BUDAPEST UNIVERSITY OF ECONOMICS
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METHOD DEVELOPMENT FOR THE STUDY OF BIODEGRADATION OF BIODEGRADABLE-LABELLED PACKAGING MATERIALS

Theses of the doctoral dissertation of

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1. INTRODUCTION

1.1 OVERVIEW

The packaging directive No. 94/62/EC dealing with the treatment of packaging materials and packaging waste, which aims at the decrease of the environmental pollution caused by packaging materials, was accepted by the European Parliament and Commission on the 20/12/1994. This was the first legal norm to provide special rules and quantitative goals on a well definable amount of materials, which was further extended for other products (cars, electronic hardware, etc.) later on. However, this packaging directive – like all the others – was considered only a recommendation for the EU countries harmonising the national rules on packaging activity and waste to decrease the relevant environmental pollution. National governments were to set up a system for waste management enabling all possible ways of waste utilisation, i.e.: prevention (first and foremost), reuse, recycling, and energy recovery. The definition of organic recycling was also created that was focusing at the utilisation the biodegradable components of packaging materials by either aerobe composting or anaerobe biogas production.

Several European countries can exploit the application of the biological treatment of solid organic waste under controlled conditions carried out as either aerobe composting or anaerobe methods for (packaging) waste management. The main reason behind this choice is the possibility to mix the usual input (green and household organic waste) of composting plants and biogas factories with by-products from food industry, paper-based and biodegradable polymer-based packaging materials, etc.

At the moment, directives and threshold values are elaborated only for the composting treatment of packaging materials, but not for the anaerobe organic recycling methods. However, there are some laboratory standards available for the study of polymers, but the practical experience gained on this field is not considered sufficient for the determination of threshold limits, and the apparent governmental support of composting evidently hinders the set-up of missing parameters. On the other hand, the traditional composting is also reinforced by the sophisticated qualification process that the possible input materials are to go through to be compostable-labelled. First, the composition of materials intended for composting must be known and they must not contain toxic components; second, they must be considered biodegradable by standard laboratory tests; third, they disintegration in biological waste treatment plants must be proved; and four, the resulting compost should possess at least the same quality it would reach in the case of exclusively green waste-based input materials.

The widespread use of plastics resulted in the significant increase of the amount of plastic waste. The deposal, treatment and recycling processes require more and more efforts from the organisations responsible for environmental protection. Thence, R&D devoted to the production of biodegradable (and in the long run, compostable) materials from renewable sources are of paramount importance. However, the standardised testing of biodegradability of this new type of materials in laboratory scale is facing several problems at the moment. On the one hand, there is no measurement set-up available in national level (Hungary) capable to monitor biodegradation processes for a longer period of time (e.g. several months) usually required in real practice. On the other hand, there is no international accordance in the competence of aquatic tests derived from the biodegradation study of chemicals on the examination of the degradation of mostly water-insoluble polymers.

1.2 AIMS OF THE PHD ACTIVITY

- After evaluating the relevant & up-to-date international references, the development of a measurement set-up based on the application of solid test media was planned that is capable to determine quantitatively the biodegradation of test materials by measuring the amount of consumed O_2 or evolved CO_2, according to the available standard methods.
- As there is no certified reference material available on this field of research, the newly developed system was to be adapted to measure either pulverulent test materials widely tested and accepted in interlaboratory comparison exercises or real samples in film form to assess ready biodegradability, according to local and international requirements.
- Taking into consideration the fact that there is a practical need for the study of biodegradability of samples in not only film but in other forms that can not be tested in aerated systems because of their composition or quantity, the critical comparison of non-standardised methods applicable for the assessment of biodegradation was also planned.

2. MATERIALS AND METHODS

2.1 SAMPLES

The description of the samples studied is given as follows:

- Microcristalline cellulose Avicel® PH-101 (Fluka; Buchs, Switzerland); this pulverulent material was applied as positive reference material in all studies.
- Unbleached papers with or without surface treatment: (i) “Dunasack N (DN)” paper base; (ii) “Dunasack N (DN)” paper base one-side covered with PE layer; (iii) “Dunasack N (DN)” paper base one-side covered with polylactic acid/polycaprolactone co-polymer layer. These samples were produced by “Dunapack” Paper-mill of Nyíregyháza (Hungary) according to a contract signed with the Ministry of Education in the frame of an application named “Production of environmental friendly packaging materials”. This project was also assisted by the Department of Applied Chemistry (Debrecen University), the Paper Research Institute Ltd. (Budapest) and the CFRI (Budapest) between 2000 and 2002.
- Starch (k) or aliphatic polyester (af) based foils: NF 803 (k), NF 01U (k), BF 103/51 (k), M-Bi SG 130 (k), M-Bi IP 816 (k), FARDIS (af), FARDIS /biodegradable-labelled/ (k). These foils were imported from Novamont Ltd. (Italy) by “Biopack 2001 Csomagolóanyag-gyártó és Kereskedelmi” Ltd. (Bőcs, Hungary) in the frame of an application named “Development of the technology for the production of biodegradable hard packaging materials” contracted with the Ministry of Education.

2.2 METHODS

After determining the total dry solid and carbon contents of the test materials, they were cut into smaller sized pieces according to the test method chosen and they were mixed in either compost or soil mix (both quantified and qualified previously) to assemble the following measuring set-ups:

- ***In-house developed aerated measuring system***

The development of the system in question was based on the experiences gathered in the measurement of biological activity of soils and on solid phased standardised biodegradation tests recommended by technical papers on previous interlaboratory comparisons and practical applications. On the other hand, a measuring system created by Szegi (1973) served as the most important practical background for the development of the aerated system. The original set-up had to be modified and adapted to the new application through an optimisation process carried out with the help of a reference material.

- ***BSB digi-CO_2***

The device "BSB digi" (SELUTEC GmbH, Mössingen-Öschingen, Germany) is basically an 18-chanelled respirometer intended for the determination of BOD (Biological Oxygen Demand) through the quantification of O_2 consumed. This respirometer is optionally capable to continuously detect CO_2 after the conversion of the basic device. According to the relevant literature and information from Selutec it turned out that no BOD systems had been applied in solid phase biodegradation tests before, for all that this possibility is structurally not excluded. I carried out this new application in the Department of Environmental Process Engineering, International Graduate School Zittau (Germany). After the modification, the system was optimised with a positive reference material (microcristalline cellulose Avicel) usually applied in interlaboratory tests and measurements were carried out on starch-based biodegradable foils. The samples also covered test materials developed for serving as national laboratory reference material at CFRI and some surface-treated paper samples studied previously in the in-house developed aerated system.

- ***Studies on samples embedded in compost***

One of the earliest and most obvious biodegradation tests is to monitor the weight loss and the change of total dry solids content of test materials embedded either in compost or in soil mix. This method has not been standardised, because the results derived do not usually reflect the biodegradation behaviour of test materials; however, it is still in use, especially as a screening test applied by companies developing biodegradable polymers.

Another optional method to assess the biodegradability of test materials is to determine viable cell counts (e.g. the number of starch-degrading microbes in the case of starch-based samples) responsible for degradation processes. According to the facts that (i) most of soil-derived microbes can not be quantitatively determined in laboratory circumstances, (ii) the group of microbes responsible for the degradation of a test material can not be limited to the activity of some special (countable) species, and finally, (iii) standardised methods are not focused on the examination of microbial activity, the determination of colony forming units of bacteria, yeasts, fungi, and starch-degrading microbes was carried out only during the degradation of the laboratory reference material.

3. RESULTS AND DISCUSSION

3.1 RESULTS DERIVED FROM THE MEASUREMENTS CARRIED OUT ON THE IN-HOUSE DEVELOPED AERATED SYSTEM

Optimisation of operational parameters with positive reference material

The aim of this experiment was to determine the optimal sample / compost ratio, temperature and aeration flow rate to achieve at least the critical degree of degradation of 70% of Avicel, the positive reference material usually applied in biodegradation tests. The final results were obtained as follows: (i) 2 g reference material should be mixed in 80 g compost in the incubator flasks; (ii) temperature should be set to 37°C and (iii) an aeration flow rate of 30-50 ml min^{-1} should be applied.

When working with either newly developed systems or other ones adapted for new applications, the tests carried out with the help of such reference materials may help not only to optimise operational parameters but to assess the precision and reliability of the measuring set-ups. On the other hand, the use of reference materials offers the possibility to compare the results determined by different systems.

Along with the use of a pulverised positive reference material I also made an attempt at screening for a (laboratory) reference material in film form that can be used for the assessment of biodegradability of starch-based foils. The screening was carried on commercially available products that were biodegradable-labelled by the manufacturer previously – namely, the use of a film-formed reference material would help to evaluate the results obtained by the new and non-standardised test methods emphasising to study the test material in the form it is intended to reach environment. According to my results, the foil sample named "BF 103/51" proved to be the optimal choice.

Biodegradation study of surface-treated paper samples

The aim of the surface treatment was to cover the paper sample with an environmental friendly and hydrophobic layer to replace non-biodegradable PE. To achieve this goal, a special copolymer layer developed by the Department of Applied Chemistry (Debrecen University) was applied and the biodegradability of this compound was tested together with the paper base itself. Taking into consideration that our department joined this project just during the development of the aerated measuring set-up described above, the study provided the possibility to check its sensitivity, i.e. whether the system is capable to differentiate between treated and non-treated samples by degradation curves.

The degradation of paper base was obviously hampered by the PE layer, as the final degree of degradation did not even reach 25% after the plateau phase. When testing the copolymer layered paper sample it turned out that the lag phase was extended; however, the continuously rising degradation curve observed at the end of the test period indicated the presumably better degradation potential (i.e. more access for microbiological activity) of the copolymer layered paper sample compared to the untreated paper base.

3.2 THE ADAPTATION OF THE „BSB DIGI CO_2" RESPIROMETER FOR THE ASSESSMENT OF BIODEGRADATION

The conventional BOD measurement set-up had to be modified in several parts as it was to be used in a new type of application:

- The radical change in the test medium (the usual aquatic phase replaced with solid media) went together with the need for trapping and recording higher amounts of CO_2. Since the volume of CO_2 traps (50 ml) could not be increased, the only possibility left was to increase the concentration of the inner basic solution.
- The theoretical amount of CO_2 had to be also taken into account when setting the highest allowable basic concentration. The reason behind this was the possibility of exceeding the CO_2 trapping capacity available in the case of all samples when the background CO_2 production combines with the amount of CO_2 originating from the (theoretically) totally degradable sample, especially when the sample amount is higher than 2 g. This case the replacement of the saturated traps is inevitable, making the whole measurement more difficult to handle and the evaluation more complicated. In order not to approach the saturation limit (100 mmol CO_2 at 4 mol l^{-1} KOH solution) of the traps containing 50 ml KOH each even during a longer test period, a selection process was run to find an adequate solid test medium possessing relatively low background CO_2 production, thus saving absorption capacity of CO_2 traps. According to the experiences of the German department, soil mix of good quality was chosen whose quality parameters (the amount of organic matter, pH, water content) established by the manufacturer fulfilled all requirements set up in international standard methods for the assessment of biodegradation.

Optimisation of the measurement set-up with the help of a powdered reference material

The optimisation process of the measurement set-up was focused on two input variables, namely on the temperature setting and on the amount of sample mixed in the reaction vessel. As the volume of the reaction vessels was fixed, 80 g of soil mix was introduced in each case to provide an adequate volume of head-space, according to the results provided the in-house developed aerated measuring set-up. The temperature settings of 20°C and 35°C, as well as the soil mix /sample weight ratios, were set similarly to the settings previously applied in the aerated system, i.e. the measurements on microcristalline cellulose Avicel (positive reference material) were carried out with 2 g – 4 g – 8 g of Avicel embedded in 80 g compost at 20°C and with 2 g – 4 g of Avicel embedded in 80 g compost at 35°C.

The evaluation of the measurement set-up based on the degradation curves of Avicel revealed that the system could be applied for solid phase biodegradation tests at the higher temperature setting only, because the degree of degradation exceeded the usually required 70% only the case when the experiments were carried out at 35°C with the embedding of 2 g test material. Taking into consideration that (i) soil mix was used for test medium purposes instead of compost and (ii) a still not steady-state degree of degradation of 89.3±3.2% was achieved at 35°C that totally fulfils all relevant requirements, it can be concluded that there is no point in further increasing the test temperature either for long-term operation or in the point of view of the test medium quality.

Study of real samples with the help of the modified measuring set-up

The optimised system was applied for the study of foil and paper samples. The experiment on starch-based foils mixed first in the test medium attracted the attention (i) to the importance of the careful selection of testing temperature and (ii) to the fact that the application of a reference material mismatching the form of the sample may result in false assessment on the direct applicability of the optimised working conditions of the measurement set-up. The ongoing study of paper samples proved to be important from the point of view of two aspects as it not only demonstrated perfectly the degradation process of an unquestionably compostable material in the system but highlighted the impact of the form of the test material on the final assessment: the paper sample – however definitely compostable – in film form cut into small pieces could not reach the actually required 70% limit of the degree of degradation in the measuring system that made the pulverulent Avicel degrade up to 89%.

3.3 CHARACTERISATION OF THE STUDY ON SAMPLES EMBEDDED IN COMPOST

The screening studies addressed in the dissertation were used not only for preliminary or optional examination purposes contributing to the results provided by the aerated systems, but – along with microscopic observations – played a crucial role in the assessment of biodegradation of special formed samples that can not be tested in the instrumental way. Taking into consideration (i) this analysis based on the method of comparison usually involves the examination of several samples at a time and (ii) it is focused on the selection of easily disintegrating samples possessing higher surface microbial activity, there is no point in assessing absolute biodegradability.

Notwithstanding, these – actually quite simple – measurements and results are usually de-emphasised and considered optional when testing (e.g. foil) samples easy to study in aerated systems, albeit that they may provide surprisingly useful information on biodegradability.

3.4 NEW SCIENTIFIC RESULTS (THE THESES)

1. A solid phase method easy to scale up was developed according to the relevant standards for the assessment of biodegradation by adapting and modifying a test intended for the determination of biological activity of soils. The measuring set-up was optimised with the help of a reference material usually addressed in interlaboratory comparisons and validated by reaching the required 70% limit of degree of degradation. The applicability of the system for routine analyses was proved by the measurement of real samples (e.g. starch-based foils, surface-treated paper.)

2. A BOD measuring system exclusively applied for aquatic biodegradation tests in former times was modified and adapted to carry out solid test application in laboratory scale with high precision and low uncertainty. Such an application of any BOD-systems has never been published before. The adapted measuring set-up was calibrated for the new application and its applicability for routine analyses was proved by the analyses of real samples.

3. A series of independent tests was set up for the assessment of biodegradation of special real samples that can not be tested with standardised methods. The applicability of these (often referred optional) tests was proved by analysing real samples along with standardised methods as well. The combined use of the tests in question is concerned capable to provide useful information on the biodegradability of samples without addressing standardised methods.

4. Based on an extended study presented in the dissertation, the starch-based biodegradable foil BF 103/51 (Novamont®, Italy) was selected and recommended for the role of a laboratory reference material in the assessment of biodegradation of starch-based real samples supplied in film form.

4. PRACTICAL APPLICATION OF THE METHOD DEVELOPMENT PRESENTED IN THE DISSERTATION AND POSSIBILITIES OF FURTHER INVESTIGATIONS

The in-house developed aerated measurement set-up has already been involved successfully in the assessment of biodegradation of imported biodegradable-labelled packaging materials and in the study of starch-based hard packaging materials covered with special hydrophobic layer developed at CFRI. The set-up proved to be robust, i.e. it was not affected by the installation conditions, thus it became a device easy to install at any indoor place and easy to scale up to the local needs. The precision and the uncertainty characteristics of the measurement set-up could be ameliorated principally by replacing manual titration processes by an automated titration manager. Further amelioration can be achieved by better isolation so as to decrease CO_2 loss and to increase signal/background ratio, e.g. by replacing rubber cocks holding the glass aeration tubes and closing the reaction flasks with special inserts. Background CO_2 production may be decreased by replacing traditional organic test media (compost, soil mix) with inert carriers such as vermiculite, thus enabling the calculation of carbon balance really lacked in usual solid tests. Another challenge to face is the assessment of biodegradation of samples (e.g. glues) difficult to mix in the given test media; this case, the application of an inert carrier like a piece of PTFE may serve as a base for the introduction of the sample to analyse similarly to usual ones.

The measurement set-up presented in the dissertation may become a valuable part of routine analysis after packaging materials made of the samples determined biodegradable by the set-up meet the requirements of the scaled-up disintegration tests as well – since the final goal is to assess compostability, not only biodegradability.

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