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ASSESSING BIODEGRADABILITY OF PVAL/ STARCH BLENDS IN AN ANAEROBIC ENVINRONMENT

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ABSTRACT
Research was conducted into biological degradation of PVAL modified samples, mixed with starch in an anaerobic environment. The test of biodegradability was performed in an aqueous environment under anaerobic conditions with digested activated sludge from municipal wastewater treatment plant. Evalution of biodegradation was based on methane and carbon dioxide produced in the gas phase and TOC determination. Pure PVAL (Mowiol 5-88) was degraded from 7 %, degradation of WAXY starch was 74 %. PVA mixed samples, which contained 42 % WAXY starch, 32,8% PVA Mowiol 5-88 and 25,2 glycerine reached 66 – 74 % degradation , The blends which contained 21% WAXY starch, 62 % PVA Mowiol 5-88 and 17 % glycerine was found only 29 % degradation. There was demonstrated that the value of percentage anaerobic degradation was proportionate to the representation of biodegradable components in the sample.
Keywords: biodegradation, anaerobic, PVAL/starch, blends, polyvinyl alcohol, water enviromnent

1. INTRODUCTION
The environmental fate of PVA, one of the very few vinyl polymers soluble in water, was investigated due mainly to its large utilization in textile and paper industries, which generate considerable amounts of PVA-containing wastewaters. A detailed investigation of the anaerobic biodegradability of PVA was carried out by Matsumura et al. [1], using anaerobically preincubated microorganisms deriving from both river sediments and activated sludge from municipal sewage plants. In that study medium-high molecular weight (14 kD) PVA samples as well as low molecular weight (2.2 kD) samples were submitted to the indicated microbial inoculum under strictly anaerobic conditions.
The rate and extent of PVA biodegradation were monitored during the experiment by measuring biogas (carbon dioxide) evolution, TOC determination of the anaerobic cultures, and SEC evaluation of the polymer molecular weight and molecular weight distribution.
In the presence of anaerobic microorganisms from river water sediments, the overall CO_2 production promoted by cultures fed with low molecular weight PVA was similar to that recorded in the presence of D-glucose, used as a reference compound. Both rate and extent of CO_2 evolution were affected by PVA molecular weight, with lower values being observed for the higher molecular weight sample [1]. The percent biodegradation was evaluated by the actual to initial TOC ratio of the anaerobic cultures. The resulting values were consistent with the gas production. The overall biodegradation of the low molecular weight sample correspond to about 75%, whereas the high molecular weight samples

reached lower levels (50–60%) during comparable incubation times. Lower but still significant biodegradability was recorded for both PVA samples in cultures inoculated with anaerobic sludge microorganisms The anaerobic biodegradation of PVA was investigated by monitoring the biogas evolution and TOC decrease in anaerobic respirometric tests performed in the presence of a microbial inoculum consisting of river sediment [2]. The potential biodegradability of disodium methylenemalonate/vinyl alcohol block copolymer was also investigated under these conditions. A 60% PVA biodegradation was estimated by TOC decrease after 4 months of incubation, a value slightly larger than that of the malonate-type copolymer. In agreement with previous results, the copolymer propensity to biodegradation increased with the fraction of vinyl alcohol repeating units. In contrast with the above investigations, PVA was found to show only minor degradation, ranging between 0 and 12% in 77 days, in anaerobic tests using digestion sludge according to ISO and ASTM standard procedures [3]. Starch-based materials originally attracted a great deal of interest because of their low cost, real biodegradability, and renewable origins. [4].

2. EXPERIMENTAL

Biostability of tested samples (granulate and blends based on PVA and starch WAXY) was observed in an anaerobic aqueous environment employing: laboratory equipment (capacity the apparatus is 20 positions). Biodegradability procedure was assessed the basis of methane and carbon dioxide production and TOC (total organic carbon) determination.

Experimental conditions:

Samples (testet PVA films) was inserted into 300ml flask and 100 ml liquid phase (mineral medium (*$MgSO_4$; $CaCl_2$; $FeCl_3$; $(NH_4)SO_4$; phosphoric buffer; trace elements: B^{3+}, Fe^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Mo^{6+}) were utilized in the research. Mixed microbial culture was used as a source of microorganisms – activated anaerobic sludge from municipal wastewater treatment. Dry matter od sludge was 3-4 g/l. pH 7,2. The content of bottles was bubbled with nitrogen 10 min. to eliminate oxygen and then hermetic covered and inserted in thermostat at 35 °C.

Gas chromatography was used for determining the total gas production (methan and carbon dioxide).
Gas chromatography - Chrom -5, column filled with Porapack QS, length 3.6meter, diameter 3 mm
Detector: Termal conductivity detector - TCD, temperature 100°C
Carrier gas : helium 99,999%, flow rate 30 ml / min
Termostat: 50°C, injector: 100°C
Calibration: mixed gas 4,05% CH_4, 0,798% CO_2, 95,152% N2 –Linde Technoplyn a.s., CR

Description of tested materials :

material	Strach (g)	GLY/ TPS (g)	PVA (g)	GLY / Mowiol (g)	TOC (%)
N/17/15	21	9	61,6	8,4	45,6
N/17/17	42	18	35,2	4,8	41,4
N/21/23	21	9	61,6	8,4	42,7
N/21/25	42	18	35,2	4,8	42,4
N/27/31	42	18	32,8	7,2	39,9
N/29/35	42	18	32,8	7,2	37,2

3. RESULTS AND DISCUSSION

Evalution of biodegradation was based on methane and carbon dioxide produced in the gas phase.

$$D_c = \frac{(CO_2)_t - (CO_2)_b + (CH_4)_t - (CH_4)_b}{Th_C} \cdot 100$$

where
$(CO_2)t$ production of CO_2 in gas phase in sample [mmol]
$(CO_2)_b$ production of CO_2 in gas phase - blank, [mmol]
$(CH_4)_t$ production of methane in gas phase - sample, [mmol]
$(CH_4)_b$ production of methane in gas phase- blank [mmol]
Th_C … theoretically production of C, [mmol]

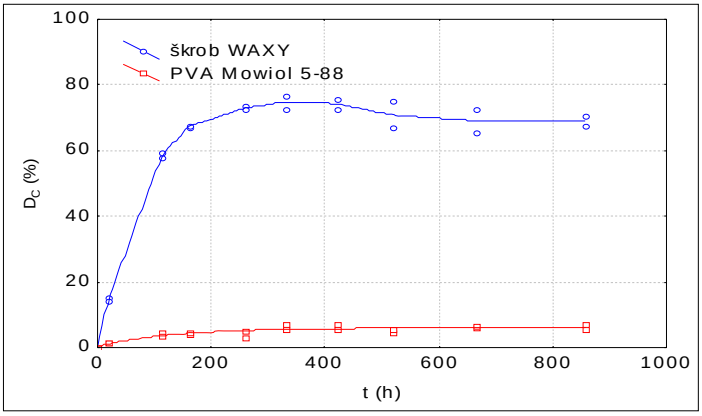

Figure 1. Biodegradability of tested sample (starch WAXY and PVA Mowiol 5-88) calculated fromh ratio(%) of CO_2 and CH_4 in gas phase to theoretically production

Poly(vinyl)alcohol Mowiol 5-88 was found to show only minor degradation 7% during 880 hours tests using digestion sludge. Starch WAXY was degraded from 77 %. There is big diference between biodegradability of polysacharide (starch) and Poly(vinyl)alcohol

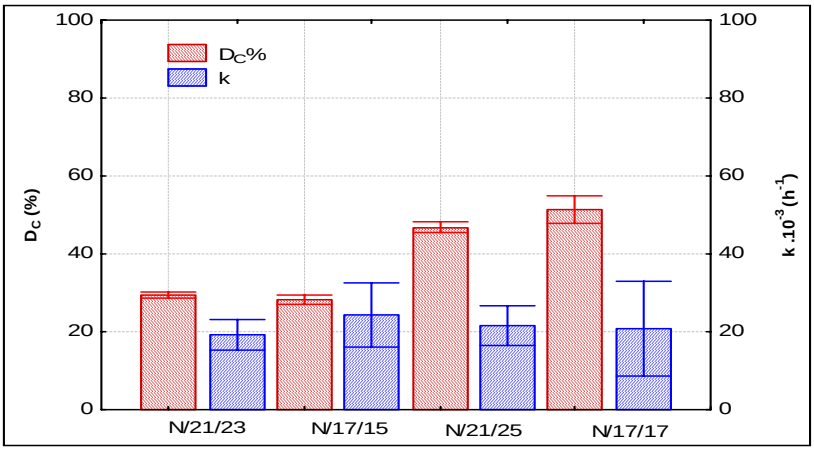

Figure 2. Biodegradability D_c calculated from ratio (%) of CO_2 and CH_4 in gas phase to theoretically production and kinetic constants of 1st order equation describing biodegradation of tested sample PVA/starch

Anaerobic biodegradation of PVA blends, PVA (Mowiol 5-88), starch WAXY and glycerol percentage of removal according to CO_2 and CH_4 production ($\mathbf{D_C}$) to theoretically production is showed in Table 1

tested material	Starch (%)	Glycerole (%)	PVA Mowiol 5-88 (%)	TEST 1 (v t=900hod)		k.10^{-3} (h^{-1})	TEST 2 (v t=550hod)		k.10^{-3} (h^{-1})
				D_C %	**D_t %**		**D_C %**	**D_t %**	
PVA N/17/15 (Meritena 100)	**21**	**17,4**	**61,6**	---	---	---	**28**	**29**	*24,3*
PVA N/17/17 (Meritena 100)	**42**	**22,8**	**35,2**	---	---	---	**51**	**53**	*20,9*
PVA N/21/23 (WAXY)	**21**	**17,4**	**61,6**	---	---	---	**29**	**30**	*19,4*
PVA N/21/25 (WAXY)	**42**	**22,8**	**35,2**	---	---	---	**47**	**49**	*21,4*
PVA N/27/31 (WAXY)	**42**	**25,2**	**32,8**	**54**	**64**	*17,9*	**48**	**56**	*20,7*
PVA N/29/35 (WAXY)	**42**	**25,2**	**32,8**	**63**	**73**	*12,8*	**55**	**66**	*21,1*
PVA Mowiol 5-88	---	---	**100**	**10**	**17**	**9,1**	**6**	**7**	*7,3*
starch WAXY	**100**	---	---	**---**	**---**	**---**	**72**	**77**	*19,1*
glycerol	---	**100**	---	**67**	**80**	**10,9**	**68**	**73**	*10,4*

Tab. 1 Anaerobic biodegradation of PVA blends, PVA, starch and glycerol - percentage of removal according to CH_4 and CO_2 production (D_C), total degradation (D_t) and kinetic constants of 1st order equation

4. CONCLUSION

The biodegradability PVA/starch blends in anaerobic environment was based on determination of production methane an carbon dioxide by analysing with gas chromatography and TOC determination. PVA (Mowiol 5-88) was found to show only minor degradation 7% - 17 % in an anaerobic tests using digestion sludge. Starch was degraded from 77 % and glycerol from 80 %. Biodegradability of PVA blends, which contained 42% WAXY starch, 32,8% PVA (Mowiol 5-88) and 25,2 glycerine reached 66 – 74 % . The samples contained 21% WAXY starch, 62% PVA (Mowiol 5-88) and 17% glycerine was found 29 % degradation. There was demonstrated that the value of percentage anaerobic degradation was proportionate to the representation of biodegradable components in the sample.

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