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Biological degradation of PVA/CH blends in terrestrial and aquatic conditions

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Abstract

A new material, the water soluble blend of poly-vinylalcohol and collagen hydrolysate (PVA/CH) was developed in Slovakia. Results from a recent biodegradation study including three blend variants differing in the collagen content are presented. Two different biodegradation tests, one in compost environment, the other at aquatic conditions and additional compost analysis after degradation of the polymer have been done. Degradation rates were determined for both test systems and the carbon conversion rates were calculated by drawing up a carbon balance out of the aquatic test. The results proofed positive influence of collagen hydrolysate on degradation but also show a relatively low biological degradability of PVA under the applied test conditions. At least, no negative influence on the compost composition was detected.

Keywords: Biodegradable plastics; Biodegradability; Poly-vinylalcohol; Collagen hydrolysate

1. Introduction

Biodegradable plastics are becoming more and more an issue in research, development and in practical use. They play an important role towards environmental friendly materials and packaging and can improve the environmental impact of different products. Besides that they can solve some complex problems in agriculture, medicine, packaging industry and (bio)waste management. Multi-step test schemes have to be applied and test criteria have to be met to assure the claimed properties of new materials, such as the European standard EN 13432 for biodegradable packaging. A test scheme for agricultural applications is currently under development (CEN, technical committee 249) but is not finished now. But it is to expect, that a demonstration of biodegradability and of material disintegration will be the minimum requirement in all future schemes.

The new water soluble plastic blend made of poly-vinylalcohol and collagen hydrolysate (PVA/CH) is an unique mixture of synthetic and biogenic materials. Its properties offer potential for several practical applications in agriculture ranging from portion-packaging of pesticide chemicals through sieving tapes till mulching foils as well as for packaging of contaminated cloths in hospitals. The positive impact of such biodegradable plastics usage was described on global, regional and local level (Fritz et al., 2001). Ongoing from applications as listed, the most important characteristic of the investigated materials are their biological degradability and the impact of their residues and biodegradation metabolites on natural ecosystems as well as their impact on the composting process and on water treatment systems. Those properties had to be analysed by a comprehensive study.

Biodegradable packaging waste would preferably be collected and treated together with biowaste and will undergo an aerobic, thermophilic composting process. Materials used for portion-packaging or mulching films will biodegrade on site at ambient temperature. To cover those different degradation scenarios, two biodegradation test systems had to be applied. The modified Sturm-test (ISO FDIS 14852) was chosen to represent aerobic biodegradation at ambient temperature. It was the only test system found allowing to measure and calculate a carbon balance (Hund, 1994). For simulating a compost environment the laboratory composting test, prEN

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14046, as mentioned in the general standard EN 13432, was chosen.

2. Methods

2.1. Materials

Stabilised compost was taken from the agricultural composting plant Pixendorf (Austria) which treats local, source separated biowaste ('Biotonne'). After collection it was sieved through a 10 mm screen. Some selected analysis data of that compost are given in the last line of Table 1.

The raw material PVA was produced in Slovakia, at CHZ Nováky, and had a molecular weight of 40,000–45,000. The 4% solution in water showed a viscosity of 10 mPa/s at 20 °C.

The raw material collagen hydrolysate was obtained from a leather company in Zlín (FT), Czech Republic, commercially available under the product name Hykol E. The collagen had a molecular weight of up to 10,000 and a nitrogen content of 14% on dry matter base.

Three blends of PVA/CH, developed at the KPK, CHTF-STU (Slovakia), were used with different rate of collagen content: 16.8% collagen in HK 70/193, 12.5% collagen in HK 92/260 and 0% (pure PVA) in HK 76/199. All three materials were produced by blow extrusion in laboratory scale and were provided as water soluble, colourless, optically clear foils of about 35 μm thickness.

As a reference substance and to confirm the validity of both, the laboratory composting system and the Sturm-test, cellulose (Fluka, No. 22181) was used.

2.2. Terrestrial biodegradation analyses

The standard method prEN 14046 was followed, only minor changes had been necessary to adapt to the available laboratory equipment. The degradation tests were performed in closed, aerated glass vessels of about 3 l total volume positioned inside a heating oven and kept at a constant temperature of 58 °C (±1 °C). Aeration was done in a rate of 90–100 ml/min per vessel with normal compressed air. Between 70 and 110 g (12% in mass on dry weight basis) of each one of the materials was initially mixed with 900 g of three month old almost mature biowaste compost. The three materials, the cellulose reference and the control were tested in three parallels each, so all together 15 vessels were used. The exhaust air was passed through bottles filled with 400 ml of 0.5 M NaOH solution to absorb the released carbon dioxide separately from each degradation vessel. The NaOH solutions were replaced periodically and the absorbed carbon dioxide was measured by titration with 0.1 M HCl. Biodegradation was calculated by summing up the amounts of released CO_2 for each vessel and set into relation to the theoretical amount of CO_2 assuming a full conversion of all sample carbon into CO_2. The test runtime was limited to 94 days, until the plateau phases (no significant CO_2-production) were reached in all vessels.

After the degradation test aqueous eluates were made from all of the compost samples according to the DIN S4 procedure: One part compost dry matter plus ten parts water were mixed during 24 h by overhead shaking at room temperature. After a short settlement the turbid supernatant was decanted through a 63 μm sieve (removing swimming particles) and centrifuged for 30 min at 3 g. The clear supernatant was used for further chemical analysis.

2.3. Preparation of an inoculum to be used in the aquatic degradation test

For use in the aquatic degradation tests an inoculum was prepared from compost by the following procedure: About 500 g of compost (the same as described above) was suspended in about 2 l of hand-warm tap water and stirred for two hours. After 30 min sedimentation the turbid supernatant was passed through a 63 μm sieve to remove swimming particles and centrifuged for 20 min at 3 g to obtain the micro-organisms in a pellet. That

Table 1
Analytical results of water eluates from compost samples after the laboratory composting test

Sample (% CH content)	pH	Conductivity (mS/cm)	Colour[a] ($E_{485\ nm}$)	DOC (mg/l)	NO_3 (mg/l)	TKN (mg/l)
1. HK 76/199 (0%)	7.51	3.09	3.36	2030	273	12.8
2. HK 92/260 (12.5%)	7.41	3.80	2.64	1360	376	13.3
3. HK 70/193 (16.8%)	7.58	3.57	3.94	1610	246	13.1
4. Cellulose	7.35	4.14	0.97	541	649	13.2
Control (compost treated)	7.81	2.89	4.60	1590	136	13.0
Fresh compost (before test)	8.10	3.51	2.78	638	277	13.4

DOC = dissolved organic carbon, NO_3 = nitrate, TKN = total Kjeldahl nitrogen.
[a] The colour was measured as light extinction at a wavelength of 485 nm and could be seen as a rough indicator for the amount of water soluble humic substances.

pellet was re-suspended in 100 ml tap water, stirred and aerated carefully for 24 h and analysed for pH (7.8) and dry matter (1.02%). That procedure assured to obtain an active inoculum with a micro-organism composition close to that of compost and comparably low concentrations of other biodegradable organic matter.

2.4. Aquatic biodegradation analyses, modified Sturm-test

The biodegradability of the polymer materials was determined in a modified Sturm-test system using a compost micro-organism inoculum. The standard method ISO FDIS 1452 was widely followed, almost no changes were necessary to be able to draw up a proper carbon balance. The test is a continuously stirred, aerobic, aqueous system performed in gas washing bottles at 35 °C. Aeration was done using CO_2-free compressed air from a pressure bottle (synthetic air) in a rate of about 50 ml/min. The test mixture contained an inorganic medium, the organic test material (the sole source of carbon and energy) with concentrations close to 1200 mg/l of organic carbon (see Table 2) and 1 ml of the inoculum described above. Similar to the system used for the composting test (see above) the CO_2-evolution was followed by periodic measurement of the released carbon dioxide in the exhaust air. The biodegradation was calculated by relating the measured to the theoretical amount of CO_2.

3. Results

The obtained degradation rates during the 94 days of laboratory composting were 39% for HK 70/193 (high CH content), 46% for HK 76/199 (pure PVA), 40% for HK 92/260 (lower CH content) and above 100% of theory for cellulose. The dynamics of the degradation progress could be seen from Fig. 1. The CO_2-evolution started within the first 24 h with initial high rates slowing down and almost stopping at the seventh day. The discontinuity around test day 12 derived from opening of the vessels and manual homogenisation by stirring. The reactivation initiated a new phase of high microbial activity. Later homogenisation procedures did not affect the dynamics that much. At the end of the composting test the sample pieces had been found in all vessels in high amount. That residuals did show a significantly changed visual appearance and changed physical and chemical behaviour, since they appeared opaque white, soft elastic and they were not water soluble any longer.

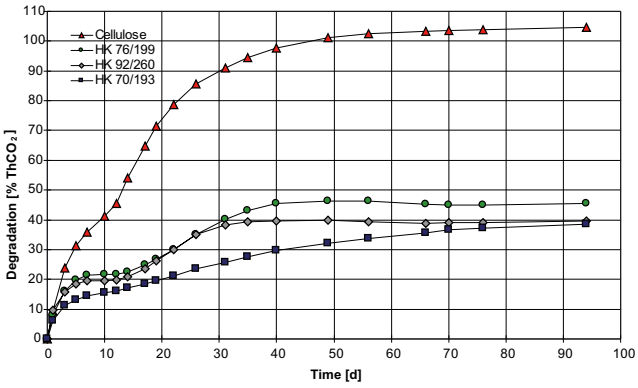

Fig. 1. Biological degradation of PVA/CH at compost conditions (laboratory composting method, CO_2-evolution), % values calculated on base of theoretical amount of CO_2 from sample carbon content. PVA/CH blends: HK 76/199 (0% collagen), HK 92/260 (12.5% collagen), HK 70/193 (16.8% collagen).

Analysis results of the remaining compost samples taken from the vessels at the end of the test are given in Table 1. The analysed parameters did show almost the same results for the three different sample blends and differed only slightly from those of the control compost. The reference compost in which cellulose was degraded did show a high conductivity but low colour and dissolved organic carbon at the same time.

During the 48 days in the Sturm-test the material HK 70/193 (high CH content) reached 25%, HK 76/199 (pure PVA) reached 17%, HK 92/260 (lower CH content) reached 24% and cellulose reached 84% degradation based on the theoretical amount of CO_2-evolution. The dynamics of the degradation progress could be seen

Table 2
Carbon balance from the Sturm-test degrading PVA/CH blends. TOC was measured from homogenised content of the test bottles including suspended particles. All % values are given on base of the initial carbon content (the sum differs from 100% because of analytical inaccuracy and probable losses)

Sample (% CH content)	TOC start (mg/l)	TOC end (mg/l)	C converted into CO_2 (%)	C remaining insoluble (%)	C remaining solved (%)
1. HK 76/199 (0%)	1290	974	17.0	1.2	74.3
2. HK 92/260 (12.5%)	1253	796	23.9	1.7	61.9
3. HK 70/193 (16.8%)	1243	761	24.5	1.3	60.0
4. Cellulose	1063	81	83.9	6.5	1.1
Blind	41	33	–	–	–

Converted carbon was calculated from the periodically measured evolved CO_2, insoluble carbon was determined from centrifugation pellets and solved carbon from centrifugation supernatants at the end of the degradation tests (48 days).

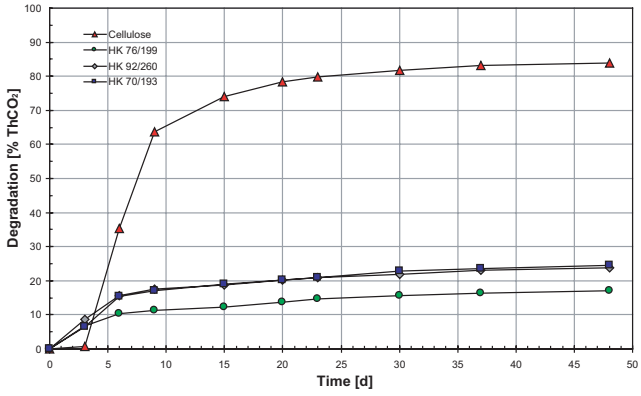

Fig. 2. Biological degradation of PVA/CH at aquatic condition (Sturm-test, CO_2-evolution), % values calculated on base of the theoretical amount of CO_2 from sample carbon content. PVA/CH blends: HK 76/199 (0% collagen), HK 92/260 (12.5% collagen), HK 70/193 (16.8% collagen).

from Fig. 2. The centrifugation supernatants (prepared for chemical analysis) at end of the test were optically clear and colourless.

To evaluate the degree of carbon conversion into the three possible end products CO_2, new biomass and residual dissolved carbon separate TOC and DOC analysis (total and dissolved organic carbon) were done from the bottle contents after 48 days of Sturm-test. The results are shown in Table 2. The carbon content of insoluble particles could not analytically differentiated between grown biomass and insoluble residues of the original samples. Nevertheless, because of the water solubility of the PVA/CH-samples it was considered as biomass only. The analysis results were the basis for drawing up a carbon balance. The sum of CO_2–carbon, converted insoluble (biomass) and unconverted dissolved (sample) carbon should be the same as the amount of carbon initially put into the system with sample and inoculum. The recovery was around 90% in all bottles, reflecting both analytical inaccuracies and a probable CO_2 loss. The direct result of the carbon balance was, that the biomass, expressed as the insoluble carbon content, was very low in all three sample bottles, indicating a low biomass growth and indirectly a low content of biodegradable organic matter. Most of the initial sample carbon was found in the DOC, that means it was not assimilated by the micro-organisms.

4. Discussion

In general, the biodegradation rates of PVA/CH blends were striking low in both test systems. The higher temperature of the laboratory composting test may have caused a partial hydrolysis of the PVA polymer, resulting in a little higher biodegradability (van der Zee, 1997). But even then the CO_2-conversion rate did not exceed 46%. The materials were initially water soluble but had not been dissolved before adding them to the compost at the start of the composting test. Only very little free pore water was available in the compost matrix, following the recommendations in the prEN 14046. Even if the conditions were optimal for the biodegradation process, the water content was obviously not high enough to dissolve the PVA. Before degradation started (during the lag phase) and even before the material had a chance to dissolve in the compost pore water the PVA/CH became, surprisingly, insoluble.

The weak biodegradability could be partly caused by the chemical structure of the PVA (unknown stereo regularity of hydroxyl groups) or by the degree of polymerisation (comparably high molecular weight). The change of the visual appearance and mechanical properties (which were not further quantified) could have been caused by the increased temperature during the composting process or by chemical means, such as the denaturation of the collagen compound or reactions of the components with humic acids or other organic or inorganic contents of the compost. The degradation value of over 100% for cellulose was a result of the so called 'priming' effect, which is well known to appear by introducing an easy degradable substance into almost mature compost (Dalenberg and Jager, 1989; Tuomela, 2002).

Analysis results from the remaining compost after degradation of the materials and cellulose reference did show that a higher amount of water soluble organic substances (DOC) and humic substances (colour) was formed in those vessels which treated PVA or PVA/CH. Other parameters, such as conductivity, nitrate and TKN were much less influenced by the type of sample treated but were at least slightly different to the results obtained from the control compost. Nevertheless, the conductivity increase was much higher due to biodegradation of cellulose than it was due to biodegradation of the PVA/CH samples. All those observed effects were most probably caused by stimulation of the micro-organism population and keeping the temperature constant at 58 °C till end of the test. The ripening phase which occurs naturally during several weeks at mesophilic temperature when humic substances are polymerised (Danneberg, 1970) is not part of the laboratory composting test.

While the collagen content did not have a significant influence on the degradability in the composting test, there could be a pattern observed in the Sturm-test: the higher the collagen content of a PVA/CH blend was (HK 70/193 with 16.8% collagen), the higher degradation rates were achieved. Nevertheless the degradation rates (conversion into CO_2) of all PVA/CH blends were significantly lower than in the composting tests, which was most probably the influence of the test temperature. In the Sturm-test the positive influence of the collagen

hydrolysate on the total CO_2-conversion was noticeable. The same effect was detected earlier also at anaerobic condition (Lešinský et al., 2000).

From the results of the carbon balance analysis (Table 2) it could be interpreted, that neither a denaturation of the PVA/CH blend nor any significant formation of biomass did occur during the 35 °C Sturm-test. The water soluble materials kept their properties and are found almost totally in solution (DOC). Under the applied test conditions the cellulose was completely converted into CO_2 and new biomass, no priming effect appeared.

For further evaluation it must be considered, that the used PVA contained about 16% Glycerine (added as softener), which is fully biodegradable. If the theoretical amount of CO_2 from the Glycerine is subtracted from the practically measured CO_2-evolution, the degradability of the pure PVA was much lower. The net biodegradability of the pure PVA was not more than 30% under composting conditions (58 °C) and about 1% in aquatic environment (35 °C). PVA should therefore be considered as not biodegradable in environments with low temperature.

5. Conclusions

The results of those experiments showed unexpected low degrees of biodegradability of the investigated PVA/CH blends under two different conditions and environments. The tested material variants did not significantly influence the composting process or lower the compost quality. Even if no residues other than undergraded PVA are to expect, a need for closer material analyses which may proof the reason for the low biodegradability is clearly identified. Further studies of the degradability of PVA/CH blends in soil (to address agricultural applications) and by activated sludge (for wastewater treatment plants) should extend the current results by including additional natural and technical biodegradation conditions. In advance of any practical use in agriculture or other public applications additional investigations and most probably a change in the polymer structure of the PVA component are needed. A label for biodegradability should not be printed on products composed of PVA and CH in compositions like the tested ones.

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References

Dalenberg, J.W., Jager, G., 1989. Priming effects of some organic additions to ^{14}C-labelled soil. Soil Biol. Biochem. 21, 443–448.

Danneberg, O.H., 1970. Huminstoffaufbau und Stickstoffumbau während der Rotte von Maisstroh. Ph.D. Thesis, University of Natural Resources and Applied Life Sciences, Vienna.

EN 13432, 2001. Requirements for packaging recoverable through composting and biodegradation—test scheme and evaluation criteria for the final acceptance of packaging. CEN Brussels.

Fritz, J., Link, U., Braun, R., 2001. Environmental impacts of biobased/biodegradable packaging materials. Stärke/Starch 53 (3–4), 105–109.

Hund, K., 1994. Entwicklung von biologischen Testsystemen zur Kennzeichnung der Bodenqualität. Study No. 94-011, Environmental agency, Berlin.

ISO/FDIS 14852, 1999. Determination of ultimate aerobic biodegradability of plastic materials in an aqueous medium—method by analyses of evolved carbon dioxide. ISO Genf.

Lešinský, D., Alexy, P., Bakoš, D., Kolomazník, K., Javorekova, S., 2000. Research and production of biodegradable polymers in Slovakia. Proceedings of the Food Biopack Conference, Copenhagen, pp. 96–98.

prEN 14046, 2003. Evaluation of the ultimate aerobic biodegradability and disintegration of packaging materials under controlled composting conditions—method by analysis of released carbon dioxide. AFNOR Paris.

Tuomela, M., 2002. Degradation of lignin and other 14C-labelled compounds in compost and soil with an emphasis on white-rot fungi. Ph.D. Thesis, University of Helsinki.

van der Zee, M., 1997. structure-biodegradability relationships of polymeric materials. Ph.D. Thesis, University Twente.