

Influence of Technological Process on Biodegradation of PVA/Waxy Starch Blends in an Aerobic and Anaerobic Environment

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Abstract Improving biodegradability of PVA/starch blends is a reality already documented by a number of works. Admittedly, mechanical properties of products (for example, tensile strength) are somewhat worse, but suitable composition optimizing or chemical modifying of starch may eliminate the problem to a large degree. This work is an attempt to find another potential effect influencing biodegradability, that of technological procedure for producing films from these blends on an extruder. The procedure with a so-called pre-extrusion step (two-stage) and dry-blend (single-stage) produced blends of slightest differences in achieved biodegradability (virtually within limits of experimental error) in aerobic (76 vs. 79%) as well as anaerobic breakdown (48 vs. 52%). Conversely, morphological analysis exhibited superior homogeneity of films prepared by the two-stage process; their tensile strength was also higher.

Keywords Polyvinyl alcohol (PVA) · Starch · Waxy · Blend · Aerobic · Anaerobic · Environment · Technological process

Introduction

Starch is a renewable and biologically fully degradable polymer. Its biodegradation rate is determined by a number of its properties (particle size, processing temperature, moisture content), also by its content of pro-oxidants, photoaccelerators or free-radical initiators. However, starch is no ideal filler. It does not possess sufficiently good physico-chemical and processing properties; its blends are mostly brittle. Reasons for its employment are as follows: this cheap filler of high purity is available with ease from a number of crops (naturally renewable material) and its treatment before actual application in plastic is possible.

In a number of studies, polymer blends were prepared on the basis of PVA containing different kinds of natural starch (corn, wheat, rice, potato and others) [1–9]. For example, El-Mohdy [1] modified blends of PVA (wheat starch or thermoplastic starch) by electron beams irradiation, and described their mechanical properties and biodegradation. Study of mechanical properties revealed a significant influence of amylose content on properties of resultant films. It was also proved that presence of amylopectin increases water solubility of blends. In most cases, however, mechanical properties of blends on the bases of PVA become worse with added starch.

For this reason, a whole series of studies were published on chemically modifying starch [10–14]. In general, chemical modification of starch can apply, for example, esterification or oxidation; but methods employed most are etherification and methylation. Chemical modification of starch in most cases admittedly leads to markedly improving physico-chemical properties of blends, but presents higher manufacturing costs. Nevertheless, authors of quite a number of studies fail to follow influence of

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technological processing as well as chemical modification of starch on biodegradability of resultant mixed film.

It follows that a whole number of polymeric blends based on PVA and starches (natural or chemically modified) are known, but research into biodegradability of PVA combined with starch bearing trade name WAXY [15] from genetically modified plants has not been undertaken yet. It is essential that the starch contains a low percentage of linear chains (amylose content below 1%), which has a strong bearing on technological processing of PVA/starch blends. WAXY starch of low linear chain content is thermally more stable and better plasticizable; easier incorporation into PVA blends is thus achieved. Lawton described in his work [16] the influence of particular starch types on mechanical properties of mixed films based on PVA (98% hydrolysis), studied films were prepared by merely casting aqueous solutions; however, the author did not study biodegradability of these mixed films.

The objective of this study was to assess the influence of technological procedure when incorporating WAXY starch into PVA, chiefly on biodegradability of resultant polymeric blends in an aerobic and anaerobic aqueous environment.

Experimental

Materials and Chemicals

Materials used for tests were currently available commercial products: MOWIOL 5–88 (PVA), viscosity 5.5 ± 0.5 mPa s, hydrolysis degree—8 mol%, produced by Kuraray, Germany; WAXY starch (W)—corn starch of amylose content <1%, produced by Cerestar, Benelux; GLYCEROL (G)—delivered by H.C.I. Slovakia; STEARIN III—mixture of stearic and palmitic acid, specified for pharmaceutical purposes, produced by SETUZA, Ústí nad Labem, Czech Republic; SUPERNATANT 22 S—precipitated silicon dioxide for pharmaceutical purposes, produced by DEGUSSA, Germany.

All other employed chemicals used were of analytical purity, produced or delivered by the Lachema Co, Brno, Czech Republic.

Preparation of Films

The preparation of films is described in Fig. 1. Additives added to PVA/G blend: mixture of palmitic and stearic acid—Stearin III, 0.3% per PVA; silicon dioxide, Sipernat 22 S, 0.25% per PVA. Additives added to W/G blend: Stearin III, 1% per starch; water, 10% per glycerol.

Method A: PVA/WAXY Blend with Pre-Extrusion Step (PVA/W-ES)

Plasticizing PVA with glycerol: Weighed ingredients of blend were mixed together and blended. The blend was placed in a heated hot-air drier for 25 min at 130 °C. Blends were prepared under laboratory conditions on a twin-screw extruder ($\phi = 16$ mm, L/D = 40). Individual polymers containing glycerol were pelletized under conditions as follows: temperature profile in extrusion of W/G (from feed hopper to extrusion head) was 100/140/150/160/170/180/160/140/140/140 °C and screw speed was 200 rpm, in extrusion of PVA/G it was 160/170/180/189/190/190/190/190/180/180 °C and screw speed was 220 rpm. Pelletized blends PVA/G and W/G were mechanically blended in the desired concentration ratio and processed under conditions as follows: temperature profile 150/160/170/170/180/180/180/175/175/175 °C and screw speed 220 rpm. During the process, a vacuum venting zone placed in segment 34D was employed to remove abundant humidity.

Method B: PVA/WAXY Blend from Dryblend (PVA/W-DB)

WAXY starch was mechanically mixed with glycerol in a laboratory mixer. Into the glycerol/starch blend thus prepared a pre-plasticized blend of PVA with glycerol was added and all was mechanically mixed. The PVA/W-DB pellets were prepared on a twin-screw extruder under laboratory conditions as follows: temperature profile: 150/160/170/180/180/180/175/175/175 °C and screw speed 220 rpm (Table 1).

Mechanical Properties of PVA/W Blends

Mechanical properties—tensile strength and elongation at break were measured on Metrotest 5 kN device, in accordance with standard STN ISO 527 [17] at cross head speed 1 mm/min in strain range 0–3%, and at 50 mm/min in strain range >3%, at laboratory temperature. Test specimens were prepared from extruded strands and tested two days after extrusion. Strand dimensions were: length 100 mm and diameter 2 mm. Five test specimens were measured from each sample. Maximal tensile strength and elongation at break were read from the stress/strain curve.

Morphological Analysis

Specimens for scanning electron microscopy (SEM) were prepared by fracturing after cooling to temperature of liquid nitrogen. The fracture surface of sample of specimens was observed using the Tesla BS-300 electron microscope with digitalizing unit Tescan. Operating

Fig. 1 Scheme of films preparations under laboratory conditions on a twin-screw extruder ($\varphi = 16$ mm, $L/D = 40$)

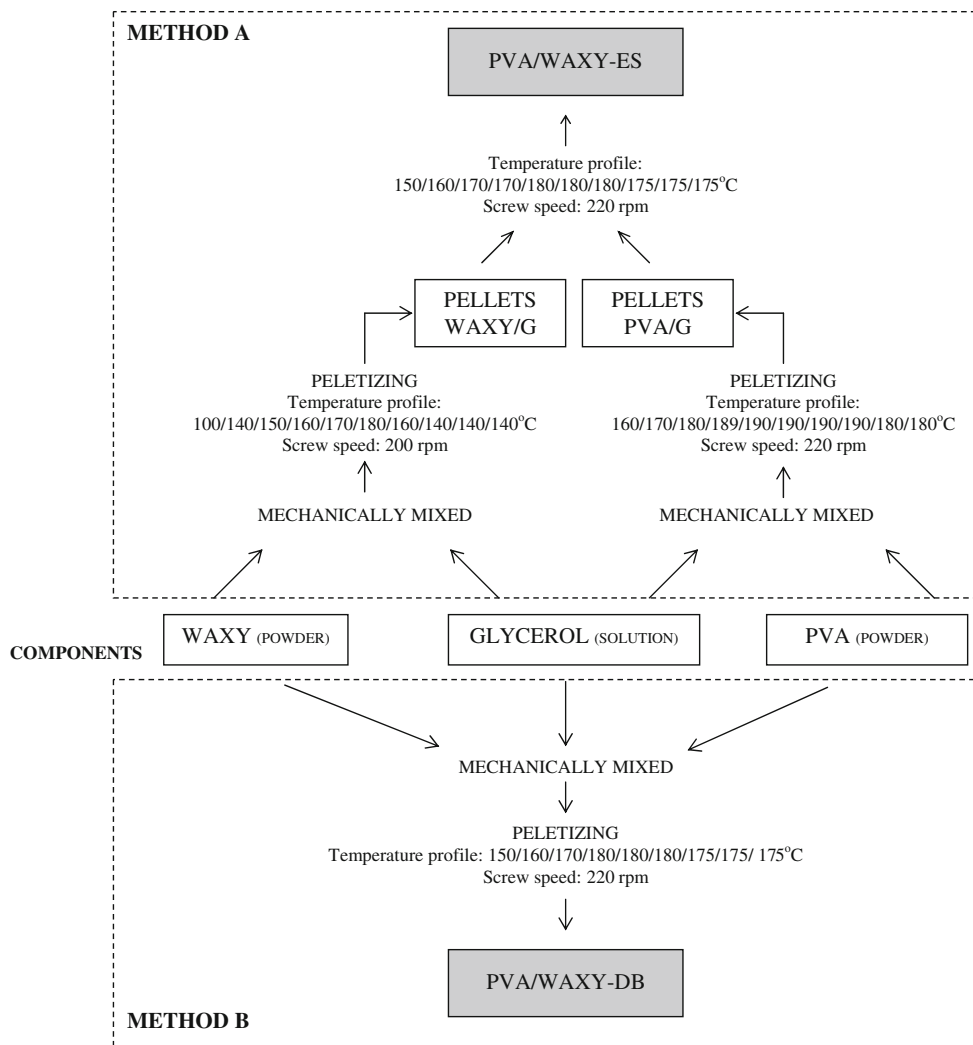


Table 1 Composition of blends (films) PVA/WAXY starch in wt.%

| Sample | W starch | PVA | G | W/G | PVA/G |
|----------|----------|------|------|-----------------|-----------------|
| PVA | – | 100 | – | – | – |
| PVA/G | – | 82 | 18 | – | – |
| W/G | 70 | – | 30 | – | – |
| PVA/W-ES | – | – | – | 60 ^a | 40 ^a |
| PVA/W-DB | 42 | 32.8 | 25.2 | – | – |

^a Pellets

voltage was 20 kV. Pictures were made using software WinTip 3.1

Equipment and Apparatus

Equipment employed for tests and analyses, among others, was as follows: mechanical properties—tensile strength and elongation at break were measured on Metrotest 5 kN

device; SEM pictures were taken by means of Tesla BS-300 electron microscope with digitalizing unit Tescan and operating under software WinTip 3.1; biodegradability of tested films was investigated in an aerobic environment by means of microrespirometer MicroOxymax O₂/CO₂/CH₄ (Columbus Instruments Corp, USA); biodegradability in anaerobic environment was assessed through produced CH₄ and CO₂ determined in gaseous phase with modified “bottle” laboratory apparatus by means of GC (HP 7890, Agilent Technologies) in packed column PORAPAK QS with TCD [18]; organically bound carbon in solid samples was determined by means of analyzer TOC 5000A—solid sample (Shimadzu Corp, Austria).

Aerobic Biodegradability Test [19, 20]

Biodegradability of tested granulated materials (Table 1) was investigated in an aqueous aerobic environment in the

presence of a mixed microbial culture—activated sludge from the municipal wastewater treatment plant, by means of microrespirometer MicroOxymax O₂/CO₂/CH₄ (Columbus Instruments Corp, USA) on the one hand, and of the Zahn-Wellens test on the other.

Initial dry matter concentration of activated sludge was 500 mg/L, that of substrate was 200 mg/L. Substrate in the form of pellets was always dosed directly into reaction suspension. Preparing the activated sludge suspension and all diluting made used of a mineral medium [20, 21].

Level of pH was kept during the test within a 7.0 ± 0.5 interval. Samples of the suspension for determining pH and dry matter of biomass were always withdrawn at start and end of test. Endogenous respiration was investigated at the same time.

The basic biodegradability criterion was ratio of actually produced CO₂ arising during microbial breakdown to the theoretical quantity given by balance of carbon present in sample, expressed as D_{CO_2} (%) according to Eq. 1:

$$D_{CO_2} = \frac{(nCO_{2\text{sample}} - nCO_{2\text{blank}})}{ThCO_2} 100, \quad (1)$$

where $nCO_{2\text{sample}}$ is quantity of CO₂ produced during breakdown of substrate (mmol), $nCO_{2\text{blank}}$ is quantity of CO₂ produced during endogenous respiration of microorganisms (mmol), and ThCO₂ is theoretical production of CO₂ coming under total substrate breakdown (mmol) as determined through balance of organically bound carbon in mixed film.

A complementary criterion was determining percentage of removed PVA [20]. Biodegradation of sole PVA contained in mixed films was also under observation employing the Zahn-Wellens test [20]. At determined intervals, a sample of activated sludge suspension was withdrawn; residual WAXY starch and activated sludge were removed and PVA concentration was then determined through spectrophotometry [22].

Anaerobic Biodegradability Test [23]

Biodegradability of tested granulates (Table 1) in an aqueous anaerobic environment was studied in the presence of a mixed microbial culture supplied in the form of partly digested sludge from anaerobic stabilization of residual activated sludge from the municipal wastewater treatment plant.

Preparation of solutions and all components utilized a mineral medium [5, 23]. Tested samples were dosed into test bottles of 250-mL volume so that each bottle contained ~20 mg carbon in 100 mL liquid phase. Starting concentration of “anaerobic” sludge dry matter was 3 g/L. Filled bottles were bubbled through with nitrogen for ~5 min, then sealed gastight and immersed in water bath

tempered to 35 ± 1 °C. Contents of bottle were continuously stirred during test. Anaerobic biodegradability was surveyed through produced CO₂ and CH₄. Both produced gases were subjected to final analysis employing gas chromatography (GC-HP 7890) with TCD [18]. Analysis of actual samples mostly used 0.2-mL quantities of gas phase withdrawn at determined time intervals. Percentage of biologically removed substrate— D_C (%) was evaluated through produced CO₂ and CH₄—Eq. 2:

$$D_C = \frac{(\text{CO}_2)_{\text{sample}} - (\text{CO}_2)_{\text{blank}} + (\text{CH}_4)_{\text{sample}} - (\text{CH}_4)_{\text{blank}}}{TC_{\text{theor}}/M_C} 100, \quad (2)$$

where $(\text{CO}_2)_{\text{sample}}$ is quantity of CO₂ produced during breakdown of substrate (mmol), $(\text{CO}_2)_{\text{blank}}$ is average quantity of CO₂ released in bottle during endogenous respiration of microorganisms (mmol), $(\text{CH}_4)_{\text{sample}}$ is quantity of CH₄ produced during breakdown of substrate (mmol), $(\text{CH}_4)_{\text{blank}}$ is average quantity of methane released in bottle during endogenous respiration of microorganisms (mmol), TC_{theor} is quantity of total (theoretical) carbon in dry matter of tested sample (g/g) and M_C is atomic mass of carbon (g/mol).

Individual courses of aerobic and anaerobic biodegradation were processed applying program STATISTICA Cz 6.1. Measured dependencies $D_{CO_2} = f(t)$ and $D_C = f(t)$ were described by a regression equation for first-order substrate kinetics—see Eq. 3:

$$D = D_{\text{max}} \left[1 - e^{-k(t-t_{\text{lag}})} \right], \quad (3)$$

where D_{max} is a regression coefficient representing limit value D_{CO_2} , or D_C in infinite time (%), k is value of “rate” constant (h^{-1}), t_{lag} is the shift on time axis showing lag phase (h). A similar procedure was described, for example, in work [21] evaluating aerobic biodegradability.

Additivity

Assessing whether the final biodegradation degree at a certain time was given by sum of biodegradations of particular components or whether interactions (positive or also negative) occurred in the system, the so-called additive rule was applied, checking if final results characterizing biodegradability of blends (for example, rate constants, degradability percentage) corresponded to weight presence of particular components. Thus, relations of experimental data and values calculated according to regression equation for substrate kinetics Eq. 3 and additivity rules according to Eq. 4 were analyzed, e.g. $k_{D_{CO_2}}$

$$k_{D_{CO_2}} = w_1k_1 + w_2k_2 + \dots + w_nk_n, \quad (4)$$

where individual values k to k were calculated according to Eq. 3 for components, 1w to $^b w$ represented mass fractions of individual components in relevant blend (Table 1). Calculated dependencies and particular values are indicated in tables and figures. A similar approach was used in work [21].

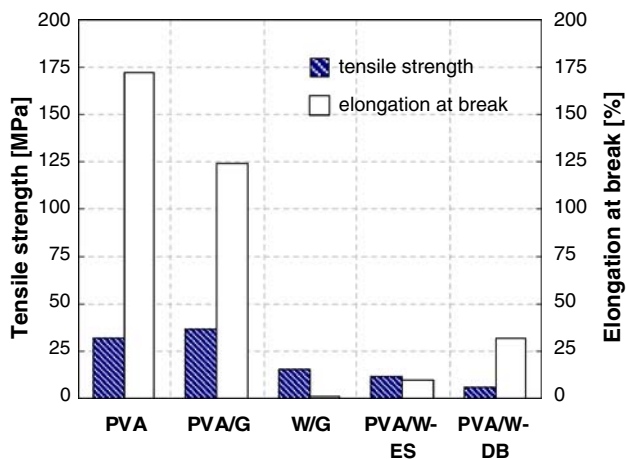
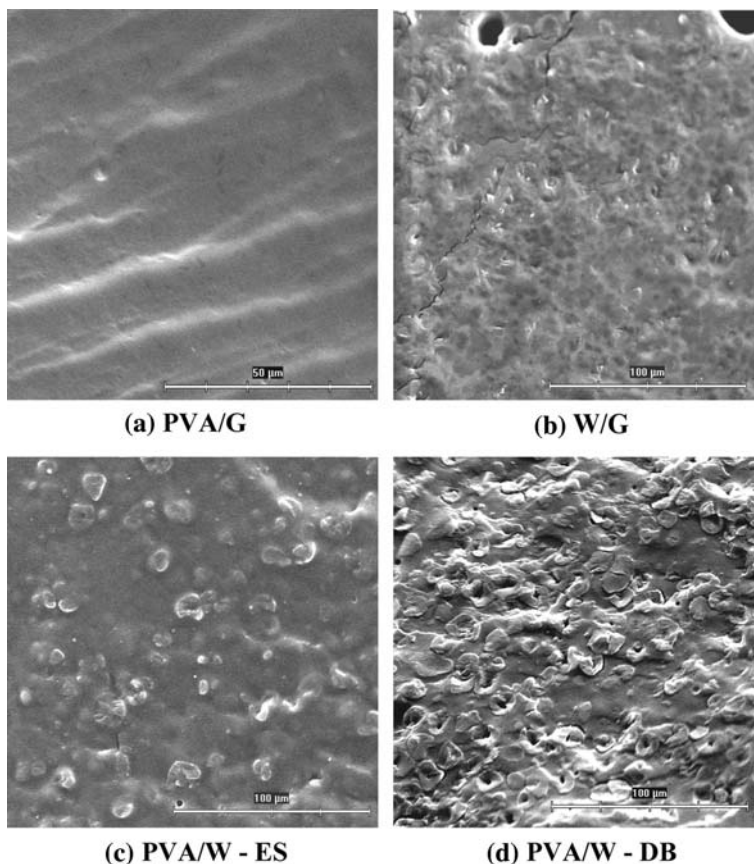


Fig. 2 Influence of technological procedure for preparing PVA/W blends on tensile strength (MPa) and elongation at break (%)

Fig. 3 SEM pictures of fracture surfaces of blend PVA/G (a), W/G (b), of blend (d) of polyvinyl alcohol and starch prepared from dry blend (PVA/W-DB) and of blend (c) of polyvinyl alcohol and starch prepared by two-stage process with so-called pre-extrusion step (PVA/W-ES)



Results and Discussion

Mechanical Properties

Evaluating parameters were tensile strength and elongation at break, as determined through procedures described in the Experimental part. Tensile strength of blends PVA/W-ES and PVA/W-DB, as compared to sample of blend PVA/G, decreased ~3.3 times and 5 times; elongation at break 12 times and 4 times. Reduced tensile strength displayed particularly worsened mechanical toughness of the blend (Fig. 2).

Morphological Analysis

From SEM pictures of fracture surfaces (Fig. 3) it follows that plasticized PVA (PVA/G) has typical single-phase structure without visible non-homogeneities. Sole WAXY starch, even after plastifying (W/G), contained a certain quantity of starch grains imperfectly plasticized.

Comparing samples prepared by mixing two granulates (PVA/W-ES) with samples prepared by single-stage mixing from a common dry blend (PVA/W-DB), it may be said that superior blend homogeneity as well as superior mixing-in of starch grains was achieved in the two-stage

process, i.e. when granulates W/G and PVA/G were prepared in the first stage, to be subsequently blended together in the second stage.

Aerobic and Anaerobic Degradability of PVA/W Blends

As already said in the introduction, the objective of this study was assessing which technology for preparing polymeric PVA/W blends from the viewpoint of biodegradability is more favorable, whether two-stage blend preparation with pre-extrusion step (PVA/W-ES), or preparation of PVA/W blend from a dry blend (PVA/W-DB).

With a view to intended application of PVA-based mixed films (for example, in packing of infectious hospital

material), evaluation selected for the study was biodegradation in an aqueous aerobic and anaerobic environment (in conditions corresponding to processes in wastewater treatment plants).

When describing biodegradation of mixed polymeric packing materials, it was first necessary to know behavior of individual components in the selected biodegradation environment. Figures 4 and 5 indicate courses of aerobic and anaerobic biodegradation of WAXY starch and PVA (Mowiol 5–88, hydrolysis degree 88%) in the presence of a mixed microbial culture of aerobic (Fig. 4) or anaerobic origin (Fig. 5). Biodegradation of glycerol (data not presented here) as plasticizer occurred, as expected, very quickly in both cases (lag phase shorter than 5 h); during the test, 78% breakdown in an aerobic environment and 67%

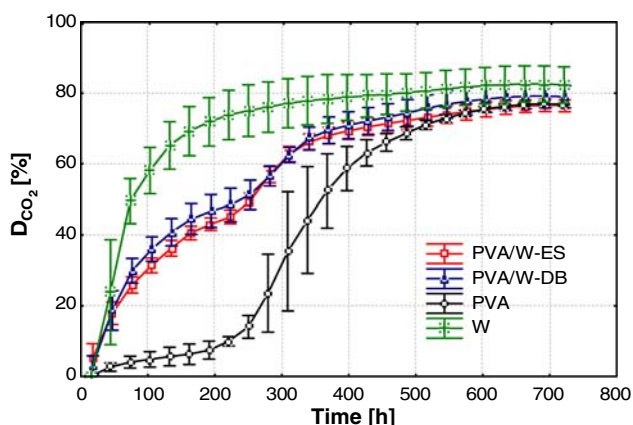


Fig. 4 Produced CO_2 serving to evaluate aerobic biodegradation course of polyvinyl alcohol, starch, of PVA/W blend prepared from common dry blend (PVA/W-DB) and of PVA/W blend prepared by two-stage process with so-called pre-extrusion step (PVA/W-ES); (\pm SD)

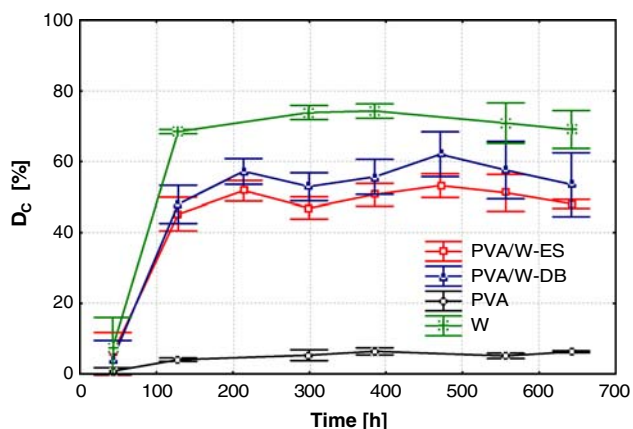


Fig. 5 Produced CH_4 and CO_2 serving to evaluate anaerobic biodegradation course of main blend components, of PVA/W blend prepared from common dry blend (PVA/W-DB) and of PVA/W blend prepared by two-stage process with so-called pre-extrusion step (PVA/W-ES); (\pm SD)

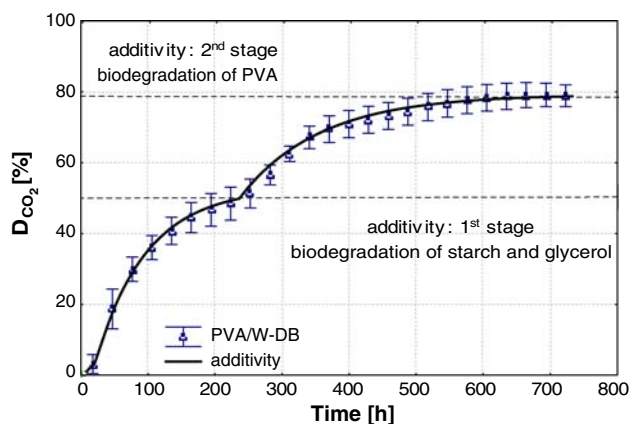


Fig. 6 Comparison of calculated additive and measured course of aerobic biodegradation of PVA/W blend prepared from common dry blend (PVA/W-DB) from reaction suspension in presence of activated sludge, by produced CO_2 ; (\pm SD)

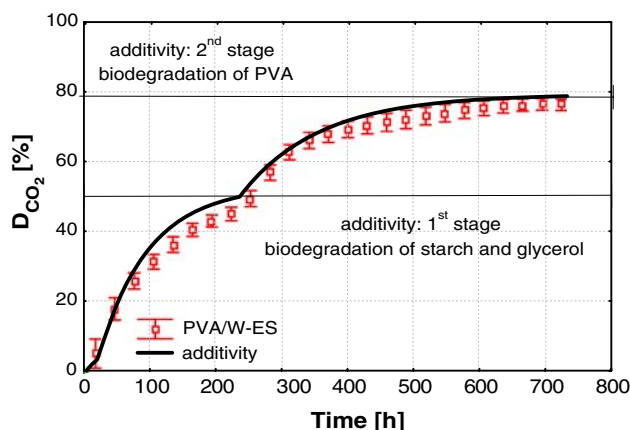


Fig. 7 Comparison of calculated additive and measured course of aerobic biodegradation of PVA/W blend prepared by two-stage process with so-called pre-extrusion step (PVA/W-ES) from reaction suspension in presence of activated sludge, by produced CO_2 ; (\pm SD)

breakdown in an anaerobic environment took place. Breakdown rate constants (k) were similar in both cases— $\sim 10 \times 10^{-3} \text{ h}^{-1}$. Other additives (mixture of palmitic and stearic acids—Stearin III, silicon dioxide—Sipernat 22 S) are added to the blends for better technical processing and in relatively low concentrations. For this reason, they were paid no attention from the point of view of biodegradability.

In the biodegradation of WAXY starch in presence of activated sludge from municipal wastewater treatment plant, a 20-h lag phase was recorded in an aerobic environment, while biodegradation proceeded immediately in an anaerobic environment. At end of test (residual dissolved organic carbon was lower than 10 mg/L), 80% breakdown was achieved in aerobic environment and 72% breakdown in an anaerobic environment. Breakdown rate

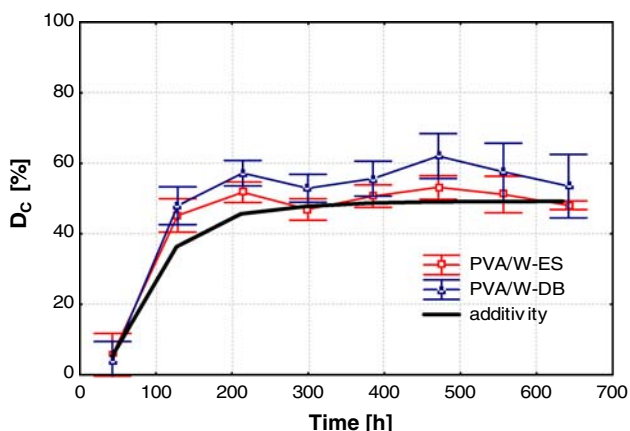


Fig. 8 Comparison of calculated additive and measured course of anaerobic biodegradation of PVA/W blend prepared from common dry blend (PVA/W-DB) and of PVA/W blend prepared by two-stage process with so-called pre-extrusion step (PVA/W-ES); (\pm SD)

constants ranged around $k = 15 \times 10^{-3} \text{ h}^{-1}$ in both aerobic and anaerobic environment. The level achieved with natural corn starch (data not presented) under aerobic conditions was always $\sim 90\%$ degradation, with WAXY starch in that time an $\sim 10\%$ lower breakdown degree was attained. This difference could have been caused by different amylose content.

Biodegradation of PVA in an anaerobic environment (Fig. 4) displayed a “standard” course [21]; degradation lag phase (proceed acclimation of mixed culture) was ~ 10 days and 80% biodegradation already occurred in 25 days. In an anaerobic environment (Fig. 5), admittedly no breakdown lag phase was recorded, merely 6% PVA biodegradation (Eq. 2) took place during the test [5].

Biodegradation of PVA/W-ES and PVA/W-DB blends (Figs. 6 and 7) in an aerobic environment was, as expected, a two-stage process; breakdown of readily degradable components (glycerol and WAXY starch) occurred in the first stage and breakdown of PVA itself took place in the second stage. In the first stage, 50% degradation of both blends occurred, corresponding to starch and glycerol contents; $\sim 80\%$ degradation was attained at the end of test in second stage. Presence of readily degradable components, from viewpoint of produced gases, thus exerts no negative influence on biodegradation of PVA itself.

From Fig. 8 it followed that an $\sim 48\%$ and 52% anaerobic breakdown took place with samples PVA/W-ES and PVA/W-DB respectively during a 650-h test.

The mass presence of components in samples was 42% WAXY starch, 25.2% glycerol and 32.8% PVA Mowiol 5–88. As was already recognized in previous tests [21], a relation was found also in this case between values D_{CO_2}

Table 2 Limit values of aerobic and anaerobic biodegradation (\pm SD) of main blend components; PVA/W blends prepared from common dry blend (PVA/W-DB) and PVA/W blends prepared by two-stage process with so-called pre-extrusion step (PVA/W-ES)

| Sample | D_{CO_2} max or D_C max \pm SD [%] | $t_{lag} \pm$ SD [h] | $k \pm$ SD [10^{-3} h^{-1}] |
|-----------------------------------------|------------------------------------------|----------------------|-----------------------------------------|
| <i>Aerobic biodegradation—1st stage</i> | | | |
| PVA | 79.15 ± 1.54 | 234.6 ± 6.57 | 8.10 ± 0.78 |
| W | 80.09 ± 0.57 | 20.46 ± 3.35 | 15.4 ± 1.07 |
| G | 78.08 ± 0.24 | <5 | 9.61 ± 0.21 |
| PVA/W-ES | 51.86 ± 1.01 | <5 | 9.22 ± 0.43 |
| PVA/W-DB | 57.26 ± 1.82 | 7.43 ± 2.05 | 9.77 ± 0.80 |
| <i>Aerobic biodegradation—2nd stage</i> | | | |
| PVA/W-ES | 76.12 ± 0.32 | 138.2 ± 6.11 | 9.5 ± 0.46 |
| PVA/W-DB | 79.21 ± 0.54 | 143.8 ± 10.1 | 9.0 ± 0.68 |
| <i>Anaerobic biodegradation</i> | | | |
| PVA | 6.12 ± 0.4 | <5 | 7.25 ± 1.9 |
| W | 72.3 ± 1.2 | <5 | 19.0 ± 2.3 |
| G | 67.0 ± 3.1 | <5 | 10.9 ± 1.8 |
| PVA/W-ES | 48.3 ± 0.8 | <5 | 20.7 ± 2.7 |
| PVA/W-DB | 52.6 ± 1.6 | <5 | 21.1 ± 5.1 |

SD Standard deviation

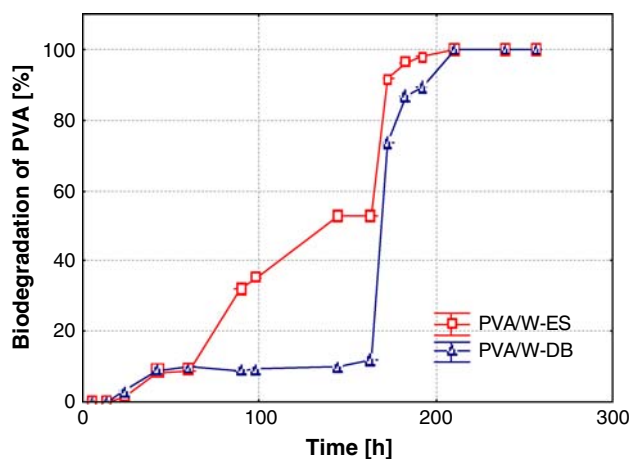


Fig. 9 Percentage of PVA removal from reaction suspension under aerobic conditions in presence of activated sludge, from PVA/W blend prepared from common dry blend (PVA/W-DB) and from PVA/W blend prepared by two-stage process with so-called pre-extrusion step (PVA/W-ES)

and D_C (%) and composition of given sample (Tables 1, 2). This fact was also confirmed by calculations according to so-called additivity rule—Figs. 6–8. The indicated biodegradation course of blends PVA/W-ES and PVA/W-DB was additive in both aerobic as well as anaerobic environment, hence accordingly to presence of individual components in blends.

When the aerobic biodegradation of blends was monitored by spectrophotometric PVA determining (Fig. 9), a slightly untypical two-stage degradation of PVA was noticed in the PVA/W-ES blend: PVA breakdown already occurred after 50 h.

The differences between biodegradation of PVA prepared by two steps and PVA prepared by one step technology can be probably explained by two effects. Two extrusions of PVA in presence of glycerol can ensure better plasticizing effect accompanied by increasing of amorphous phase portion. Amorphous PVA is more readily to biodegradation as crystalline phase. On the other hand, two extrusion steps can induce larger degradation process of base polymer which can be connected with oxidation of PVA chain. It can leads to increasing of concentration of carbonyl and/or carboxyl groups. Both mentioned effects can be factors improving accessibility of PVA to biodegradation. In this time we do not have experimental data for confirmation of above mentioned hypothesis, but it will be focused of our interest in the future work.

Conclusion

In course of tests was demonstrated the significant influence of blends preparation on degradation of PVA

(confirmed spectrophotometrically at 690 nm of the PVA-iodine complex), which was observed in blend prepared by two stage process with pre-extrusion step.

On the other hand, from viewpoint of biodegradability evaluated on basis the gases production, the difference between biodegradation course of blends poly(vinyl alcohol)/WAXY starch with pre-extrusion step and poly(vinyl alcohol)/WAXY starch from dryblend in an aerobic and anaerobic environment is negligible. This is also confirmed by limit values of biodegradability evaluated through first-order substrate kinetics (Table 2). A different method of incorporating WAXY starch in poly(vinyl alcohol) showed no marked influence on resultant biodegradation of mixed films.

With a view to further development of formulations and technological procedure in processing PVA/WAXY starch blends, our observation may be assessed as positive as the technological procedure of preparation does not affect biodegradability of studied blends. Hence, this factor will in no way limit technological conditions for preparing blends and their processing.

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