in more complex microorganisms environment.

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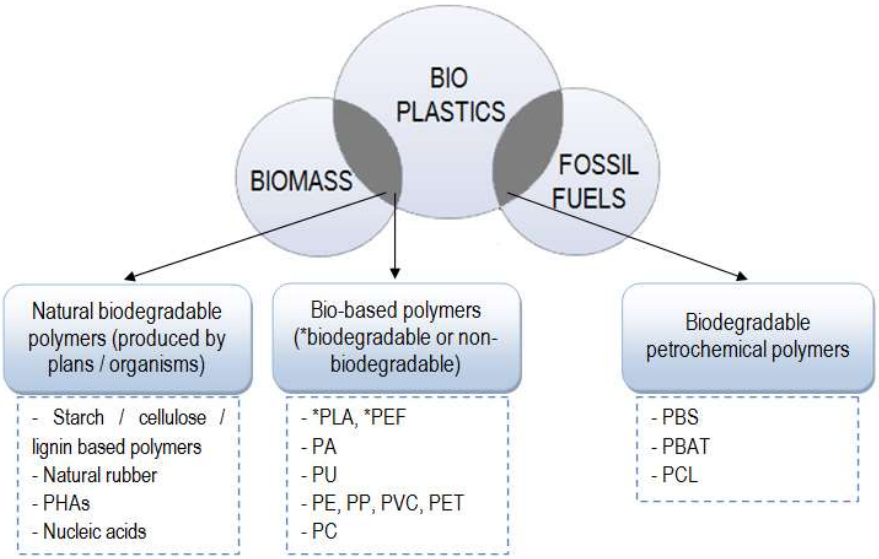


Figure 1. Division and examples of "bioplastic" term, taking into account source of raw materials and biodegradability.

Fig 2

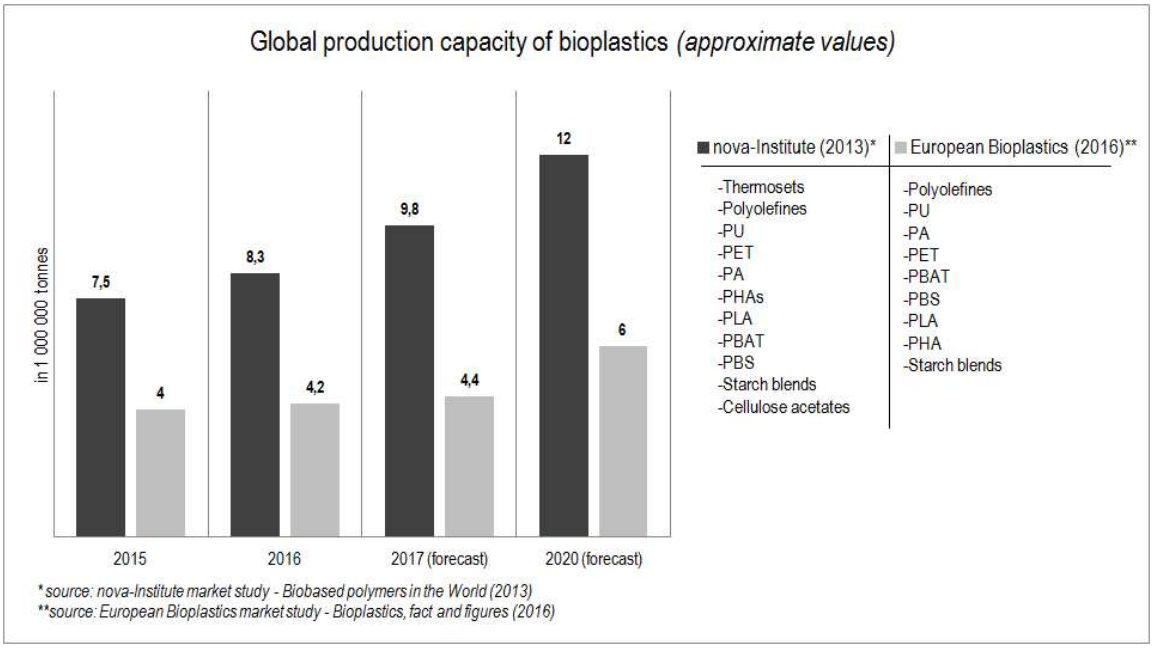


Figure 2. Approximate data and forecasts of global production capacity of bioplastic.

Fig 3

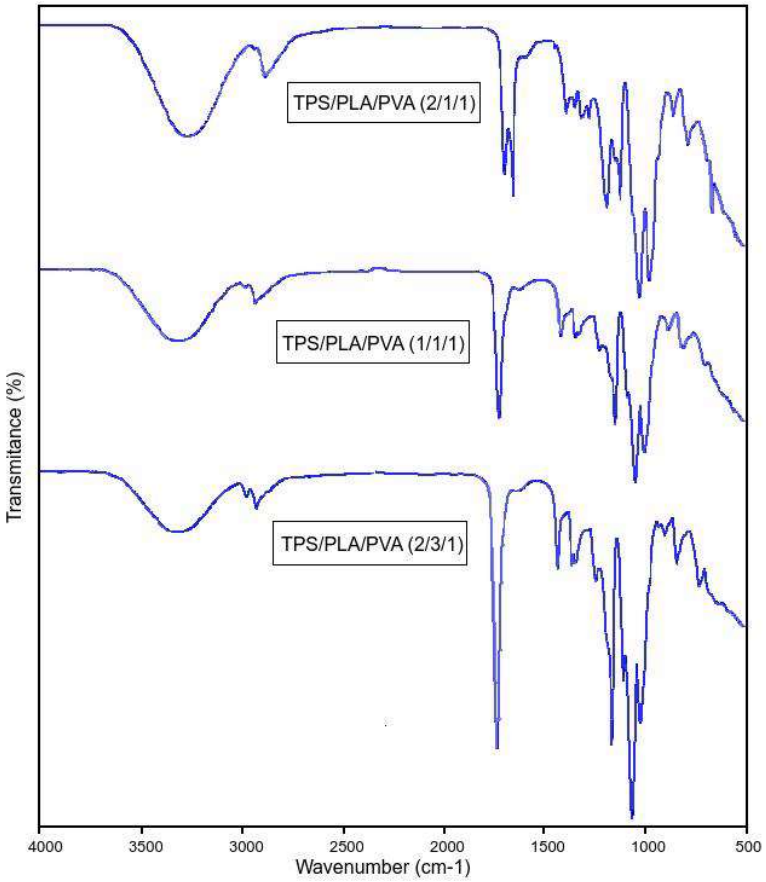


Figure 3. FTIR spectra of selected TPS/PLA/PVA compositions.

Fig 4

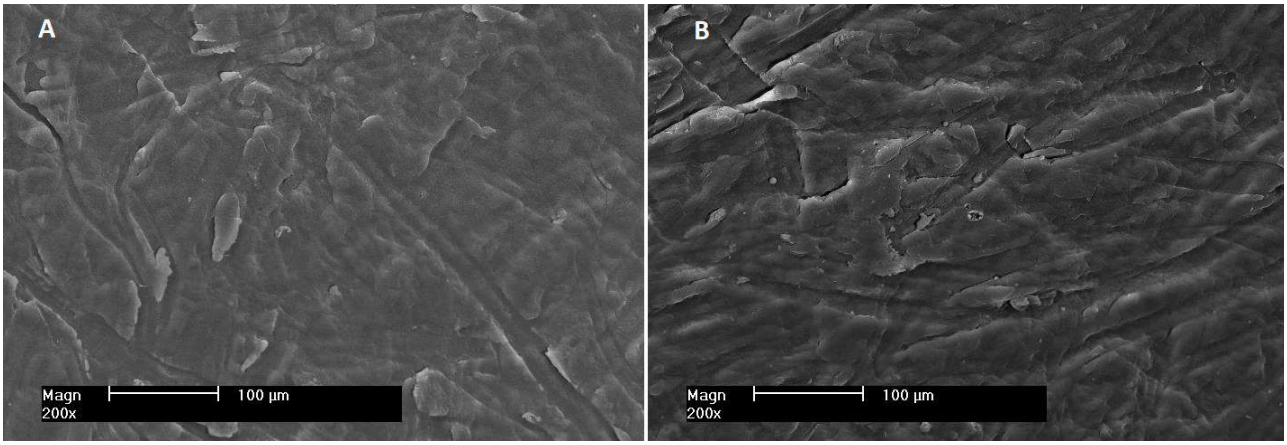


Figure 4. Surface appearance of TPS/PLA/PVA(1/1/1)-190/100 film a) day after compression process b) after one year of storage. SEM images (200x).

Fig 5

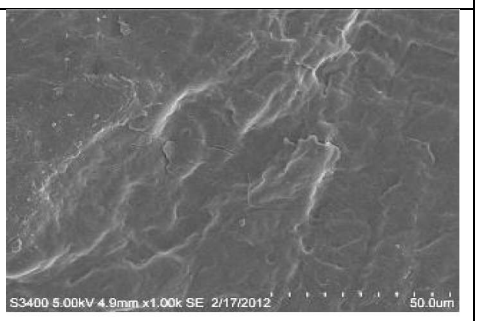
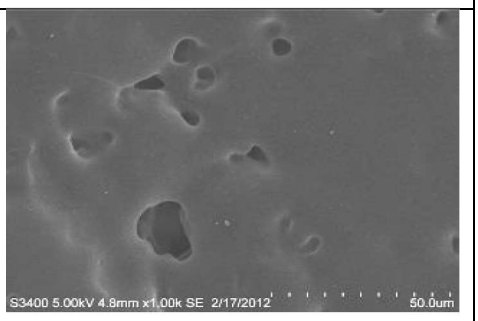
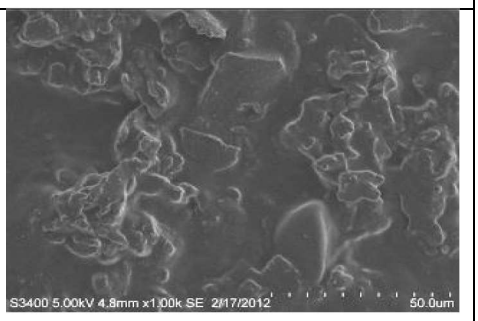
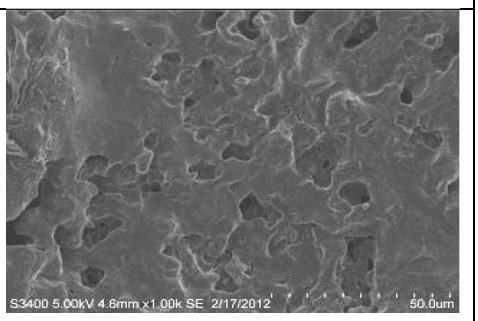
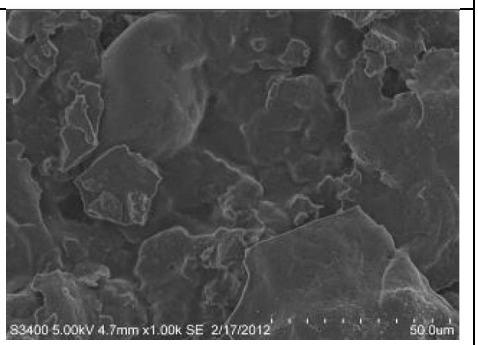
Etching process	**TPS/PLA/PVA(1/1/1) -190/100 SEM (x1000)**
a) Blind sample (before etching process)	
b) Drop of dichloromethane (the contact time<1 min)	
c) Drop of water (the contact time< 1 min)	
d) Full immersion in dichloromethane (the contact time: 15 min)	
e) Full immersion in water (the contact time: 15 min)	

Figure 5. Scanning electron microscopy images (x1000) of TPS/PLA/PVA(1/1/1)-190/100 films after etching with dichloromethane or water.

Fig 6

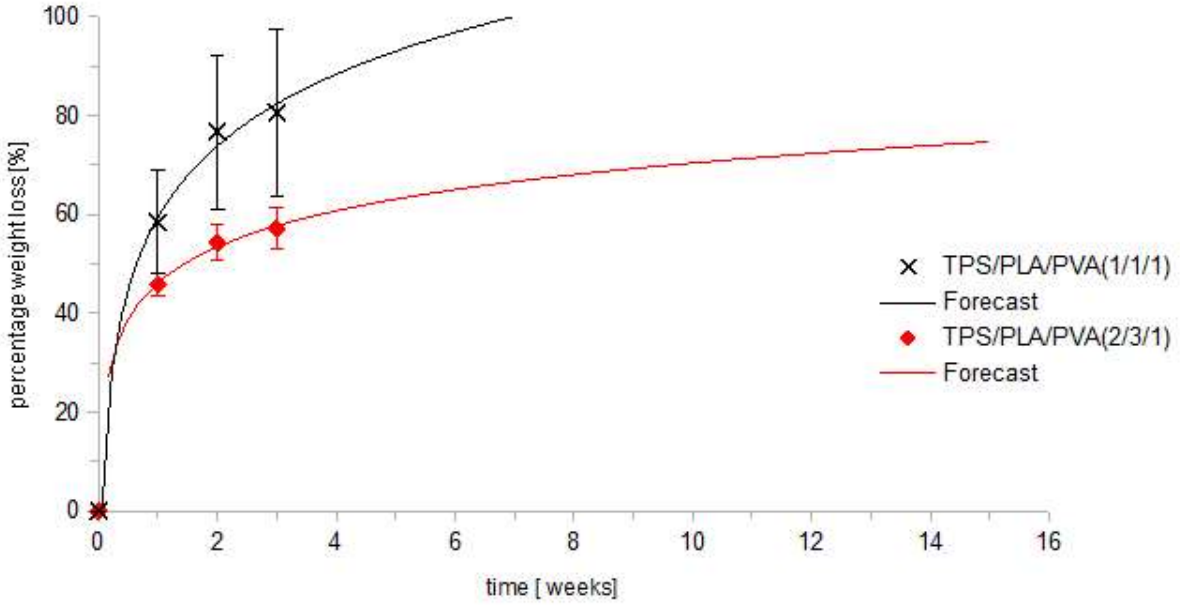


Figure 6. Weight loss behavior of TPS/PLA/PVA compositions with 3 monthly forecast results.

Fig 7

Figure 7. Changes in TPS/PLA/PVA(1/1/1) sample visual aspect under the influence of *Pseudomonas aeruginosa* bacteri, a) the first day of incubation, b) after 21 days of incubation

Fig 8

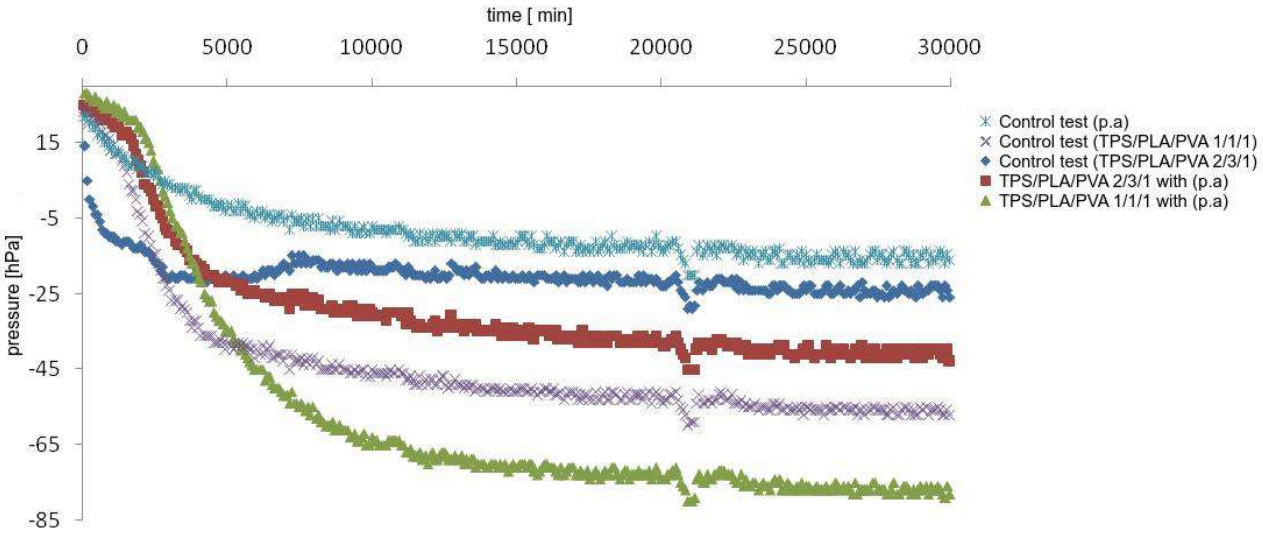


Figure 8. Pressure measurement curve 21 days incubation with *Pseudomonas aeruginosa* bacterial population.

Fig 9

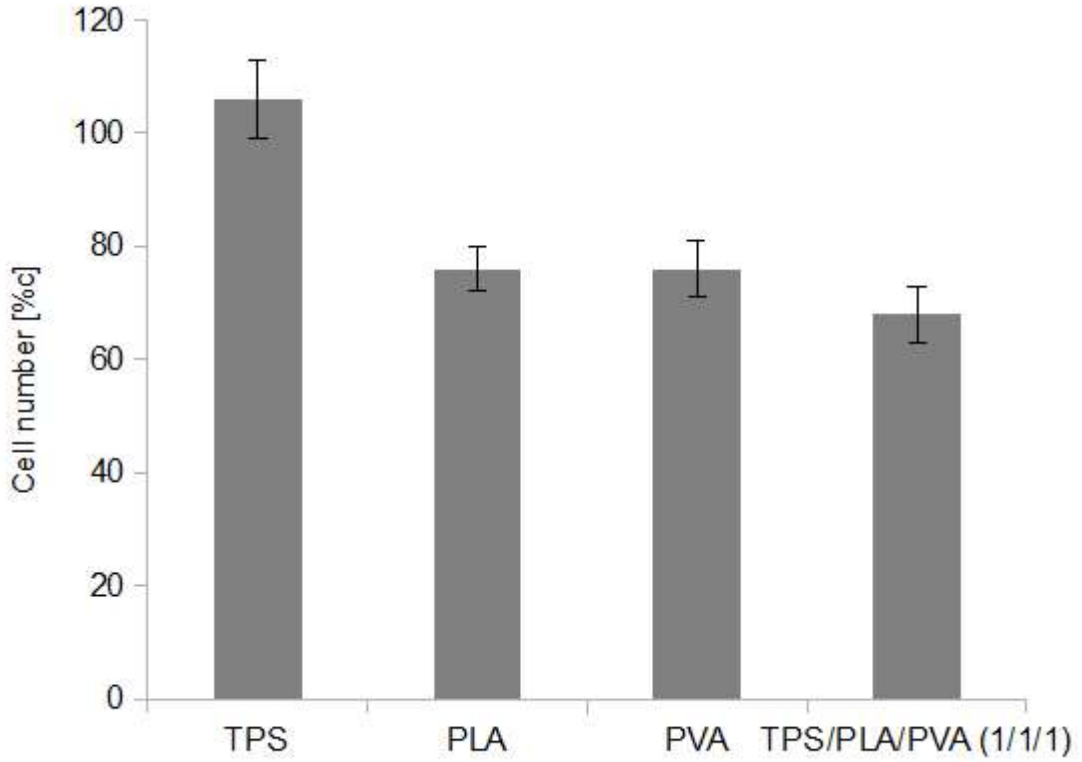


Figure 9. The influence of the TPS/PLA/PVA(1/1/1) composition and their components on the *Phaeodactylum tricornutum* cell number during 14 days of incubation in seawater.