INVESTIGATION OF THE INITIAL DEGRADATION STAGE AND TENSILE STRENGTH OF POLYLACTIDE AND ITS COMPOSITES WITH EGGSHELLS

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Abstract

The degradation rate of the composite polylactide (PLA) – eggshell powder (ESP), depends on many factors. The main are porosity, particle distribution, the weight load of ESP and chain length, the microstructure of bio-based and biodegradable PLA polymer. Bio-additives introduced to polymer matrix may have an impact on mechanical properties of the composite. Natural bone structure inspires to design mimicry materials. Materials which combine inorganic and organic components are of highly complex structure.

The paper focuses on the investigation of tensile strength and the initial stage of degradation of PLA and its composites with ESP in two media, i.e. H_2O and PBS. ESP was obtained by grinding, stirring with mixture 14.5 wt.% NaOH and 85.5 wt.% ethanol, and drying. Samples containing: 0, 10 and 20 wt.% of ESP were prepared. Dumbbell-samples were made by injection molding, and their mechanical properties were measured. Tensile results suggest that Young's modulus increased and tensile strength decreased as the amount of ESP is increased. Conductivity and pH of incubation media differed according to the material composition. SEM-EDS observations of PLA-ESP composites after fracture test were performed, and showed good adhesion between ESP and the polymer matrix. Influence of the incubation in H_2O and PBS on PLA and PLA--ESP composite surface degradation was checked. The PLA-ESP composites are characterized by a combination of unique properties, which may be suitable to use them as an eco-friendly packaging or medical material.

Keywords: *polylactide, eggshells, bio-composite, degradation, tensile strength*

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Introduction

Composite materials are made from the combination of two or more components, which allows achieving a new functional material. At the moment researchers focus on investigating new bio-composites for different purposes. Characteristics of the final material depends on many factors as size and amount of additive, its orientation, and adhesion to the matrix [1,2]. As an example: bone is strong and elastic. This duality is due to the complex structure of inorganic and organic phases, mainly collagen and hydroxyapatite [3-6]. Of course, there are many various methods for modifying polymers with particle reinforcement [1]. For example, PLA is a very popular biodegradable bio-based polymer, which can be used as an alternative to other non-biodegradable synthetic polymers [7]. PLA polymer may have a semi-crystalline or amorphous structure, which assures the possibility of physical properties modification. Many medical devices are made from PLA because of its unique properties [8]. PLA is not osteoconductive and has lower elastic modulus than bone. One of the methods of increasing the modulus of elasticity may be the manufacturing of a composite containing inorganic particles e.g. ESP. ESP addition to PLA matrix may bring its mechanical properties closer to those of bone, which can be very useful for medical application. ESP is also a cheap and easily available source of calcium. This type of material can avoid the need for a second surgery as well [2]. Kasuga et al. described the influence of calcium carbonate ($CaCO_3$) particles on PLA properties [9]. They showed that elastic modulus depends on the amount of additive. Young's modulus increased significantly to 4-6 GPa, i.e. comparable to that of natural bone by addition of 30 wt.% of $CaCO_3$ [9]. According to Ramakrishna et al., Young's modulus of cortical bone in the longitudinal direction is 17.7 GPa, and that of cancellous bone is 0.4 GPa. The tensile strength is approximately 133 MPa and 7.4 MPa for cortical and cancellous bone, respectively [5]. Some additives can also modify PLA degradation rate, which can differ depending on the size, shape, isomer ratio and temperature. Half-life time for PLA varies from 6 months to 2 years [10].

According to the previous studies, the amount of thrown chicken eggshells is significant, especially in the countries where egg production is well developed; in some articles, eggshell waste is described as an environmental problem [6,11,12]. What makes ESP an interesting additive for polymer composites is its chemical composition and availability [1,11]. ESP consist of $CaCO_3$ set on collagen and glycosaminoglycans films [6]. In various articles, some combinations of ESP with different polymers were described. Shuhadah and Supri investigated composites with low-density polyethylene (LDPE) and according to their study, the tensile strength of LDPE-ESP composites decreased and Young's modulus increased with increasing amount of ESP [1]. An interesting effect was observed in Asha and Sekhar work, where tensile strength of polyamide (PA) was higher or constant as the amount of ESP increased, and it depended on the type of PA matrix [12]. Petit et al. focused on testing degradation of polycaprolactone-ESP (PCL-ESP) composites; it was noted that soil pH, heat and an aerobic environment accelerate the degradation process, while an anaerobic and moisture-saturated environment delays this process, as compared with the composting system used as control [11].

TABLE 1. Literature review of types of ESP surface treatment processes and impact of ESP content on composite mechanical properties.

Reference	Material	Parameters changes	Surface compatibilization method
Shuhadah, Supri [1]	LDPE-ESP	↑ %ESP ↓ tensile strength ↑ %ESP ↑ Young's modulus	- wash - dry - grind to obtain 63 μm particles - dry in oven at 80ºC - mix with 10% NaOH, decant - dry - stir with mixture of 6% of isopthalic acid and ethanol - dry in 80ºC to constant weight
Timob [6]	Epoxy-ESP (nano particles)	2-4% nano-ESP ↑ bending modulus & strength 5/10% nano-ESP ↓ bending modulus & strength	- boil in 100ºC for 6 h - blend - wash with H_2O and then ethanol - dry at room temperature - mill - wash, stir etc. with absolute ethanol several times - vacuum dry at room temperature for 24 h
M.G. Petit, Z. Correa, M.A. Sabino [11]	PCL-ESP		- wash - dry - grind in a cryogenic mill (<190ºC)
A. Asha, V.C. Sekhar [12]	PA-ESP	ESP influence the tensile strength depending on the type of polyamide	- wash - dry - grind to a powder to obtain 100 μm particles - mix with NaOCl solution, stir for 30 min, decant, wash with distilled water - stir with 6% isophtalic acid in ethanol for an hour - dry in 140ºC to obtain constant weight

An important aspect is converting eggshells into particles, which can be added as an additive to the polymer matrix. Unmodified eggshells surface is hydrophilic [1,6]. Available articles mention various methods of eggshells powder surface compatibilization to the polymer matrix, which are described in TABLE 1. For example, treatment eggshells with NaOH solution leads to deproteinization of the material. Application of an isopthalic acid allowed the surface treatment of ESP, which was also compared by Shuhadah and Supri with unmodified eggshells [1]. Mechanical properties of polypropylene-ESP were investigated by Dhaliwal et al. They concluded that eggshells modification with isophthalic acid improved interfacial bonding [13].

This paper is focused on the investigation of tensile strength and the initial stage of PLA and PLA-ESP composite degradation in two media. This experiment allows considering the bio-based composite as an eco-friendly packaging or medical application material [6,7,12].

Materials and Methods

The tested bio-composite was made from PLA matrix (Ingeo, NatureWorks grade 3251D) and 0, 10, 20 wt.% ESP addition. ESP was prepared from hens organic eggshell.

The procedure of ESP preparation was started by washing hens eggshell in distilled water. Next stage was drying in Memmert drier at 100 ± 5ºC for 30 ± 1 min. Pulverisation was prepared in an electric grinder for 30 ± 1 min to obtain uniform particle distribution. Finally, ESP was sieved with sieves. Surface treatment was achieved in 14.5 ± 0.1% NaOH solution, and magnetic stirring for 30 ± 1 min was used for better removal of organic remnants. Then ESP was washed with distilled water and dried at 100 ± 5ºC for 30 ± 1 min. The last step of surface compatibilization was stirring for 30 ± 1 min in pure methanol. Cleaning was achieved by decanting and washing ESP with distilled water. Finally, drying was accomplished in the Memmert drier at 100 ± 5ºC for 60 ± 1 min.

PLA was dried in a Memmert drier at 50 ± 5ºC to achieve a constant weight. Three material composition samples were prepared using Zamak Mercator injection machine: PLA with 0, 10 ± 1, 20 ± 2 wt.% ESP. Samples mass was 4.4 ± 0.1 g. Settings of the injection process are listed in TABLE 2.

TABLE 2. Injection moulding settings of PLA and PLA-ESP composites.

Parameter	Value	Deviation	Unit
Injection time	10	0.1	[s]
Injection force	10	0.1	[kN]
Mould temperature	25	1	[ºC]
Injection moulding temperature mass	220	1	[ºC]

Tensile test

Dumbbell-samples were tested on universal testing machine Zwick 1435. The tensile test was performed at a speed of 2 mm/min, at room temperature (sample dimension 40 mm x 4 mm x 4 mm). Force-displacement data were registered, and tensile strength and Young's modulus were calculated. Samples were tested after injection and after one-week degradation in distilled water and PBS, and the average results and standard deviation were reported.

Degradation process

Degradation of samples was tested in two media: distilled water and phosphate-buffered saline (PBS). PBS was prepared by using 8 g NaCl, 0.2 g KCl, 1.44 g Na_2HPO_4, 0.24 g KH_2PO_4, 0.133 g $CaCl_2 \cdot 2H_2O$, 0.10 g $MgCl_2 \cdot 6H_2O$, mixing with distilled water to obtain a solution of 800 ml, and then a pH value in the range 7.2-7.4 was achieved by adding HCl and water.

The pH and conductivity values were measured for two suspension sets. Suspensions were made with dry to wet ratio 1:10. The sets were as follows:

- PLA + H_2O
- ESP + H_2O
- 90 wt.% PLA + 10 wt.% ESP + H_2O
- 80 wt.% PLA + 20 wt.% ESP + H_2O
- PLA + PBS
- 90 wt.% PLA + 10 wt.% ESP + PBS
- 80 wt.% PLA + 10 wt.% ESP + PBS

The first set was stored in a dryer at 37ºC. The second set was stored at 20ºC in distilled water, which mass was later measured, in a dried state and soaked, after different periods of time. This procedure allowed to measure solvent absorption and degree of degradation.

Conductivity, pH and mass changes

Solution conductivity was measured with ELMETRON microcomputer conductivity meter CC-315. Solution pH was measured with ELMETRON pH-meter CP-411. Measurements were made every 5 days. Mass of samples was measured with RADWAG PS 360/C/2 with an accuracy of 0.0001 g. Samples were weighed soaked for 10 and 22 days, then they were dried at 37ºC and again weighed.

Optical Microscope

Samples and eggshells were observed under a digital microscope Keyence VHX-900X with magnification 200x, which allowed evaluating surface topography.

Scanning Electron Microscope

The surface of samples before and after 3 weeks degradation was observed using NOVA NANO SEM 200 microscope with EDS. The fracture surface of the specimens was also investigated. Eggshells were also tested to determine their composition.

Results and Discussions

Injection process

After the injection process, it was observed that obtained dumbbell-shaped specimens had non-homogenous ESP distribution.

High transparency of PLA samples contained 0 wt.% ESP suggest the high volume of an amorphous phase [14]. Samples with: 10 wt.% ESP showed an injection line, for 20 wt.% ESP the homogeneity of material increased (FIG. 1).

Tensile test

Non-degraded samples with different ESP content after the tensile test are shown in FIG. 1. During the tensile test force-displacement characteristic curves were registered (FIG. 2). Their appearance indicates that samples behaved as a brittle material. Young's modulus measured from the characteristic curves increased with the increasing amount of ESP (FIG. 3). After one week degradation the parameter was increased for pure PLA, and for the composites, the differences were within the error limits (less than 5% of change).

As Young's modulus increased with the amount of ESP, the tensile strength decreased (FIG. 4). 1-week-degradation of the samples almost did not influence the tensile strength.

Visual appearance observation during degradation

The visual appearance of the samples during degradation in distilled water and PBS were observed under an optical microscope. Visible changes in the appearance of the samples did not occur, only light solution turbidity. The solution which contained a modified PLA-ESP composite was characterized by sulphur like smell, which may be connected to the presence of sulphur in eggshell.

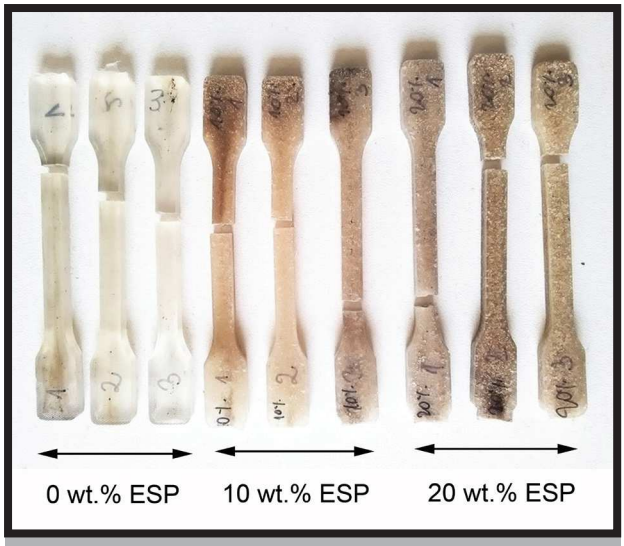

FIG. 1. Non-degraded samples after tensile test.

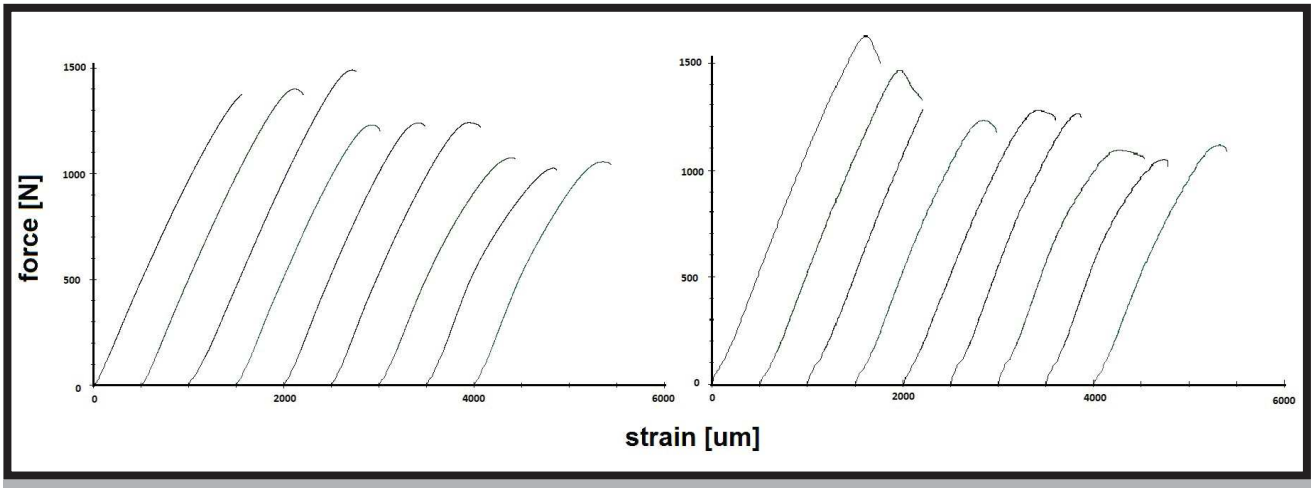

FIG. 2. Force-displacement characteristic curves for non-degraded (left) and after 1-week-degradation (right) samples. Example of samples type with 10% ESP additive.

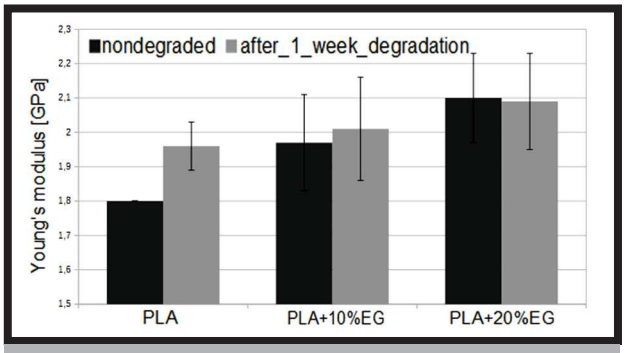

FIG. 3. Young's modulus of samples: non-degraded and after 1-week-degradation.

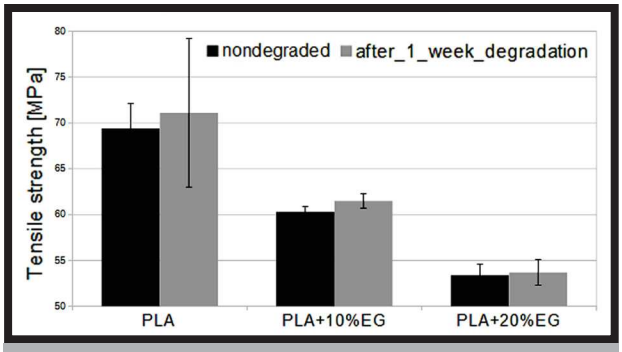

FIG. 4. Tensile strength of samples: non-degraded and after 1-week-degradation.

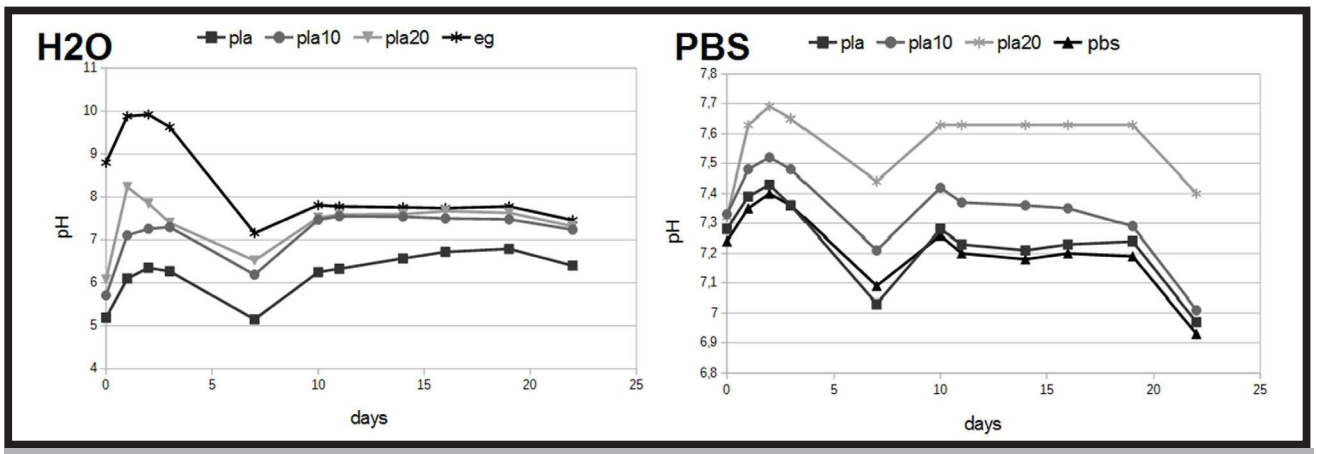

FIG. 5. Changes of pH for samples immersed in water (left) and PBS solution (right).

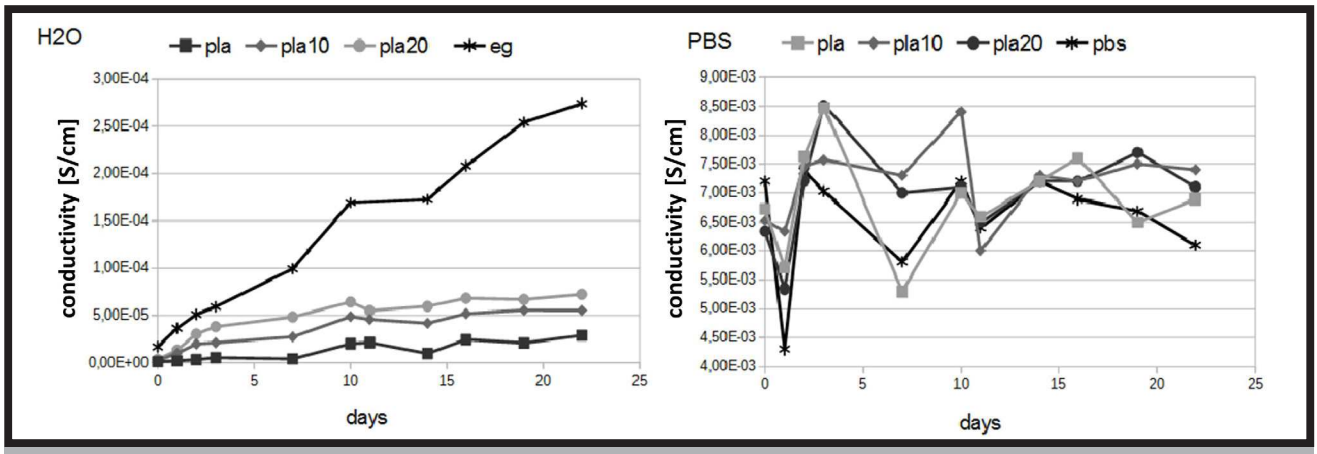

FIG. 6. Conductivity changes during degradation in water (left) and PBS (right).

pH

Up to 10 days pH of solutions was changing dynamically and then after 10 days of degradation it became constant in water (FIG. 5). Samples immersed in PBS showed decreasing pH with the time. These phenomena may be due to many possible factors, including the presence of bacteria. The highest pH value was observed for ESP solution and it can be explained with the chemical structure of ESP – which is mainly built from calcium carbonate. This also justified the fact that pH of composites increased with the increase in ESP amount. A pure solution of PLA+H_2O was acidic because of its degradation mechanism. It undergoes PLA hydrolysis, which produces lactic acid.

Conductivity

The conductivity of samples in distilled water at the beginning of the degradation was 0.5 [μS/cm] (FIG. 6). The conductivity value increased with time, intensively in the case of ESP. As ESP amount in the composite raised, the composite degradation accelerated, because conductivity was higher than in the sample with less ESP amount. It also means that the degradation time of PLA can be shortened by adding ESP. The conductivity of PBS solutions was not stable.

Mass changes

Mass change during the degradation process was investigated. The mass change during the 3 weeks was ≤ 0.0001 g.

Absorption of the solutions was measured and the results are shown in FIG. 7. Its value may be the evidence of open porosity in the composites what can facilitate the absorption of the liquids. Polylactide is hygroscopic, which is higher if it is in an amorphous state [2,15]. The value of absorptivity at the level of several percents confirms the fact. Then the value decreased and it was similar for all samples after three weeks of degradation.

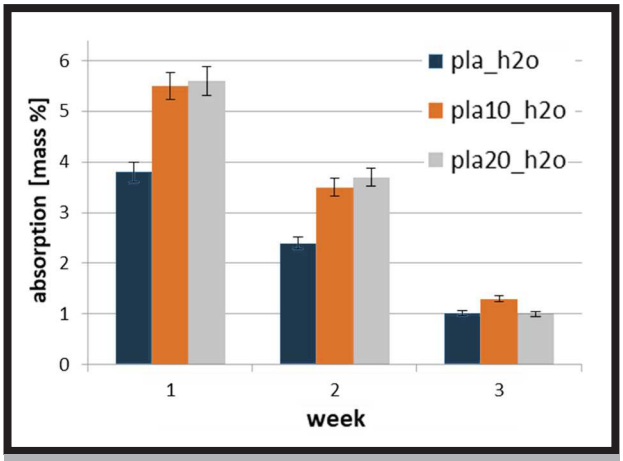

FIG. 7. Absorption of water vs time.

Scanning Electron Microscope

The SEM with EDS of non-degraded ESP surface and the ESP after 24 days of degradation in distilled water was investigated. EDS analysis showed that non-degraded ESP contains mainly: calcium, carbon, oxygen, and trace amounts of magnesium, sulphur and phosphorus.

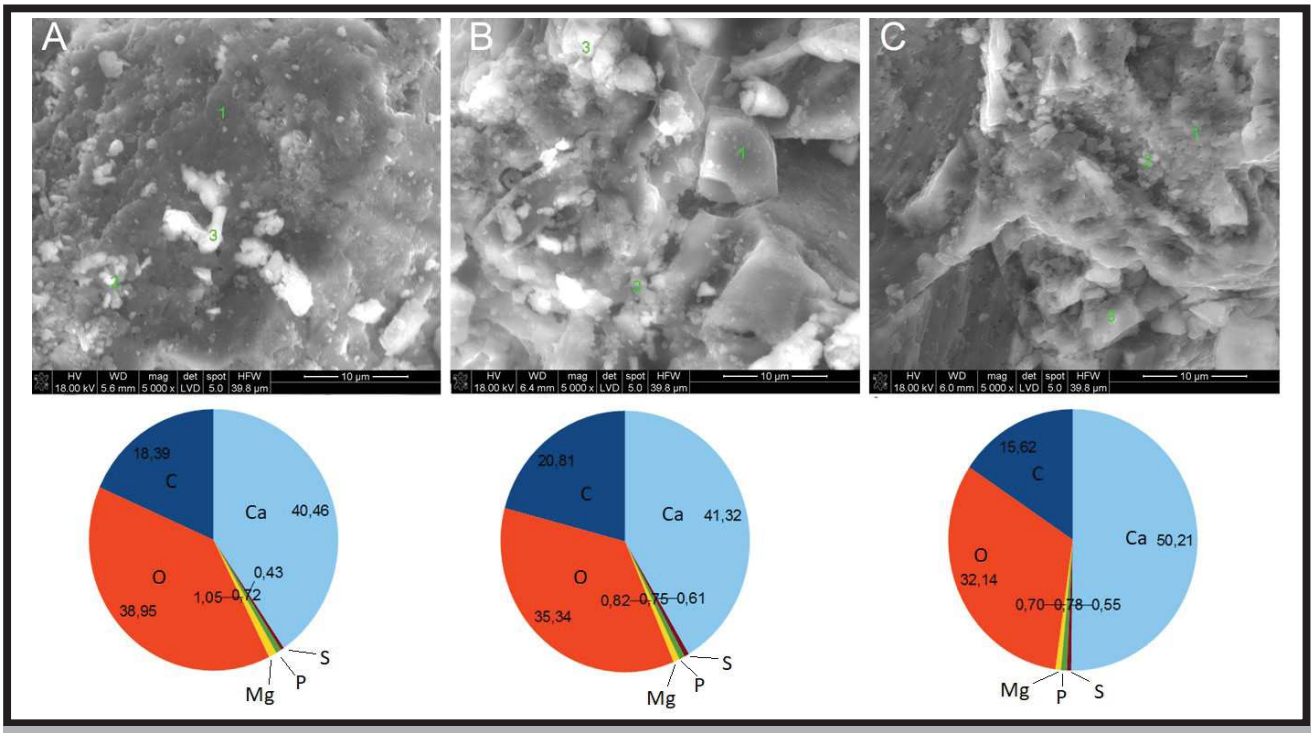

FIG. 8. SEM images of ESP and average chemical composition: A – unmodified, B – modified , C – after 24-days degradation in distilled water.

EDS analysis of the ESP showed during degradation that calcium amount increased (FIG. 8) suggesting that the organic part is removed and dissolution of calcium carbonate was occurred.

SEM surface images of the PLA and PLA-20 wt.% ESP samples (FIG. 9) have not shown visible degradation. The SEM surface image of PLA-10 wt.% ESP has shown a visible degradation of the PLA matrix. White spots on the surface are representing ESP, which was also investigated with EDS.

Fracture surfaces investigation under SEM after tensile strength measurement showed that ESP particles are strongly bond to the PLA matrix (FIG. 10).

Conclusions

1. The ESP can be a source of easily available $CaCO_3$.
2. The ESP modified PLA composite is chemically stable; in the long-term it does not cause significant acidification of the aqueous environment consisting of water and PBS.
3. Along with immersion time of PLA / ESP composites in water, salts from ESP are released to the solution.
4. The addition of ESP increased the hygroscopic properties of the composite.
5. As the ESP content in the composite increases Young's modulus of the resulting composite increases.
6. Together with the increase in the ESP content in the composite material, the strength of the composite material decreases.

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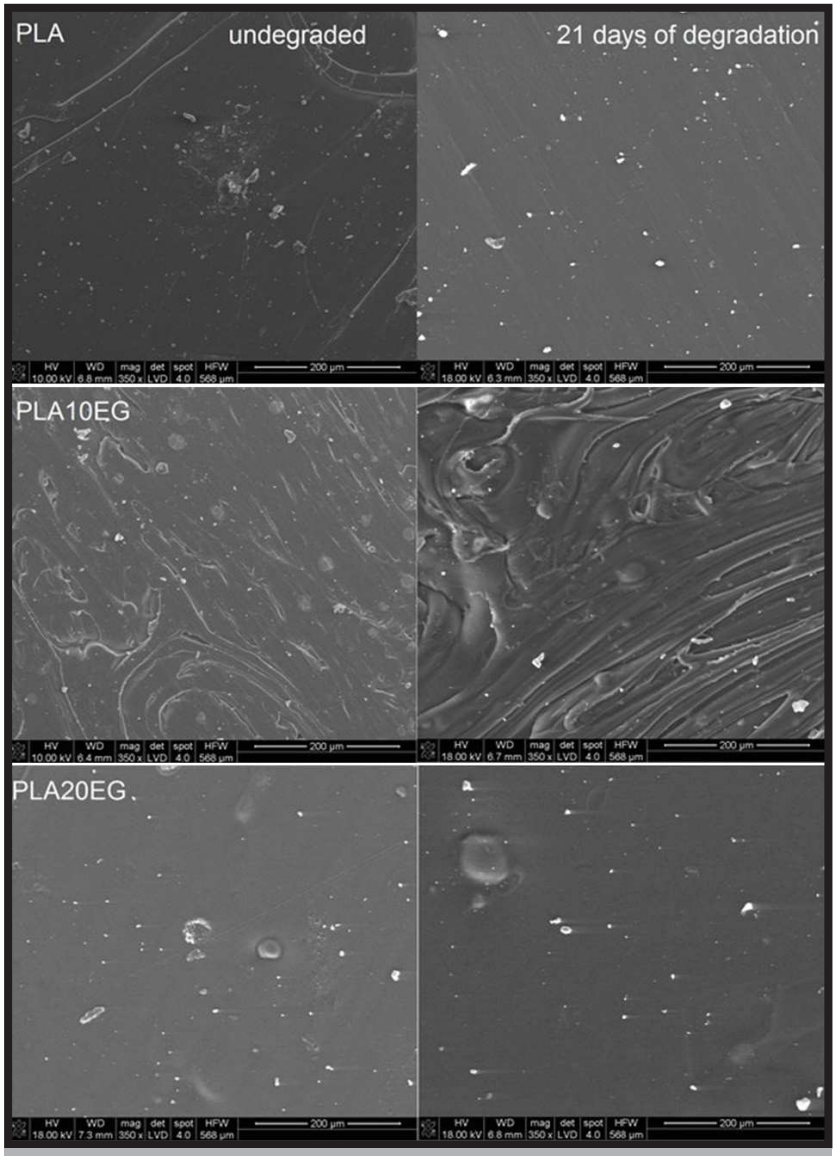

FIG. 9. SEM images of PLA-ESP samples surface before (left) and after 21-days degradation (right).

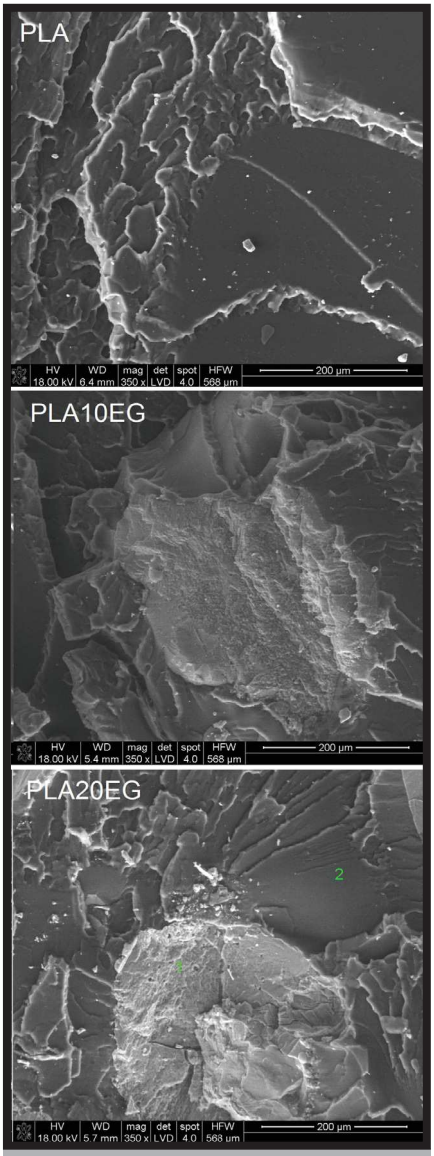

FIG. 10. SEM images of fracture surfaces of the samples after tensile test.

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