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NEW TREND OF CHARACTERISATION OF POLYMERS BIOSTABILITY UNDER AEROBIC AND ANAEROBIC CONDITIONS

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ABSTRACT
The work focuses on potential employment of MicroOxymax $O_2/CO_2/CH_4$ automatic analyzer (Columbus, U.S.A.) for assessing aerobic and anaerobic biodegradability (biostability) of composites. Convenience of the given analyzer was assessed in degradation of PVAL-based mixed films.The objective of the work was confronting results of these tests with results obtained through "classic" standard respiration procedures (measuring consumption of oxygen or production of CO_2 for the aerobic conditions and measuring production of CO_2 and CH_4 for anaerobic conditions). Standard tests already earlier revealed that a "stepwise" degradation course takes place with mixed films when unadapted inoculum is employed, which corresponds to gradual breakdown of particular components in a sequence corresponding to their biological degradation. In similar tests with analyzer MicroOxymax $O_2/CO_2/CH_4$ it was found that results of individual tests were in harmony, so that the analyzer, price disregarded, could prove to be a good alternative to existing standard tests.
Keywords: biostability, biodegradation, automatic analyzer, MicroOxymax, aerobic, anaerobic

1. INTRODUCTION
It is assumed that more than 1000 new chemical compounds – components of various products used in industry, agriculture, and households – are produced every year. Compounds that are not readily degradable accumulate in the environment and thus impair natural circulation. Therefore, biodegradability can be considered as basic criterion determining the behaviour of chemical compounds in the environment.
When quantifying the results of biodegradability, it is useful to use the basic equation of aerobic biodegradation:

$$\text{substrate (syntetic polymers)} + O_2 \xrightarrow[\text{N, P}]{\text{bacteria}} CO_2 + H_2O + \text{new biomass} \qquad (1)$$

Biodegradability can be quantified either according to the decrease of reacting compounds on the left side of Equation 1 (substrate, O_2) or according to the formation of products on the right side of the equation (CO_2, biomass). The basic parameter used to quantify biodegradability and degradation rate is the decrease of substrate determined by specific or non-specific methods (for example normalized weight loss for water insoluble polymers).

From the ecological point of view, non-specific criteria evaluating ultimate biodegradability are preferred; i.e., the substrate decrease is determined by DOC, COD, BOD, and CO_2.
The stability of compounds under anaerobic conditions may be of a pronounced ecological significance. Such compounds can accumulate in bottom sediments or in anaerobic stabilized sludges. For instance, surfactants are partially absorbed onto primary sludge and pass directly to digesters without prior biodegradation under aerobic conditions, although just the opposite is the general rule [1].
The degree and rate of degradation of a given compound are usually evaluated indirectly according to specific CH_4 and CO_2 production which is compared with the theoretical production using the classical equation (2):

$$\underset{\text{substrate}}{\underset{\text{(syntetic polymers)}}{C_nH_aO_b}} + (n - a/4 - b/2)\, H_2O \xrightarrow{\text{bacteria}} (n/2 - a/8 + b/4)\, CO_2 + (n/2 + a/8 - b/4)\, CH_4 \qquad (2)$$

However, empirical formulae of some industrial products are not known. It is more advantageous to express the results per milligram (gram) organic carbon of the compound tested. In all methods, the CO_2 and CH_4 produced from the test material are obtained by a differential measurement between test and control systems. When determining the total gas production, it is necessary to know the correction for CO_2 and CH_4 solubility in the digested liquor, to release the dissolved CO_2 forms from the digested liquor by acidification, or to quantify them by determining the dissolved inorganic carbon [1].
Nowadays, to monitor gas products of aerobic and anaerobic degradability, not only standard laboratory procedures as acidimetry, volumetry, gas chromatography are used, but also electronic manometric agents (manometric principle) in connection with computer technology. However, such arrangements sometimes do not prove required measuring sensitivity and accuracy necessary for assessing biodegradability of copolymer materials. Hence, in this work the microrespirometre Micro-Oxymax $O_2/CO_2/CH_4$ (fig.1) was employed, in which is gas components assessed paramagnetically or IR photometrically. The respirometre may be used for microbial respiration most often associated with environmental soil and water research; food science and preservation; insect respiration; tissue and skin respiration; plant research and a wide range of other applications. Hitherto, its pronounced employment in monitoring both aerobic and anaerobic biodegradability of synthetic polymers and their blend with natural compounds has not been recorded yet.

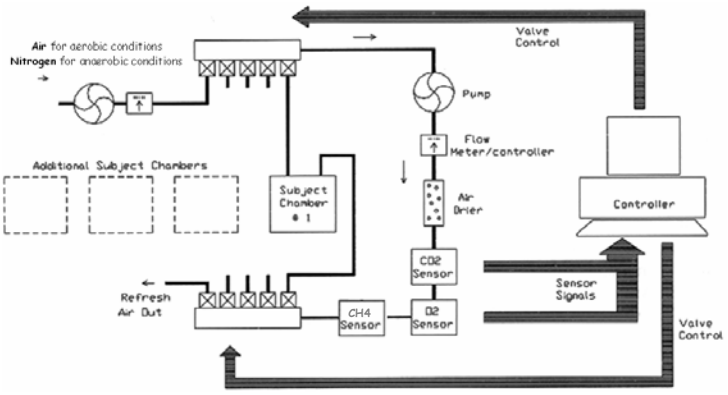

Fig. 1 Simplified diagram of the respirometer Micro-Oxymax $O_2/CO_2/CH_4$

The Columbus Instruments' Micro-Oxymax system is a highly adaptable general purpose closed circuit respirometer. The system monitors the concentration of gas contained within an enclosed head space into which the material being monitored is respiring. Periodic sensing of the gas concentration, along with an equally accurate measurement of the volume of the head space, allows calculations of incremental and accumulated values for consumption and production. Micro-Oxymax patented design principle provides a sensing threshold near $2x10^{-7}$ liter per hour. The system can be configured for single or multiple gas sensing. O_2, CO_2, CH_4, Carbon Monoxide, H_2S_2 and Hydrogen can be sensed over specially selected ranges to meet almost any application. The modular design of Micro-Oxymax allows an initial configuration for basic investigations that can be expanded later to include additional gases and/or chambers. The system automatically compensates for changes in pressure and temperature. In addition, Micro-Oxymax will initiate refreshing of the head space gas if concentrations deviate beyond operator prescribed limits.

2. EXPERIMENTAL

Biodegradability of tested samples (protein hydrolysate and blends on the basis of polyvinyl alcohol, proteinous hydrolysate, natural starch and glycerine) [2] was observed in an aerobic aqueous environment employing: microrespirometer Micro-Oxymax $O_2/CO_2/CH_4$ - current capacity the apparatus is 30 positions; laboratory equipment – biodegradability procedure was assessed the basis of CO_2 production (ASTM D5209-92) [3], which is absorbed in hydroxide solution and then titrimetrically determined, biodegradability criterion is ratio of produced CO_2 to $CO_{2\ r}$ calculated from carbon content in the original sample (%), current capacity is 7 positions; respirometer BIAL BOD 10 - manometric determination of biological oxygen demand (ČSN EN ISO 9408) [4], current apparatus capacity is 10 positions. Mixed microbial culture was used as a source of microorganisms – activated sludge from municipal wastewater treatment.

3. RESULTS AND DISCUSSION

Respirometer sensitivity is generally dependent on several factors: the first is character of used microbial culture and its concentration, the second is substrate concentration and the last is a measuring vessel capacity. Therefore, the basic information tests were accomplished at first to find suitable conditions of assessing polymer biodegradability by means of microrespirometer MicroOxymax $O_2/CO_2/CH_4$ under aerobic conditions. Anaerobic conditions required long term tests and it is the reason their results cannot be presented for the time being. Nevertheless, tests in progress are promising. Aerobic tests: reactive vessel of content 150 cm^3 used, reactive suspension content was 50 ml. Presented content and gas/liquid ratio phase were chosen in respect to comparability of results of these tests with the standard ones. The sampling interval of the gas phase was 8 hours, which was, regarding long term tests, utterly sufficient. Shorter interval would be an end in itself (useless amount of data) and consequently it could negatively influence measure accuracy (full phase dilution of testing bottles with air from hose interconnections and essential computing correction). Concentration of microbial suspension was 100 mg/l and of substrate 100 mg/l (the same conditions as with standard tests preserved).

Comparison of results of two respirometer tests according to the standard method ISO 9408 and with the employment of microrespirometer Micro Oxymax can be seen in fig. 2 (degradation procedure determined by BOD) and fig.3 (assessed by CO_2 production in % of theoretical production). Satisfactory concordance of the results was reached in both methods; 10% difference in final values D_{CO2}max and BOD was owing to used mixed microbial culture – activated sludge from municipal wastewater treatment acceptable.

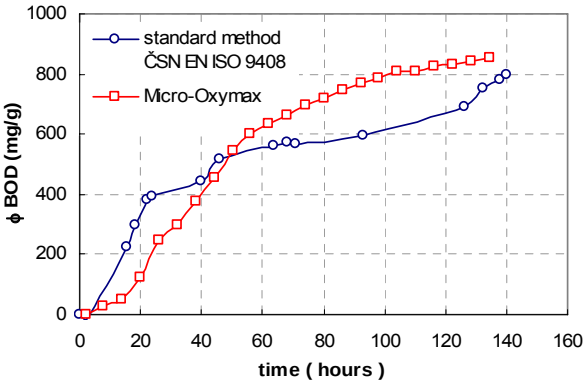

Figure 2. Biodegradability determination of proteinous hydrolysate – comparison of BOD progress of two respirometers.

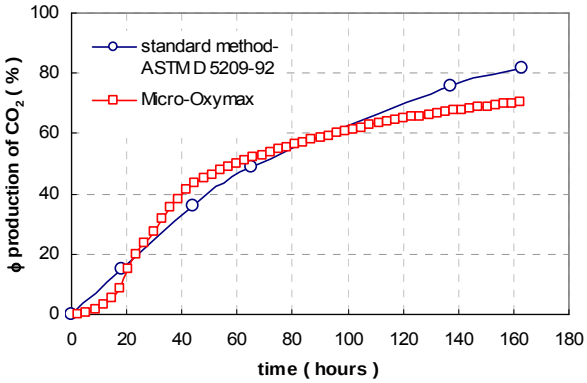

Figure 3. Percentage of proteinous hydrolysate removal according to CO_2 production-comparison of two methods progress

Taking account of the above mentioned information the PVA biodegradability and mixed foils on the basis of PVA and biopolymers were observed. As referent material collagen hydrolysate was chosen whose good biodegradability was known from the preceding tests and was also the part of tested mixed films.

From the sensor sensitivity data (apparatus manual) followed that change of CO_2 concentration in gas phase should move in interval from 0 to 1 content percentage. Not to exceed the interval, influence of inocula and substrate dosing was observed with a goal to find suitable ratio inoculum/ substrate. The result is shown in fig.4.

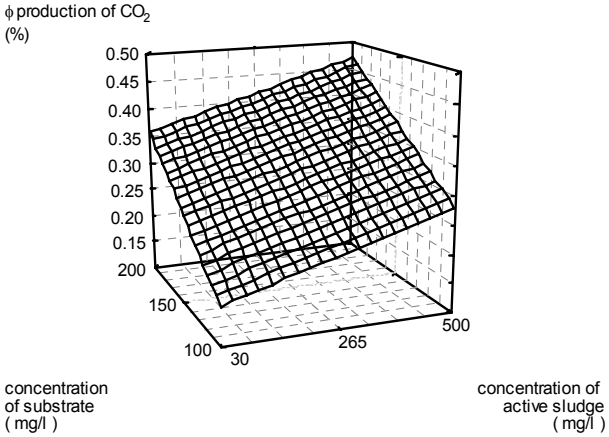

Figure 4. Influence of substrate concentration (proteinous hydrolysate) and inocula on instrument response

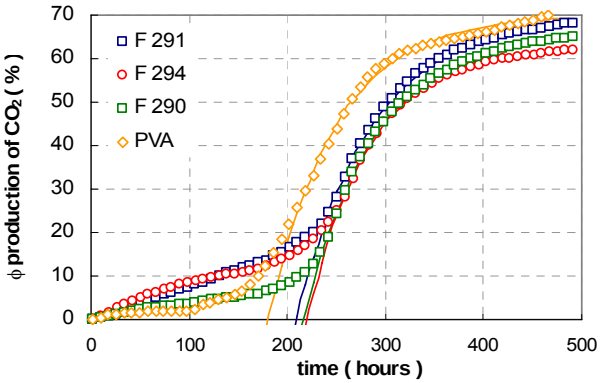

*Figure 5. Percentage of removal according to CO_2 production – D_{CO2} for foils **F291** (starch, Glycerine) **F294** (Proteinous hydrolysate, Glycerine), **F290** (Glycerine) and PVA itself – POVAL 205*

From the figure follows that suitable ratio "sludge solids/substrate concentration"was 500/200 (in mg/l). Maximal CO_2 production in the middle of the measuring extent of the apparatus (0-1 %) was ca 0.5 content % of CO2 at 8 hours sampling interval. Thus, the same conditions as with standard tests were set so the results could be mutually compared.

4. CONCLUSION

The aim of this work was the confrontation of the tests results accomplished with the employment of microrespirometer Micro Oxymax with results obtained by standard respiratory procedure. (ČSN EN ISO 9408). As the standard tests earlier found [2], with mixed foils occurs "gradual"progress of degradation using unadapted mixed microbial culture which corresponds to gradual degradation of individual components in sequence of their biodegradability. In analogical tests with analyzer MicroOxymax O_2/CO_2 it was found that results of individual tests were in harmony (fig.5) so that the analyzer, price disregarded, could prove to be a good alternative to existing standard tests.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

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