Zhang, W., Heaven, S. and Banks, C., 2018. Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste. *Polymer Degradation and Stability*. 147, 76-88
https://doi.org/10.1016/j.polymdegradstab.2017.11.005

Title: Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste

Authors: Wei Zhang, Sonia Heaven* and Charles Banks

Faculty of Engineering and the Environment, University of Southampton, Southampton SO17 1BJ, UK

*corresponding author, sh7@soton.ac.uk

Abstract

The research looked at the anaerobic biodegradation of 9 different bioplastics, all of which were commercially available and certified in Europe as compostable packaging material compliant with the biodegradation and other requirements of the EN13432 standard. A combination of testing strategies was used to assess the degree of degradation both under batch conditions, and in a simulation in which the plastics and food waste were fed daily to a digester for a period of 147 days. Two non-biodegradable plastics were used as controls, and verified the robustness of the sampling regime and the recovery of the plastic film, with errors of <1% in the final balance. The simulation allowed quantification of the weight loss of the plastics and determination of a decay coefficient for the different materials, which was then used to estimate long-term degradation. Use of a biochemical methane potential (BMP) batch test allowed estimation of the conversion of carbon into gaseous products. There was no evidence that any of the plastic films inhibited the anaerobic digestion process when continuously fed to digesters, although some inhibition occurred when the most readily degradable materials were tested at higher concentrations in batch mode. There were some interesting differences between results from the various measures of plastic degradation in the batch and simulation experiments, with batch testing in most cases suggesting a higher degree of degradation than was achieved in a semi-continuous system at a solids retention time of 50 days. The exceptions to this were two plastics that appeared to show rapid weight loss in the simulation experiment. BMP test results confirmed this was not through biological conversion of the bioplastic to gaseous carbon products, and was therefore probably due to physical disintegration. It was concluded that, of the 9 bioplastics tested, only 4 showed substantial biodegradability under anaerobic conditions. Further evidence to support the mechanism of biodegradation was obtained

by microscopy, and photomicrographs using different techniques are included to illustrate the process. Even the most degradable materials would not break down sufficiently to meet the physical contaminant criteria of the UK PAS110 specification for anaerobically digested material, if fed to a digester at 0.5% of the input load on a volatile solids basis.

Keywords

Bioplastic, anaerobic digestion, biodegradation, plastic film, food waste, co-digestion

1 Introduction

Plastic films are commonly used in food packaging as a means of protecting the food from contamination, both airborne and from manual handling; whilst at the same time allowing customers to see the contents of the package. These films may also have specific properties related to their permeability to moisture and gases, with the goal of improving the product's shelf life and its physical appearance. Other modifications include physical attributes that determine how the film can be applied and sealed. Although plastic films used in consumer-targeted food wrapping only represent a small proportion of the total plastic waste load, this fraction causes significant problems: it is particularly difficult to recover due to its non-uniform size and composition, to its presence in multi-material packaging, and to problems associated with mechanical separation in sorting plants. As a result, this material is not normally targeted by household waste segregation schemes, and is likely to be discarded in the general waste, or as a contaminant in source-segregated food waste streams. Similarly, supermarket products which are past the sell-by date are often disposed of with their packaging. It is the commercial food retailing and catering sectors that have therefore driven growth in the development and use of biodegradable biopolymers (Meeks et al., 2015) as companies seek to meet sustainability goals.

The difficulty in recycling plastic films is compounded by the fact that they often consist of several layers of different compositions; when used in food packaging they are frequently contaminated with residual food; and they are commonly found as small-format items in heterogeneous recycling streams (World Economic Forum and the Ellen MacArthur Foundation, 2017). To overcome these challenges there has been considerable interest in developing biodegradable films designed for disposal via composting or anaerobic digestion. These plastics, generally referred to as 'bioplastics', can be produced from conventional petrochemicals or from renewable biological resources; in the latter case they are termed bio-based plastics. Bio-based plastics can be synthesised from bio-based

chemical building blocks, e.g. lactic or succinic acids; through modification of natural polymers, such as starch, cellulose or chitin; or through fermentation to produce microbial polymers such as polyhydroxyalkanoates.

Anaerobic digestion is becoming increasingly popular as a means of processing food waste for energy and fertiliser recovery. The inclusion of biodegradable catering films, food wraps and card packaging in the feedstock stream would simplify collection and processing, and eliminate the need for a depackaging stage when the input materials include supermarket wastes and other packaged food materials. It is now recognised that the biodegradability of plastic films is dependent on process conditions, with significant differences reported between aerobic and anaerobic systems (Ishigaki et al., 2004; Cho et al., 2011; Mohee et al., 2008; Massardier-Nageotte et al., 2006). There are also disparities between methods for assessing biodegradability, leading to questions as to whether batch testing methods can adequately predict what will happen under real operating conditions in a full-scale bioprocessing plant (Castro-Aguirre et al., 2017).

Biodegradation of packaging materials via composting is covered by European standard EN13432 (2000) which stipulates the requirements for packaging recoverable through composting and biodegradation: the standard requires testing in accordance with EN14046 (2003) for carbon conversion to CO_2, and in accordance with EN14045 (2003) to show visual disappearance. The US ASTM standard D5338-15 (2015) covers the aerobic biodegradation of plastic materials under controlled composting conditions at thermophilic temperatures, and is based on carbon conversion to CO_2. Oxidative degradation is defined by CEN/TR1535 (2006) as degradation resulting from oxidative and cell-mediated phenomena, either simultaneously or successively. It applies to conventional plastics that contain additives to speed up oxidative degradation. Oxo-degradable materials do not conform to the EN13432 and ASTM D5338-15 standards, and are not considered compatible with composting processes. Anaerobic biodegradability of plastic materials is covered by ASTM D5511-12 (2012) and by ISO 13975 (2012), ISO 14853 (2016) and ISO 15985 (2014). All of these consider conversion of carbon in the sample to a gaseous form in batch tests, and thus do not necessarily represent degradation behaviour in continuous systems over extended periods where accumulation, leaching and/or acclimatisation may occur. These tests have a number of other limitations related to the types of inoculum used, the mixing conditions and the operational temperature and do not allow consideration of interaction with any co-substrates.

The aim of the research was to assess the extent to which selected bioplastic films were broken

down under anaerobic conditions in a mesophilic digester treating food waste. In addition to the bioplastics, card packaging was added as part of the digester feedstock, to simulate the case where a biodegradable composite packaging is co-digested with food residues in a bio-treatment process. The feedstock in the trial was formulated to contain food waste, card packaging and bioplastic at volatile solids (VS) ratios of 80:18:2 based on a likely composition for segregated waste streams arising either from homes, or from supermarkets if biodegradable packaging is included at source. The nine bioplastics used in the study had all been certified as compliant with the composting standard EN13432, and were therefore recognised as biodegradable in bio-based waste treatment processes in the EU. Their anaerobic biodegradability, biogas production potential and whether the resulting digestate would meet relevant quality standards for use in agriculture had not previously been tested. A simulation trial was chosen in preference to batch testing, as this allows acclimatisation of the inoculum; it also offers less stringent conditions, since co-digestion provides the primary carbon source as well as potentially increasing the supply of 'metabolic' co-factors that may be important in stimulating and promoting biodegradation. The drawback of this type of simulation is that it is difficult to quantify carbon conversion from the polymer alone into a gaseous form: this is recognised as the definitive means of assessing ultimate biodegradation, as opposed to primary biodegradation where the material is no longer detectable by the original analytical approach but may not have been fully mineralised. Testing of ultimate biodegradability is therefore typically carried out in batch assays although, as with aerobic testing, care is required to ensure comparability of results from different methods (Castro-Aguirre et al., 2017). To complement the results from a continuous co-digestion trial, where degradation was assessed by gravimetric methods, a batch degradation study was therefore carried out in which production of biogas and biomethane from the polymer was quantified in a biochemical methane potential (BMP) test, and compared with the theoretical value based on substrate elemental composition. A number of variants of the BMP test are available to simulate different conditions (Holliger et al., 2016): the technique has frequently been used for assessment of degradation, and forms the basis for the now-numerous batch testing strategies that have been proposed specifically for assessing the anaerobic degradation of plastic polymers. The results of the study were intended to provide comparative information on the degradation of selected biopolymers under anaerobic conditions, and to inform stakeholders on whether anaerobic digestion (AD) is a suitable treatment method for a waste stream containing packaged food material that includes carton and renewable plastic film. Although previous studies have considered the biodegradation of plastic polymers under anaerobic conditions in landfill (Abou-Zeid et al., 2001; Adamcoya and Vaverkova, 2014; Boonmee et al., 2016), and numerous batch digestion tests have been carried out (Gartiser et al., 1998; Shah 2008; Yagi et al., 2009; Cremonez et al., 2016), this is the

first reported study on degradation kinetics in a co-digestion study with feed addition and removal designed to simulate practice in a commercial AD plant.

2 Materials and Methods

2.1 Feedstock components

Bioplastics. These were provided by the manufacturers, and had been certified as EN13432 compliant by an independent body after testing in an accredited laboratory, issued with packaging product certification numbers and awarded the right to carry the scheme's certification logo. They were tested alongside non-biodegradable controls of an uncoated polypropylene (PP) film and a plain low density polyethylene (LDPE) film. All of the bioplastics were in sheet form, with the exception of a Polylactic Acid Blend (PLAB) in pelleted form. Each sheet material was measured and weighed and then accurately cut into 1 x 1 cm squares ('tokens'), the average weight of which is shown in Table 1. PLAB was used as supplied, with the average dimensions and weight of each pellet as shown in Table 1.

Food waste. To be certain of avoiding contamination with non-targeted plastic films, the trial used a synthetic food waste (SFW), formulated as described in the supplementary material, using food materials purchased in a supermarket. All packaging was removed and the materials were roughly chopped and fed through a macerating grinder (S52/010 Waste Disposer, Imperial Machine Company (IMC) Limited), then packed in 4-litre containers and stored at -20 ^{o}C. When required the SFW was allowed to thaw, stored in a refrigerator and used within 7 days.

Card packaging. To avoid any potential contamination from plastic films, unprinted card (GK unlined grey machine board 70-100% recycled fibre with bulk 1.4 cm^3 g^{-1}) was obtained from A Stevens & Co Ltd Yeovil, Somerset and shredded in an office-type cross-cut paper shredder to a particle size of ~2 cm^2. The card packaging (CP) was then macerated with water, frozen and stored until use as above.

2.2 Anaerobic Digestion trials

Anaerobic digesters. 12 digesters were used, each with a working volume of 4 L. The digesters were constructed of PVC tube with gas-tight top and bottom plates. The top plate was fitted with a gas outlet, a feed port sealed with a rubber bung, and a draught tube liquid seal through which an

asymmetric bar stirrer was inserted with a 40 rpm motor mounted directly on the top plate. Temperature was controlled at 37 ^{o}C by circulating water from a thermostatically-controlled bath through a heating coil around the digesters. Semi-continuous operation was achieved by daily removal of digestate through an outlet in the base of each digester, followed by substrate addition via the feed port. Biogas production was measured using tipping-bucket gas counters with continuous data logging. Counter calibration was checked twice weekly by collecting the gas produced over a 24-hour period in a gas-impermeable sampling bag (SKC Ltd, Dorset, UK). Gas volumes were determined using a weight-type water displacement gasometer, and corrected to standard temperature and pressure of 101.325 kPa and 0 ^{o}C in accordance with Walker *et al*. (2009).

Inoculation and pre-acclimatisation. The inoculum used was from a 75-L digester which had previously been fed for more than 300 days at an organic loading rate (OLR) of 2 kg VS m^{-3} day^{-1} on a mixture of source segregated post-consumer domestic food waste and card packaging at a ratio of 80:20% on a fresh weight basis (Zhang et al., 2012). The 75-L digester was then maintained at 36 ^{o}C without feed addition for one month to allow any undigested feed to be consumed. The resulting digestate was sieved through a 1 mm mesh to remove any plastic film, then 4 L was added to each digester. The digesters were then pre-acclimatised by feeding them for 30 days on SFW+CP.

Digester operation. After pre-acclimatisation, each digester was fed at an OLR of 2 kg VS m^{-3} day^{-1} for 147 days on a feedstock made up of 80% SFW, 18% CP and 2% of a specified bioplastic on a VS basis. This was prepared by weighing out 23.0 g of SFW and 6.2 g of CP, and adding the appropriate number of bioplastic tokens (Table 1). The solids retention time (SRT) in the digester was maintained at 50 days by removing 560 g of digestate once per week via the bottom sampling tube, while continuing to mix the vessel. Solid and liquid fractions were separated by passing the digestate through a 1 mm stainless steel mesh sieve. The solids were retained for examination, and the amount of the liquid fraction needed to restore a working volume of 4 L after feeding was returned to the digester. Feeding with the specified plastic began on the first day after acclimatisation (day 0), apart from PLAB and the control LDPE where plastic addition started on days 7 and 27 respectively: in each case the expected number of tokens taking into account daily additions and theoretical weekly losses was added to these two digesters to compensate for the delayed start.

2.4 Sampling

Plastic tokens were recovered from the digestate using a modified version of CEN/TC BT 151 (2007).

The stage of drying followed by dry sieving was omitted, as oven drying caused some deformation of the tokens. In the modified procedure the fraction retained on the sieve was washed with tap water and tokens were recovered by hand. These were then air dried for 3 to 4 days, counted and weighed. Tokens were noted as being approximately full sized, half or quarter size.

During the first 7 weeks of operation it became clear that the expected quantities of tokens were not being found in the digestate in all cases, probably due to certain tokens either floating or sinking depending on their density. To overcome this, the sampling method was modified from day 42 onwards and involved emptying the entire contents of the digester into a wide-mouthed receptacle, and removing the 560 g subsample while agitating thoroughly to ensure that all materials were in suspension. Immediately after removal of this sub-sample the remaining digestate was returned to the digester, and separated liquor added as before to maintain the working volume.

At the end of the trial each digester was emptied and its entire contents were passed through a 1 mm stainless steel mesh sieve. The solids fraction was washed and the tokens retrieved by hand sorting, then air dried, counted and weighed as previously described.

2.5 Biochemical methane potential

The biochemical methane potential (BMP) of the feedstocks was measured using 1.5-L working volume digesters continuously stirred at 40 rpm, and maintained in a thermostatic water bath at a temperature of 37 ^{o}C. Inoculum was taken from a mesophilic digester treating municipal wastewater biosolids at Millbrook Wastewater Treatment Plant, Southampton, UK. Tests were run in triplicate at an inoculum-to-substrate VS ratio of 4:1, against triplicate blanks containing inoculum only, and triplicate positive controls of alpha cellulose (Sigma Ltd, UK). Biogas was collected in calibrated glass cylinders by displacement of a 75% saturated sodium chloride solution acidified to pH 2. The height of the solution in the collection cylinder was recorded manually, with continuous data logging by a headspace pressure sensor as back-up. Gas compositions were measured each time the cylinder was refilled, and gas volumes were corrected to STP as above.

2.6 Analysis

Total solids (TS) and volatile solids (VS) were measured according to Standard Method 2540 G (APHA, 2005). Digestate pH was measured using a combination glass electrode and meter calibrated in

buffers at pH 4, 7 and 9. Alkalinity was measured by titration with 0.25 N H_2SO_4 to endpoints of pH 5.75 and 4.3, to allow calculation of total (TA), partial (PA) and intermediate alkalinity (IA) (Ripley et al., 1986). Total Kjeldahl Nitrogen (TKN) and total ammonia nitrogen (TAN) were determined using a Kjeltech digestion block and steam distillation unit, according to the manufacturer's instructions (Foss Ltd, Warrington, UK). VFA were quantified in a Shimazdu GC-2010 gas chromatograph (GC) with a flame ionisation detector and a capillary column type SGE BP-21. Calorific values (CV) were measured using a bomb calorimeter (CAL2k-ECO, South Africa). Elemental composition (C, H, N) was determined using a FlashEA 1112 Elemental Analyser (Thermo Finnigan, Italy), following the manufacturer's standard procedures. Biogas composition was measured using a Varian CP 3800 GC fitted with a Hayesep C column and a molecular sieve 13 x (80-100 mesh), and calibrated using a standard gas of 65% CH_4 and 35% CO_2 (v/v). Feedstock carbohydrate content was determined using the method of Dubois et al. (1956). Lipids were measured in accordance with US EPA SW-846 (1998), and fibre analysis was by the Fibercap method (Kitcherside et al., 2000).

Examination of samples by light microscopy was kindly performed by Prof Francisco Torrella of the University of Murcia, with confocal microscopy carried out at the University of Southampton's Imaging and Microscopy Centre (www.southampton.ac.uk/microscopy).

2.7 Assessment of the mass balance of plastic materials

As the number of tokens and the weight of plastic added daily to the digester was accurately known, the expected number and weight of tokens in the 560 g of digestate removed weekly could be estimated based on simple wash-out principles. This was done assuming either no degradation, or a first-order relationship where degradation is proportional to the weight of tokens present. The theoretical results were then compared to the actual number and weight of tokens recovered. The ratio of post-digestion weight to initial weight (the 'weight ratio') based on the number of tokens recovered was also determined. This ratio is closely related to solids destruction, but is based on the air-dried weight of the material rather than its VS content, and provides some additional information on the mode of degradation.

Recovery, counting and weighing of all of the tokens remaining at the end of the experiment enabled a mass balance to be conducted for each type of plastic over the duration of the trial. The final weight values were then used to obtain the empirical first-order decay constant for each plastic and an estimate of solids disappearance or destruction.

3 Results

3.1 Materials characteristics

Characteristics of the plastic materials are shown in Table 2. The theoretical elemental composition of both PP and LDPE is C 85.7%, H 14.3%, N 0% with a calculated calorific value of 43.86 MJ kg^{-1} TS, indicating good agreement between measured and theoretical results.

Table 3 shows the characteristics of the SFW and CP. The results for SFW were compared to typical values for three UK post-consumer source segregated domestic food waste streams (Yirong et al., 2015) and found to be very similar. The SFW contained slightly more carbohydrate and less fibre (average values for typical domestic food wastes 430 and 173 g kg^{-1} VS, respectively). The TS and VS of the SFW were slightly higher (typical domestic food waste values 24.4 and 23.3%). These small differences reflect the fact that the SFW was formulated from fresh materials, and thus contains a higher proportion of the edible components normally consumed by the customer, and proportionately less of the fractions that are typically rejected into the domestic waste stream. The properties of the CP were closely similar to those of post-consumer card packaging used in previous work (Zhang et al., 2012).

3.2 Digestion performance and stability indicators

A notable feature of the trial was that all of the digesters behaved in a similar manner, with only small differences in values for each monitoring parameter (Figure 1). pH in all digesters stabilised between 7.7 and 7.9. TAN concentrations gradually increased, but remained < 3.5 g N L^{-1} at the end of the trial (Figure 1a), below the concentration at which ammonia is considered toxic to a mesophilic methanogenic population (Schnurer et al., 2008). Total alkalinity increased with increasing TAN (Figure 1b) and around day 100 equilibrated at 25 g L^{-1} $CaCO_3$, indicating a well-buffered system; the IA/PA ratio stabilised at an average of 0.38 in all digesters. VFA concentrations were low throughout, with values in the later part of the trial around 100 mg L^{-1} (Figure 1c). These results indicated that, as expected, none of the plastics tested showed adverse effects on the acid-base balance or the operational stability of the digesters.

Volumetric biogas production (VBP) was consistent from around day 50 (Figure 1d) at around 1.4 L L^{-1}

day^{-1}, typical for this OLR and feedstock type. The biogas methane content stabilised at around 56% in all digesters from day 105 onwards. Specific methane production was around 0.400 m^3 CH_4 kg VS added (Figure 2e), again a typical value for the feed material used (Zhang et al., 2012).

The TS and VS of the whole digestate and of the solids fraction could not be measured on a weekly basis, due to the need to recover the plastic tokens. The digestate liquor VS remained constant at around 3.8 %WW (Figure 1f), however, while the wet weight of digestate solids removed each week fluctuated slightly, averaging around 13 %WW (Figure 1g). These parameters indicate that stable operation was achieved, and that the separation technique used was able to produce consistent values.

It can be concluded that the digesters showed stable performance throughout the experimental period, with a high level of conversion of feedstock VS to methane. The semi-continuous experiment was not designed to quantify additional gas production from biodegradation of the bioplastics, as at the low loadings applied the expected yield was of the same order as natural variation in overall biogas production.

3.3 Assessment of plastics destruction in co-digestion trial

3.3.1 Evidence from recovery of tokens

Figure 2 shows the number of tokens recovered each week compared to the predicted number assuming no decay. For plastics showing evidence of degradation, the number predicted using the empirically-derived first-order decay constant is also shown.

During the first 7 weeks of operation it became clear that in some cases there were discrepancies between the actual and expected number of tokens found in the digestate, probably due to tokens of certain materials either floating or sinking depending on their density. This was particularly noticeable for PP, LDPE, SBF1, CDF and PLAB. The revised sampling technique was able to prevent or reduce these irregularities, and where appropriate the actual number and weight of tokens remaining in the digester was used in modelling up to day 42.

For the PP control the subsequent recovery matched the modified theoretical prediction (Figure 2a), but in the case of LDPE the fit of observed and theoretical values was less good. The reason for this

was that, even when the digester contents were drained completely, a proportion of the LDPE tokens remained attached to the digester walls and stirrer; these were eventually accounted for in the final mass balance. The model for LDPE was therefore adjusted to reduce the number of tokens leaving the digester in the weekly digestate sample to 65% of the expected value, with the rest remaining in the digester. This empirical adjustment showed good agreement with the actual partitioning of tokens in both LDPE digesters (Figures 2b and c).

For plastics denser than the digestate liquor, until the sampling regime was changed there was a tendency to recover more tokens than predicted: this was the case for SBF1, PLAB and CDF, as can be seen in Figures 2d, e and f. For SBF1 and PLAB this was successfully addressed by modifying the sampling regime, and using the actual number of tokens recovered until the change was introduced. In the case of apparently degradable plastics such as CDF, however, no correction could be made, as part of the difference in token numbers could also be attributed to the breakdown of the material. The results of the mass balance at the end were therefore required to confirm whether the losses were due to degradation, as discussed below.

The results shown in Figure 2g-j indicated that all four of the cellulose-based films (CBM, CBHS, CBHB and CBnHS) were degraded, but to different degrees, with almost complete disappearance of the CBnHSF film. PLAF and CDF also showed a lower number of tokens than predicted (Figure 2k and l). After correcting for the sampling error up to day 42, however, the plastics SBF2, SBF1, and PLAB appeared to show little or no destruction in the AD process.

3.3.2 Evidence from weight of recovered plastic tokens and the weight ratio

Figure 3 shows the weight of tokens recovered from each digestate sample, the predicted weight based on actual number of tokens recovered and using the empirically-derived first order decay constant, and the ratio between these. As the weight ratio considers both the number and the weight of tokens displaced from the digester, it provides a useful insight into the mechanism of degradation of the plastic tokens.

After adjustment for the change in sampling methodology, there was good agreement between the calculated weights assuming no degradation and the actual weight of tokens recovered for both of the LDPE controls (Figure 3a and b) and the PP control (Figure 3c). The weight ratio for these two materials was above 1.0, indicating that these plastics may be absorbing small amounts of some

component in the digestate. The two starch-based plastics SBF1 and SBF2 also showed little or no evidence of degradation based on weight loss and weight ratio (Figure 3d and e): for SBF1 the ratio stabilised at 0.94 and for SBF2 at 1.0. The PLAF and PLAB plastics (Figure 3f and g) had very similar weight ratios, close to 1.0; but the high weight ratio and low number of tokens recovered for the PLAF suggested that the material was breaking up quite rapidly in the digester.

The most readily degraded plastic was CBnHS (Figure 3h), which showed a weight ratio of around 0.3-0.4. For CBHB (Figure 3i) the ratio was between 0.6-0.7, while the other two cellulose-based film products CBM and CBHS (Figures 3j and k) the ratio was between 0.7-0.8. These results indicate that individual tokens of cellulose film materials lose weight before disappearance or removal from the system. The CDF had a weight ratio of around 0.78, similar to that of the less degradable cellulose-based plastics.

3.3.3 Final balances and parameters from modelling

Table 4 shows the results of the final balance based on the number and weight of tokens added, removed, and present in each digester at the end of the trial. The balance between number of tokens input and finally accounted was -64 (0.7%) and +6 (0.1%) respectively for the PP and LDPE controls, confirming the accuracy of the method used.

The value of the empirical first-order decay constant for each of the bioplastics was taken as that giving the best match to the actual total weight recovered in each case. This value was then used to predict the weight of tokens removed during the run and remaining in the digester at the end. The recovery values shown in Table 4 are calculated from the weight of tokens actually removed or remaining in the digester at the end of the run, divided by the predicted weight and expressed as a percentage. The percentage recovery indicates whether the tokens were evenly distributed throughout the digestate when samples were removed. It can be seen that PP, CBM and PLAB were relatively evenly distributed (predicted recovery during run and end is 100 ± 10% of actual); whereas the uneven partitioning seen with LDPE (recovery 80% during run, 137.7% at end) also affected CBHS (89.1% and 128.5%), CBHB (74.3% and 164.9%), CBnHS (62% and 206.1%) and PLAF (67.3% and 182.6%), and to a lesser extent CDF, SBF1 and SBF2 (predicted recovery = 100 ± 20% of actual).

The empirical first-order decay constant was also used to predict the total number of tokens recovered. The values for the control plastics, SBF1, SBF2, PLAF and PLAB show good agreement

whereas for CBM, CBHS, CBHB, CBnHS and CDF the actual number recovered is considerably higher than the predicted number. This reflects the fact that the tokens lose weight as they degrade, but still remain as visible components, posing a potential problem with regard to acceptability of the digestate as a commercial product.

The weight of each material destroyed provides a basis for estimating the plastics destruction during the experiment. A further estimate of destruction was obtained by modelling the system beyond the experimental period, using first-order decay kinetics, to allow steady state conditions to be established: the difference between the input weight and predicted weight of tokens removed each week can then be used as an estimate of solids destruction potential. Table 4 shows that there was reasonable agreement between values obtained using these two methods. Differences can be attributed to several factors, one being that the simple first-order decay model assumed may not be fully adequate to describe the degradation, especially for complex multi-layer materials. The results suggested that SBF2 is not breaking down; PLAB may show slight degradation, but it is at the limit of detectability by this method; while SBF1 has a small but definite weight loss. The slight weight gain of the control plastics is also confirmed.

3.3.4 Physical status of the plastics

The recovered tokens were visually inspected. The two control plastics showed only small changes. PP showed no sign of decay or damage but tended to curl into small cylinders (Figure 4a) making counting difficult; the plastic also took on a yellowish colour, indicating absorption of some component from the digestate, which may also have accounted for the slight weight gain. LDPE showed relatively little change in shape or colour. The PLAB pellets also showed little sign of change apart from a very slight darkening in colour. Colour changes to degradable plastics have previously been reported in samples placed in landfill sites under anaerobic conditions, even though no other physical changes were noted (Adamcova and Vaverkoya, 2014)

The four cellulose-based film plastics showed different responses. CBM tokens gradually lost their metal layer and the remaining fragments appeared to become progressively smaller and more fragile, ending as a clear colourless thin film (Figure 4b). CBHS took up colour from the digestate evenly throughout the material. In CBHB the surface of the plastic showed clear signs of progressive attack at specific points, indicated by discoloured areas on the surface and around the cut edges (Figure 4c). The small number of tokens of CBnHS recovered showed little sign of damage, but

changed from a clear plastic with a shiny surface to a slightly milky semi-translucent appearance. These degradation modes reflected the material structure and components: CBnHS consists of a simple uni-layer cellulose film that is highly permeable to water vapour. CBHS has a heat-sealable layer on each surface, providing a moisture barrier; while CBM also has a metallised layer on one surface, giving improved moisture resistance. CBHB has the highest specification of moisture barrier and heat seal on both sides, making it resistant to attack until this coating is penetrated.

SBF1 and SBF2 both showed slight changes in colour, with some deformation of SBF1 tokens (Figure 4d). Signs of damage could be seen on individual tokens of both plastics, corresponding to either biodegradation or mechanical damage. PLAF and to a lesser extent CDF showed little change in appearance, remaining shiny and regular in shape, but small numbers of fragments and part-tokens were observed. When this observation is considered in conjunction with the weight data and with microscopic observations and the BMP test results, it appears likely that any tokens of PLAF and CDF found in the digestate may have been in the digester for relatively short periods; and that these materials were not biodegraded to single-carbon gaseous products, but showed rapid physical disintegration in the digester. This behaviour of PLA film materials has been previously reported under anaerobic conditions (Boonmee et al., 2016) and in composting (Arrieta et al., 2014a), and these films can be manufactured in such a way as to accelerate or retard this disintegration (Arrieta et al., 2014b).

Images of all of the plastics materials removed from the digesters on day 98 are shown in the supplementary materials (Figure S2).

3.3.5 Microscopic examination

Four of the plastics were selected for preliminary microscopic examination based on their apparent degradation characteristics. Samples were taken from the washed and air-dried material removed from the digestate, with no special measures taken to preserve microbial films. The tokens were examined using a stereoscopic microscope with surface illumination and a high power oil immersion lens with phase contrast and transmitted light. The surface of CBnHS was found to be extensively pitted and perforated in places, accounting for its loss of shine (Figure 5a). Under high power oil immersion there was evidence of bacterial colony growth at the bottom of each pit. CBHS had much more dispersed surface pitting, with pits of a larger diameter. In this case there were clear signs of the growth of rod-shaped bacteria around the immediate edge of the pit and extending into it

(Figure 5b). CBM was only observed with surface illumination, as its opacity made it unsuitable for the use of oil immersion and transmitted light; but the metal layer could be seen to be leaching away (Figure 5c). On examination of PLAF, sharp fracture lines were noted around the edges of smaller tokens, and the entire surface showed signs of crazing which was not evident in undigested material. In the sample examined no evidence of surface pitting or bacterial colonisation was seen under oil immersion and transmitted light. The CBHS was also briefly examined using fluorescent confocal microscopy: again it was possible to identify colonies of bacteria within the pitted areas, and to observe that these were within the interior cellulose layer (Figure 5d). These preliminary investigations suggest confocal microscopy is a promising technique that could help to elucidate the mechanisms and constraints on the degradation process. (See also Supplementary materials for additional images).

3.4.1 Energy balances

The BMP test is the most commonly used method for assessing the bioconversion of a substrate to methane. Methane and carbon dioxide production in the test can be compared to the theoretical methane potential calculated using the Buswell equation (Symons and Buswell, 1933), and the carbon conversion in the test material can therefore be accounted. This batch test provides favourable conditions with a guaranteed retention time which eliminates any of the 'short circuiting' that may occur in continuous systems; and also uses a high inoculum-to-substrate ratio to maximize the degradation of the sample and its conversion into gaseous end products, while reducing the potential for accumulation of inhibitory intermediate compounds. Even under these conditions the BMP value is generally lower than the theoretical methane potential, as a proportion of the carbon is converted into new biomass. The batch test hence gives a measure of the potential methane yield of the test substrate under anaerobic conditions: this value, however, is often higher than can be obtained in a fully-mixed, continuously-fed digester. The batch BMP test format is the basis for the various anaerobic biodegradability tests that have evolved to take into account different operating temperatures, types of inoculum and duration of exposure (e.g. ISO 13975 (2012), ISO 14853 (2016), ISO 15985 (2014)). In this work BMP testing took place over a period of 65 days (Table 5 – see Supplementary materials for more detailed results), at which time the rate of methane production in most samples had slowed to that of the inoculum-only control. Elemental composition data (Table 2) was used in the Buswell and Du Long equations (IFRF, 2001) to predict the calorific value (CV). The CV of dried material was also measured and used to supplement the BMP test results to confirm degradation through carbon conversion to methane. The results of these analyses were compared

using a mass balance approach (Table 5).

Measured and calculated calorific values were in reasonably good agreement, giving support to the accuracy of the elemental composition analysis. The recovery of energy in the form of methane from the four cellulose-based films (CBM, CBHS, CBHB and CBnHS) ranged from 75 to 86% of the energy potential based on the measured higher heat values, confirming the excellent degradation of these materials under the wet mesophilic test conditions used. The theoretical VS destruction during the 65-day BMP test was calculated from the actual methane yield, the carbon content of the substrate, and the methane and carbon dioxide concentrations predicted by the Buswell equation (Table 5). For the cellulose-based film plastics, the calculated solids destructions were slightly higher than expected based on the values from the semi-continuous trial (Table 3), suggesting that the measured carbon content may have been slightly low. The actual specific methane yields for CBHS, CBHB and CBnHS, however, showed very good agreement with the Buswell predictions of 0.438, 0.410 and 0.423 m^3 CH_4 kg^{-1} VS respectively, and indicated a high degree of biodegradability.

The energy recovery from PLAB (2.6%) was very close to the values for the two control plastics PP and LDPE (1.9 and 1.4% respectively), again indicating that PLAB pellets show little or no degradation in these conditions. The four remaining plastics CDF, SBF1, SBF2 and PLAF showed energy recovery values ranging from 8.9-18.8%, suggesting only partial degradation. The BMP tests for PLAB, CDF, SBF1, SBF2 and PLAF were left running until day 103. With the exception of PLAF there was little or no change in the final methane yield. PLAF continued to produce methane at a higher rate than in the first 50 days, possibly indicating that some acclimatisation to the substrate had occurred. By day 103 it had produced a further 0.119 m^3 CH_4 kg^{-1} VS added, giving a total of 0.216 m^3 CH_4 kg^{-1} VS, with good agreement between replicates. Yagi et al. (2014) also noted a long slow increase in biodegradability assessed in terms of methane yield during mesophilic batch testing of PLA powder over 277 days.

Based on the specific methane yields shown in Table 5, the bioplastic component might produce a maximum of 2% of the total specific methane production from a mixed feedstock of food waste, card packaging and bioplastic at 80:18:2 %VS as used in the current trial. This estimate is based on CBHS, the bioplastic with the highest BMP value, with the other bioplastics giving correspondingly lower contributions. The contribution of a given bioplastic to the total specific methane production is likely to be even lower if the solids retention time in the digester is less than that required for full degradation of the bioplastic.

3.5 Factors affecting digestate standard compliance

Worldwide there are a number of standards for the use of bioprocessed waste materials in agriculture and horticulture, but the UK has adopted separate specifications for aerobically and anaerobically processed materials. The UK's PAS110 Specification for anaerobic digestates (BSI, 2010) contains criteria for pathogen content, Potentially Toxic Elements (PTE), stability and physical contaminants, and was used as a reference in this work. In a mixed food waste, card packaging and plastic feedstock with the plastics present only in small quantities, these parameters are strongly influenced by the composition of the other components. As the current trial used a synthetic food waste and selected print-free card packaging, the contribution from the plastics was considered only in so far as it might affect the overall results, using a mass balance approach.

A number of other parameters such as pH, total nitrogen (N), total phosphorus (P), total potassium (K), TAN, and TS and VS are also reportable under PAS110 as they may influence digestate application rates, but have no limit values. These again are chiefly determined by the SFW and CP components of the feedstock: relevant values for the digestate pH, TAN and solids in the current trial are as seen in Figure 1.

PAS110 specifies that physical contaminants must not exceed a given proportion of the wet weight of digestate, with the proportion increasing as the digestate nitrogen concentration increases: the logic behind this is that land spreading is often limited by nitrogen load, and hence the amount of contaminant applied per unit area of land area should be the same at a given load. The plastics destruction estimated from modelling was used in conjunction with the permitted mass of physical contaminants to calculate the maximum allowable amount of each bioplastic in the feedstock. For this calculation the VS destruction of the incoming SFW was taken as 86% (experimental data - not shown), and the expected weight of digestate arising from 1 tonne of input feed was thus between 741-746 kg depending on the solids destruction for each of the bioplastics. The results are plotted in Figure 6. This example is illustrative for the conditions used in this study, as in practice the result will depend on the TS and VS of the specific incoming feed, and its VS destruction. With the 2% bioplastic VS load used in this study and the digestate TKN content of around 9 kg N $tonne^{-1}$ WW, none of the digestates would comply with the physical contaminant criteria of the PAS110 specification. With regard to these criteria, the apparent disappearance of the plastic is of more importance than whether it in fact undergoes ultimate biodegradation to gaseous products, and the approach

developed in the current work thus provides an appropriate testing methodology.

Information on the PTE criterion is provided in Supplementary materials: at the bioplastics loading required to comply with the physical contaminants specification, calculation showed that the bioplastic materials could not cause the digestate to exceed the specified limit values for PTE. The results of digestate stability testing are also provided in the Supplementary materials.

4 Discussion

The results clearly demonstrated differences in biodegradability under aerobic and anaerobic conditions: all of the bioplastics tested had been certified under the EN13432 composting standard, yet four of them converted less than 20% of their carbon into biomethane. As expected, it was not possible to quantify additional biomethane production as a result of bioplastic addition in the semi-continuous digestion trial, even where a high degree of degradation was observed, as the relative proportion of gas production from the bioplastics is low in comparison to that from the SFW+CP mixture: this is inevitable unless a much higher plastics loading is used than is likely to occur in a real mixed foodwaste stream. All of the digesters performed well during the semi-continuous trial, showing stable operation based on typical process assessment criteria, with biomethane production in the expected range for this type of substrate. It was therefore clear that none of the bioplastics caused any inhibition of the process at the loading rates used.

The extent of degradation was assessed using a number of criteria, and a summary comparison of these is given in Table 6. While these are not like-with-like comparisons, they do offer some useful insights. CBnHS and CBM showed consistently high values for all four measures applied, although the calorific recovery for CBnHS was slightly lower than the other values. CBHB and CBHS showed lower degradation in the semi-continuous test. Unfortunately the BMP tests for these materials showed some initial inhibition, possibly as a result of rapid acid production from readily degradable components, making it difficult to assess and compare degradation kinetics; but the degradation rates in the batch BMP tests appeared lower for these materials. These results are also reflected in the modelled degradation constants for each plastic (Table 4), where CBnHS has the highest value or 0.39 followed by CBM, CBHS and CBHB at 0.10, 0.06 and 0.04, respectively. There are now a number of ISO standards that use carbon conversion as a basis for assessing the ultimate biodegradation of plastic polymers under anaerobic conditions. These are each tailored to specific conditions that reflect different operating modes and types of digester, and are therefore not necessarily

interchangeable. The results from the BMP tests in the current study confirmed whether carbon conversion had occurred, and thus indicated which of the test samples were anaerobically biodegradable. In some cases, however, the rates of degradation were lower than those observed in the semi-continuous trial. This difference provides an indication of the potential limitations of batch tests, which may be subject to partial inhibition due to inappropriate inoculum-to-substrate ratios, and may be too short to benefit from adaptive acclimatisation. They are therefore suitable for assessing whether a material is readily biodegradable, but do not necessarily reveal any long-term changes in the system biology that may affect its capability and capacity for ultimate degradation.

The results for CDF, SBF1, SBF2 and PLA provided an interesting contrast to the cellulose-based film plastics. CDF and PLA both showed significant weight loss in the semi-continuous trial (59.0 and 57.5% respectively), but relatively low methane production in the 65-day BMP test (respectively 8.9 and 18.8% calorific recovery as CH_4). The results strongly suggest that the polymeric structure of the PLA and CDF is rapidly destroyed under anaerobic conditions, to an extent where the physical form is no longer recognizable; but this transformation is initially without biodegradation of any macro-molecular subunits. This view was also supported by preliminary microscopic examination of PLA. It is therefore possible to have a relatively high proportion of these materials present in a feedstock without failing the PAS110 physical contaminants criterion, but with little or no energy recovery or ultimate degradation occurring in the system. The nature and long-term stability of the macromolecular components needs further assessment in light of the current concerns over the so-called oxo-degradables, which break down into microplastics and may be highly damaging if they find their way into the environment (Thompson, 2013). Although the PLA did slowly degrade under anaerobic conditions in the BMP test, the CDF showed only a very small apparent conversion into gaseous products; the nature of its disintegration products was not investigated in the current work. Both of the starch-based polymers SBF1 and SBF2 showed low physical breakdown in the simulation experiment (7.9 and 2.1% respectively), despite a proportionately higher gas yield in the 65-day BMP test (18.8 and 10.2% calorific recovery as CH_4). The performance of PLAB on all four parameters in Table 6 was consistent and very close to that of the controls, confirming that for practical purposes no degradation is occurring under wet mesophilic anaerobic conditions. This probably reflects the fact that PLAB is a PLA-based material with a fairly low rate of breakdown, and unlike the other plastics it was in pellet form. The specific surface areas for PLAF and PLAB were calculated as ~54 and ~1.5 $mm^2\ g^{-1}$ respectively, indicating the much lower potential for microbial attack on PLAB. Yagi et al. (2013, 2014) reported relatively high degradation rates in batch tests with PLA powder (125-250 μm), especially in thermophilic conditions.

The results obtained have interesting implications for the choice of digester operating mode. The semi-continuous trial was run at a 50-day SRT, with the liquid separated and returned to the digester. This is a fairly common operating mode at commercial scale, but does not favour plastics that require a long retention time for degradation. A system operating at the very long 'natural' retention times that are possible for food waste digestion without liquid recycle might show better breakdown of plastics such as CBHB, PLAF and SBF1, by keeping them in the digester for longer and thus allowing them to achieve a higher degree of degradation. The higher methane yield achieved in the 103-day BMP test for PLAF supports this view. For the SFW used in this trial, for example, the 'natural' retention time based on feedstock addition without digestate separation and solids removal at an OLR of 2 g VS L^{-1} day^{-1} would be 139 days; the addition of dry card packaging would increase this considerably, due to its high solids content.

The results for partitioning of plastic tokens between the digestate sample and the digester are unlikely to scale up directly, but are of interest as similar behaviour will occur in an industrial plant. This means the location of the outlet and the mode of digester mixing may have a considerable effect on plastic retention: for less dense plastics, digesters with a low-level outlet may have a longer retention time while those regulated by a high-level weir may lose material more rapidly, and vice versa for denser plastics.

The advantage of the semi-continuous methodology used is that it replicates some aspects of behaviour in full-scale operational digesters which are not seen in batch tests, and provides information on the degradation behaviour with respect to standards for visual contaminants. It does not provide robust values for the specific methane yield and ultimate biodegradability of a given bioplastic, and batch tests are preferable for this purpose.

5 Conclusions

The method developed to assess the extent of degradation of bioplastic film material under anaerobic conditions with daily feed additions and digestate removal was successful in quantifying

the rates and allowing estimation of decay coefficients, which were further used to model the likely long-term destruction. Of the nine bioplastics tested only the four cellulose-based materials showed extensive biodegradation in the static BMP assay. This verified that both polylactic acid film (PLAF) and cellulose diacetate film (CDF), which were shown to be removed in the simulation trials, were initially disrupted but not degraded; it was likely that only the PLAF showed biodegradation over a longer period. None of the bioplastics inhibited or destabilised the digestion process, which ran for 177 days in total and provided some useful insights into issues relating to the physical properties of the plastic materials that are likely to affect the behaviour of full-scale systems. Although the digestion trial was run with a solids retention time of 50 days, the degree of breakdown of even the most biodegradable of the polymers tested was unlikely to meet more stringent environmental requirements for the exclusion of physical contaminants, such as those specified in the UK PASS110 for digestate utilisation. Observation of the films using light and confocal microscopy clearly showed the mechanisms of attack, and these could be related to the properties and degradation behavior of each of the materials tested.

Acknowledgements

The work was commissioned and funded through The National Non-Food Crops Centre (www.nnfcc.co.uk). The authors are very grateful to Prof Francisco Torrella of the University of Murcia and Dr Yue Zhang of the University of Southampton for provision of microscopic images.

References

Abou-Zeid, D.M., Müller, R.J. and Deckwer, W.D., 2001. Degradation of natural and synthetic polyesters under anaerobic conditions. Journal of Biotechnology, 86(2), 113-126.

Adamcová, D. and Vaverková, M.D., 2014. Degradation of biodegradable/degradable plastics in municipal solid waste landfill. Pol. J. Environ. Stud, 23(4), 1071-1078.

APHA, 2005. Standard Methods for the Examination of Water and Wastewater. 21st edition, American Public Health Association, American Water Works Association, Water Environment Federation.

Arrieta, M.P., Fortunati, E., Dominici, F., Rayón, E., López, J. and Kenny, J.M., 2014b. PLA-PHB/cellulose based films: mechanical, barrier and disintegration properties. Polymer Degradation and Stability, 107, 139-149.

Arrieta, M.P., López, J., Rayón, E. and Jiménez, A., 2014a. Disintegrability under composting conditions of plasticized PLA–PHB blends. Polymer Degradation and Stability, 108, 307-318.

ASTM D5338-15, 2015. Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures.

American Society for Testing and Materials. Available https://www.astm.org/Standards/D5338.htm, last accessed April 2017.

ASTM D55511-12, 2012. Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions. American Society for Testing and Materials. Available https://www.astm.org/Standards/D5338.htm, last accessed April 2017.

Boonmee, C., Kositanont, C. and Leejarkpai, T., 2016. Degradation of Poly (lactic acid) under Simulated Landfill Conditions. *Environment and Natural Resources Journal, 14*(2), 1-9.

BSI, 2010. PAS110:2010 *Publicly Available Specification: Specification for whole digestate, separated liquor and separated fibre derived from the anaerobic digestion of source-segregated biodegradable materials*. British Standards Institution, UK.

Castro-Aguirre, E., Auras, R., Selke, S., Rubino, M. and Marsh, T., 2017. Insights on the aerobic biodegradation of polymers by analysis of evolved carbon dioxide in simulated composting conditions. Polymer Degradation and Stability, 137, 251-271.

CEN/TC BT 151 WI, 2007. Soil, sludge and treated biowaste – Determination of impurities and stones. Impurities 2007-03-12(E) STD Version 2.1c. European Committee for Standardisation. Available https://standards.cen.eu, last accessed April 2017.

CEN/TR 15351, 2006. Plastics – Guide for Vocabulary in the Field of Degradable and Biodegradable Polymers and Plastic Items, European Committee for Standardisation. Available https://standards.cen.eu, last accessed April 2017.

Cho, H.S., Moon, H.S., Kim, M., Nam, K. and Kim, J.Y., 2011. Biodegradability and biodegradation rate of poly (caprolactone)-starch blend and poly (butylene succinate) biodegradable polymer under aerobic and anaerobic environment. Waste Management, 31(3), 475-480.

Cremonez, P.A., Teleken, J.G., Feiden, A., Rossi, E.D., de Souza, S.M., Teleken, J., Dieter, J. and Antonelli, J., 2016. Anaerobic digestion of cassava starch-based organic polymer. Revista de Ciências Agrárias (Portugal), 39(1), 122-133.

Dubois, M., Gilles, K. A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric method for determination of sugars and related substances. Analytical Chemistry 28(3), 350-356.

EN 13432 (2000) Packaging - Requirements for packaging recoverable through composting and biodegradation - Test scheme and evaluation criteria for the final acceptance of packaging. European Committee for Standardisation. Available https://standards.cen.eu, last accessed April 2017.

EN 14046 (2003) Packaging - Evaluation of the disintegration of packaging materials in practical oriented tests under defined composting conditions. European Committee for Standardisation. Available https://standards.cen.eu, last accessed April 2017.

EN 14046 (2003) Packaging - Evaluation of the ultimate aerobic biodegradability and disintegration of packaging materials under controlled composting conditions. Method by analysis of released carbon dioxide. European Committee for Standardisation. Available https://standards.cen.eu, last accessed April 2017.

Gartiser, S., Wallrabenstein, M. and Stiene, G., 1998. Assessment of several test methods for the determination of the anaerobic biodegradability of polymers. Journal of environmental polymer degradation, 6(3), 159-173.

Holliger, C., Alves, M., Andrade, D., Angelidaki, I., Astals, S., Baier, U., Bougrier, C., Buffière, P., Carballa, M., de Wilde, V. and Ebertseder, F., 2016. Towards a standardization of biomethane potential tests. Water Science and Technology, 74(11), 2515-2522.

IFRF, 2001. International Flame Research Foundation *Online Combustion Handbook* ISSN 1607-9116 (Method from Combustion File 24)

Ishigaki, T., Sugano, W., Nakanishi, A., Tateda, M., Ike, M. and Fujita, M., 2004. The degradability of biodegradable plastics in aerobic and anaerobic waste landfill model reactors. Chemosphere, 54(3), 225-233.

ISO 14853 (2016) Plastics -- Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system -- Method by measurement of biogas production. International Organization for Standardization. Available www.iso.org/standard/67804.html, last accessed July 2017.

ISO 15985 (2014) Plastics -- Determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic-digestion conditions -- Method by analysis of released biogas. International Organization for Standardization. Available www.iso.org/obp/ui/fr/#iso:std:63366, last accessed July 2017.

ISO 13975 (2012) Plastics -- Determination of the ultimate anaerobic biodegradation of plastic materials in controlled slurry digestion systems -- Method by measurement of biogas production. International Organization for Standardization. Available www.iso.org/standard/54396.html, last accessed July 2017.

Kitcherside, M.A., Glen, E.F., Webster, A.J.F., 2000. FibreCap: an improved method for the rapid analysis of fibre in feeding stuffs. Animal Feed Science and Technology 86, 125-132.

Massardier-Nageotte, V., Pestre, C., Cruard-Pradet, T. and Bayard, R., 2006. Aerobic and anaerobic biodegradability of polymer films and physico-chemical characterization. Polymer Degradation and Stability, 91(3), 620-627.

Meeks, D., Hottle, T., Bilec, M.M. and Landis, A.E., 2015. Compostable biopolymer use in the real world: Stakeholder interviews to better understand the motivations and realities of use and

disposal in the US. Resources, Conservation and Recycling, 105, 134-142.

Mohee, R., Unmar, G.D., Mudhoo, A. and Khadoo, P., 2008. Biodegradability of biodegradable/degradable plastic materials under aerobic and anaerobic conditions. Waste Management, 28(9), 1624-1629.

Ripley, L.E., Boyle, W.C., Converse, J.C., 1986. Improved alkalimetric monitoring for anaerobic digestion of high strength wastes. Journal of the Water Pollution Control Federation 58, 406-411.

Schnürer, A. and Nordberg, A., 2008. Ammonia, a selective agent for methane production by syntrophic acetate oxidation at mesophilic temperature. Water Science and Technology, 57(5), 735-740.

Shah, A.A., Hasan, F., Hameed, A. and Ahmed, S., 2008. Biological degradation of plastics: a comprehensive review. Biotechnology Advances, 26(3), 246-265.

Symons, G.E., Buswell, A.M., 1933. The methane fermentation of carbohydrates. Journal of the American Chemical Society 55, 2028-2036.

Thompson, R., 2013. Plastics, Environment, and Health. In Gabrys, J., Hawkins, G. and Michael, M. (Eds.), *Accumulation: The Material Politics of Plastic.* Routledge, London.

US EPA SW-846 (1998). Method 9071B: n-hexane extractable material (HEM) for sludge, sediment, and solid samples. Test methods for evaluating solid waste, physical/chemical Methods.

Walker, M., Zhang, Y., Heaven, S. and Banks, C., 2009. Potential errors in the quantitative evaluation of biogas production in anaerobic digestion processes. Bioresource Technology, 100(24), 6339-6346.

Yagi, H., Ninomiya, F., Funabashi, M. and Kunioka, M., 2009. Anaerobic biodegradation tests of poly (lactic acid) under mesophilic and thermophilic conditions using a new evaluation system for methane fermentation in anaerobic sludge. International Journal of Molecular Sciences, 10(9), 3824-3835.

Yagi, H., Ninomiya, F., Funabashi, M. and Kunioka, M., 2013. Thermophilic anaerobic biodegradation test and analysis of eubacteria involved in anaerobic biodegradation of four specified biodegradable polyesters. Polymer Degradation and Stability, 98(6), 1182-1187.

Yagi, H., Ninomiya, F., Funabashi, M. and Kunioka, M., 2014. Mesophilic anaerobic biodegradation test and analysis of eubacteria and archaea involved in anaerobic biodegradation of four specified biodegradable polyesters. Polymer Degradation and Stability, 110, 278-283.

Yirong, C., Heaven, S. and Banks, C.J., 2015. Effect of a trace element addition strategy on volatile fatty acid accumulation in thermophilic anaerobic digestion of food waste. Waste and Biomass Valorization, 6(1), 1-12.

Zhang, Y., Banks C.J. and Heaven S., 2012. Co-digestion of source segregated domestic food waste to improve process stability. *Bioresource Technology*, 114, 168-178.

Table 1 Plastic materials used in trial

	Abbreviation	Average weight (mg)	No. of tokens in daily feed [a]
		10 x 10 mm square	
Polypropylene film	PP	2.61	61
Low density polyethylene film	LDPE	5.14	31
Cellulose-based metallised film	CBM	3.42	54
Cellulose-based heat-sealable film	CBHS	4.28	43
Cellulose-based high barrier heat-sealable film	CBHB	6.68	27
Cellulose-based non heat-sealable film	CBnHS	6.24	30
Cellulose diacetate film	CDF	6.50	26
Starch-based film blend 1	SBF1	2.17	76
Starch-based film blend 2	SBF2	4.29	38
Polylactic Acid Film	PLAF	3.71	43
		Pellet	
Polylactic Acid Blend	PLAB	24.7	7

[a] No. of tokens fed to each digester in semi-continuous trial (duplicate digesters used for LDPE).

Table 2 Characteristics of the plastic materials

	TS	**VS**	**Calorific value**	**C**	**H**	**N**
	%WW [a]	%WW	MJ kg^{-1} TS	%VS	%VS	%VS
PP	99.7	99.7	46.61	85.46	14.92	0.00
LDPE	100.0	99.8	46.56	84.78	15.22	0.00
CBM	87.5	86.7	17.85	47.09	5.49	2.54
CBHS	87.4	87.1	17.83	47.60	5.70	0.00
CBHB	90.1	89.8	17.18	44.56	6.22	2.12
CBnHS	85.9	85.6	18.15	47.03	5.56	1.34
CDF	95.3	95.0	20.14	52.32	5.31	0.00
SBF1	97.6	97.6	22.16	60.01	6.59	0.00
SBF2	97.0	97.0	24.20	60.74	6.97	0.00
PLAF	99.6	99.5	18.35	51.21	5.49	0.00
PLAB	99.7	94.6	22.87	57.44	6.30	0.00

[a] WW = wet weight

Table 3 Characteristics of SFW and CP

	Units	SFW	CP
pH		4.78	-
Total solids (TS)	%WW	29.8	29.1
Volatile solids (VS)	%WW	27.9	23.2
VS as %TS	%TS	95.5	79.8
Total Kjeldahl nitrogen (TKN)	g kg^{-1} VS	28.6	1.46
Calorific value (CV)	MJ kg^{-1} TS	21.57	14.34
Crude proteins	g kg^{-1} VS	179	-
Lipids	g kg^{-1} VS	143	-
Carbohydrates	g kg^{-1} VS	631	-
Hemicellulose	g kg^{-1} VS	86	-
Cellulose	g kg^{-1} VS	7.4	-
Lignin	g kg^{-1} VS	20	-
Elemental C	%VS	54.09	43.64
Elemental H	%VS	7.19	5.70
Elemental N	%VS	2.84	0.0

Table 4 Final balance results based on no. and weight of tokens and experimentally determined values for degradation constants

	PP	LDPE	CBM	CBHS	CBHB	CBnHS	CDF	SBF1	SBF2	PLAF	PLAB
No. of tokens added	8906	4293	7884	6278	3942	4380	3796	11096	5548	6278	999
Actual no. of tokens in digester at end	3137	2256	565	918	1038	286	671	3638	1992	1327	320
Actual no. of tokens removed in run	5705	2043	1540	1826	1230	320	1261	7082	3337	1274	655
Predicted total no. of tokens recovered [a]	8906	4293	1721	2141	1679	289	1556	10227	5436	2670	969
Actual total no. of tokens recovered	8842	4299	2104	2743	2268	606	1932	10720	5329	2601	975
Balance (no. at end + no. out – no. in)	-64	6	-5780	-3535	-1675	-3774	-1864	-376	-219	-3678	-24
No. of tokens destroyed	0.7%	-0.1%	73.3%	56.3%	42.5%	86.2%	49.1%	3.4%	3.9%	58.6%	2.4%
Weight added (g)	23.29	22.06	26.97	26.89	26.34	27.32	24.68	24.05	23.78	23.31	24.69
Predicted weight in digester at end (g) [a]	7.93	7.88	1.59	2.55	3.18	0.47	2.86	6.90	7.60	2.81	7.36
Actual weight in digester at end (g)	8.56	10.85	1.67	3.28	5.25	0.98	3.40	7.64	8.69	5.13	7.86
Recovery at end	107.9%	137.7%	104.7%	128.5%	164.9%	206.1%	119.0%	110.8%	114.3%	182.6%	106.8%
Predicted weight removed in run (g) [a]	15.35	14.19	4.29	6.62	8.04	1.33	7.26	15.24	15.70	7.10	16.58
Actual weight removed in run (g)	15.51	11.38	4.22	5.90	5.97	0.82	6.71	14.50	14.60	4.78	16.08
Recovery in run	101.0%	80.2%	98.3%	89.1%	74.3%	62.0%	92.5%	95.2%	93.0%	67.3%	97.0%
Actual total weight recovered (g) [b]	24.08	22.23	5.89	9.17	11.22	1.80	10.12	22.14	23.29	9.91	23.93
Balance (end + out – in)	0.79	0.16	-21.09	-17.72	-15.12	-25.52	-14.57	-1.91	-0.49	-13.40	-0.76
Weight destroyed	-3.4%	-0.7%	78.2%	65.9%	57.4%	93.4%	59.0%	7.9%	2.1%	57.5%	3.1%
1^{st}-order degradation k	0.00	0.00	0.10	0.06	0.04	0.39	0.04	0.00	0.00	0.04	0.00
VS destruction potential [c]	0.0%	0.0%	82.7%	72.3%	64.7%	94.9%	66.2%	12.4%	2.9%	64.8%	6.2%

[a] Based on 1st-order degradation coefficient

[b] Actual total weight recovered = Actual weight in digester at end + Actual weight removed in run

[c] Based on value from longer-term modelling with 1st-order degradation coefficient

Table 5 Energy balance value of materials

	Empirical formula				Theoretical CH_4 content of biogas (Buswell)	Calculated CV	Measured CV	Actual CH_4 yield in 65-day BMP test	Recovery as CH_4 in 65-day BMP test	% Recovery of measured CV	Calculated solids destruction
	C mole	H mole	O mole	N mole	%	MJ kg^{-1} VS	MJ kg^{-1} VS	m^3 CH_4 kg^{-1} VS	MJ kg^{-1} VS	%	%
PP	7.12	14.80	-0.02	0.00	76.1	44.40	46.68	0.025	0.89	1.9	2.0
LDPE	7.06	15.10	0.00	0.00	76.7	44.43	46.58	0.018	0.64	1.4	1.5
CBM	3.92	5.44	2.81	0.18	47.7	17.39	18.03	0.374	13.40	74.3	88.9
CBHS	3.96	5.65	2.92	0.00	49.4	17.44	17.90	0.433	15.50	86.6	98.3
CBHB	3.71	6.17	2.94	0.15	49.4	17.04	17.23	0.404	14.48	84.0	98.0
CBnHS	3.92	5.52	2.88	0.10	48.3	17.26	18.28	0.410	14.69	80.4	96.4
CDF	4.36	5.26	2.65	0.00	49.9	19.08	20.20	0.050	1.80	8.9	10.3
SBF1	5.00	6.53	2.09	0.00	55.9	23.89	22.20	0.113	4.05	18.3	18.0
SBF2	5.06	6.91	2.02	0.00	57.1	24.64	24.22	0.069	2.46	10.2	10.6
PLAF	4.26	5.44	2.71	0.00	50.1	18.80	18.39	0.097	3.47	18.8	20.2
PLAB	4.78	6.25	2.27	0.00	54.5	22.44	24.09	0.017	0.62	2.6	3.0
Card packaging (CP)	3.63	5.65	3.17	0.00	47.7	15.70	14.34	0.274	9.81	68.4	70.3
Foodwaste (SFW)	4.50	7.13	2.24	0.20	55.6	22.42	22.59	0.471	16.89	74.8	83.7

Table 6 Comparison between different measures of plastics degradation from semi-continuous, BMP and analytical tests

% destruction or recovery values based on:	Semi-continuous		65-day BMP	
	Measured mass balance at end of run [a]	Long-term modelled value [b]	Carbon balance [b]	Calorific recovery [b]
PP	-3.4	0.0	2.0	1.9
LDPE	-0.7	0.0	1.5	1.4
CBM	78.2	82.8	88.9	74.3
CBHS	65.9	72.1	98.3	86.6
CBHB	57.4	64.7	98.0	84.0
CBnHS	93.4	94.9	96.4	80.4
CDF	59.0	66.4	10.3	8.9
SBF1	7.9	12.4	18.0	18.3
SBF2	2.1	2.7	10.6	10.2
PLAF	57.5	64.7	20.2	18.8
PLAB	3.1	6.2	3.0	2.6

[a] see Table 4; [b] see Table 5

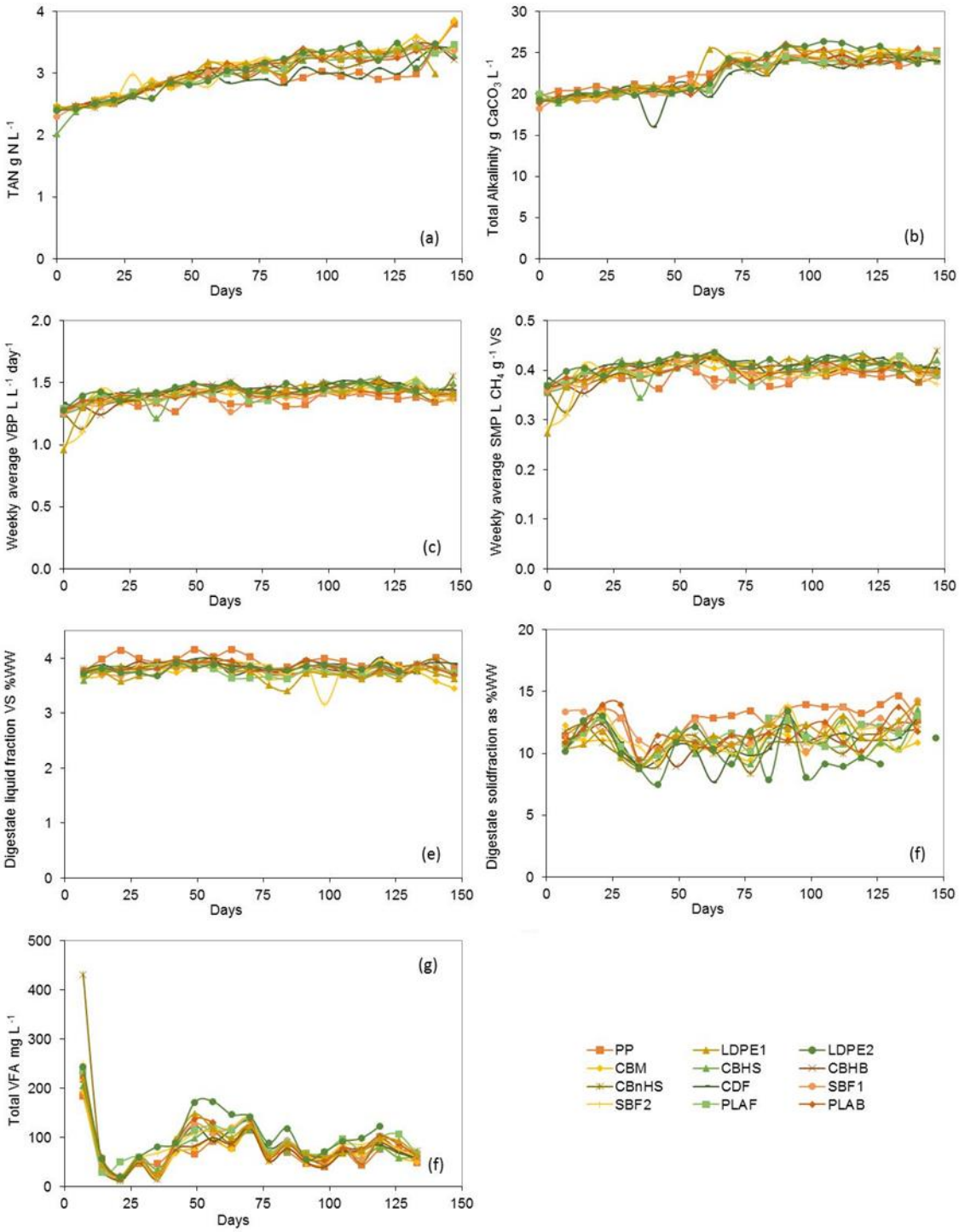

Figure 1 Digester monitoring parameters during the experimental period: (a) TAN, (b) Total Alkalinity, (c) total VFA, (d) volumetric biogas production, (e) specific methane production, (f) digestate VS and (g) wet weight of digestate solids

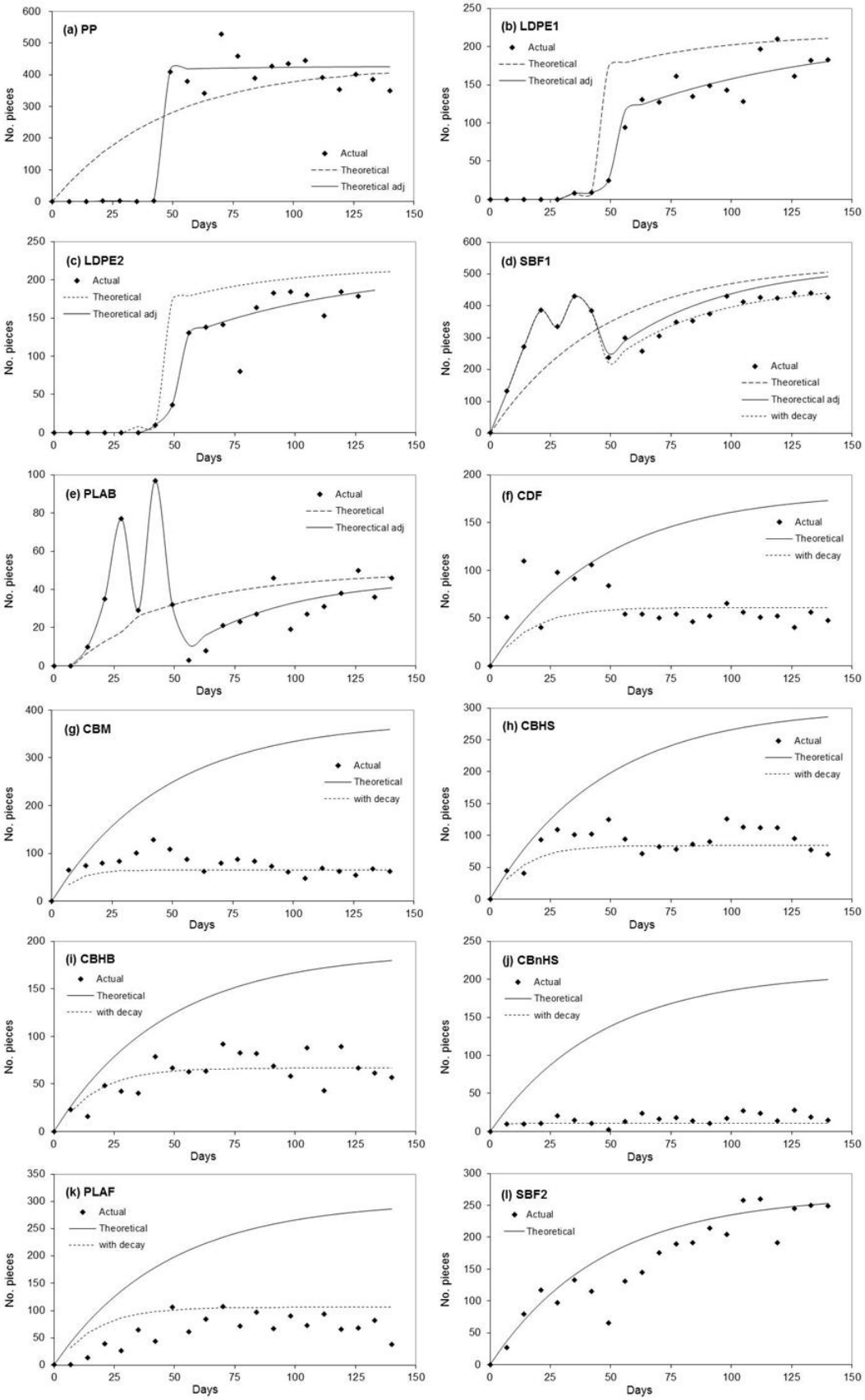

Figure 2 No. of plastic tokens recovered from digestate sample, predicted no. assuming no destruction, and predicted no. modelled using an empirical first-order decay coefficient for (a) PP, (b) LDPE1, (c) LDPE2, (d) SBF1, (e) PLAB, (f) CDF, (g) CBM, (h) CBHS, (i) CBHB, (j) CBnHS, (k) PLAF, (l) SBF2.

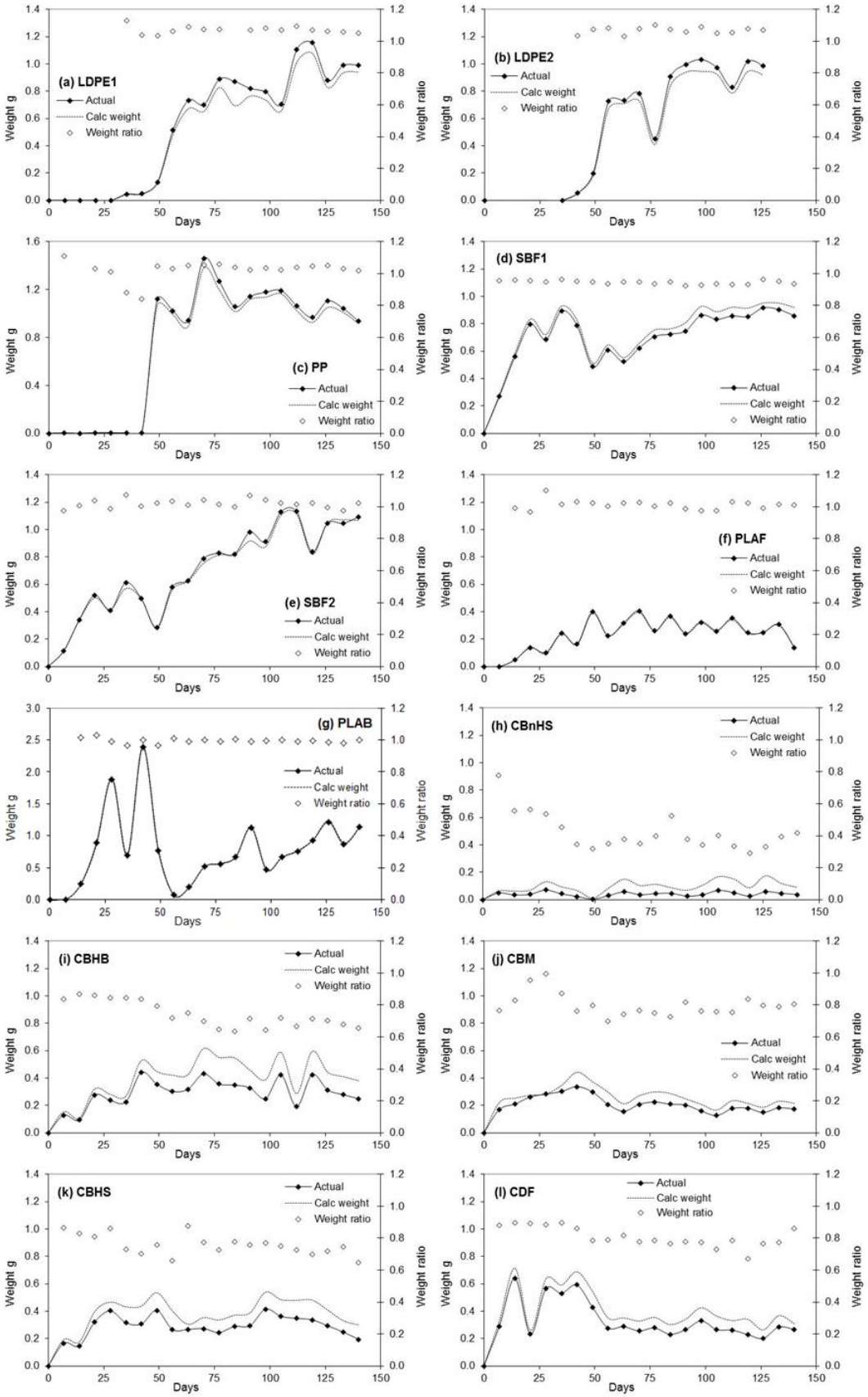

Figure 3 Weight of plastic tokens recovered from each digestate sample, predicted weight based on actual number of tokens recovered, and ratio between these values, for (a) LDPE1, (b) LDPE2, (c) PP, (d) SBF1, (e) SBF2, (f) PLAF, (g) PLAB, (h) CBnHS, (i) CBHB, (j) CBM, (k) CBHS and (l) CDF.

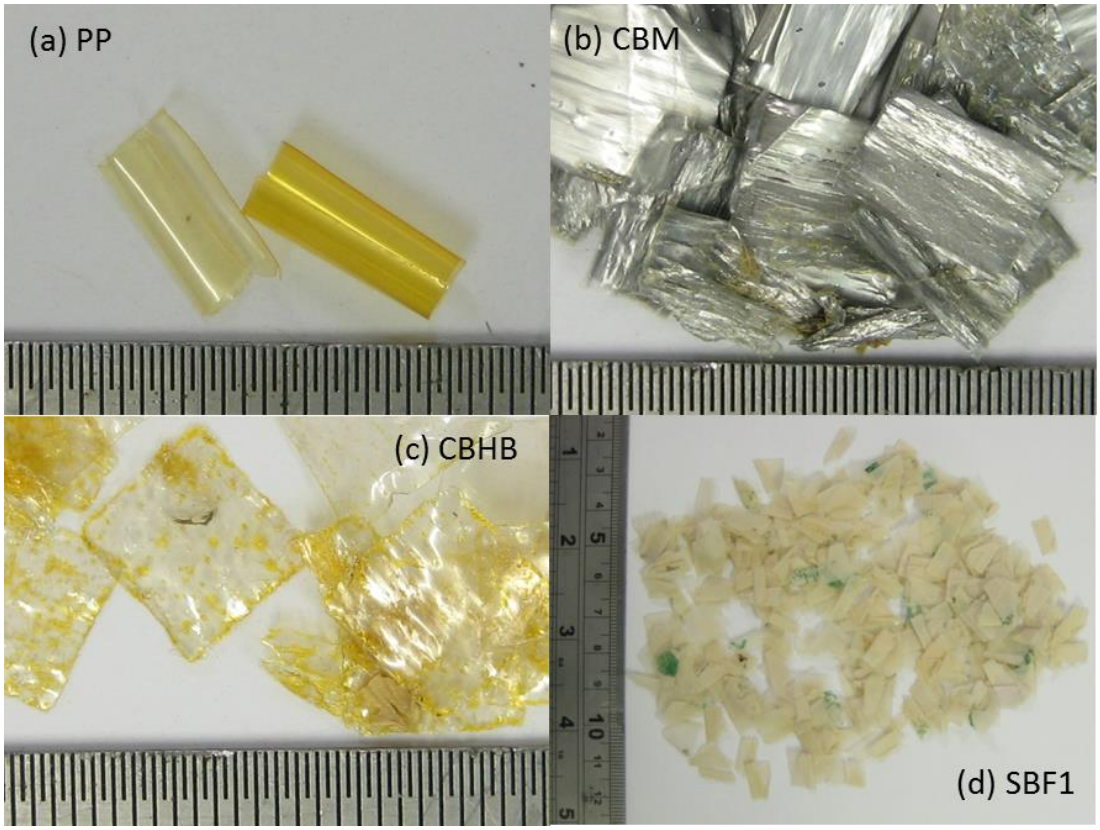

Figure 4 Photographic images of selected examples of plastics removed in digestate on day 98: (a) PP, (b) CBM, (c) CBHB, (d) SBF1

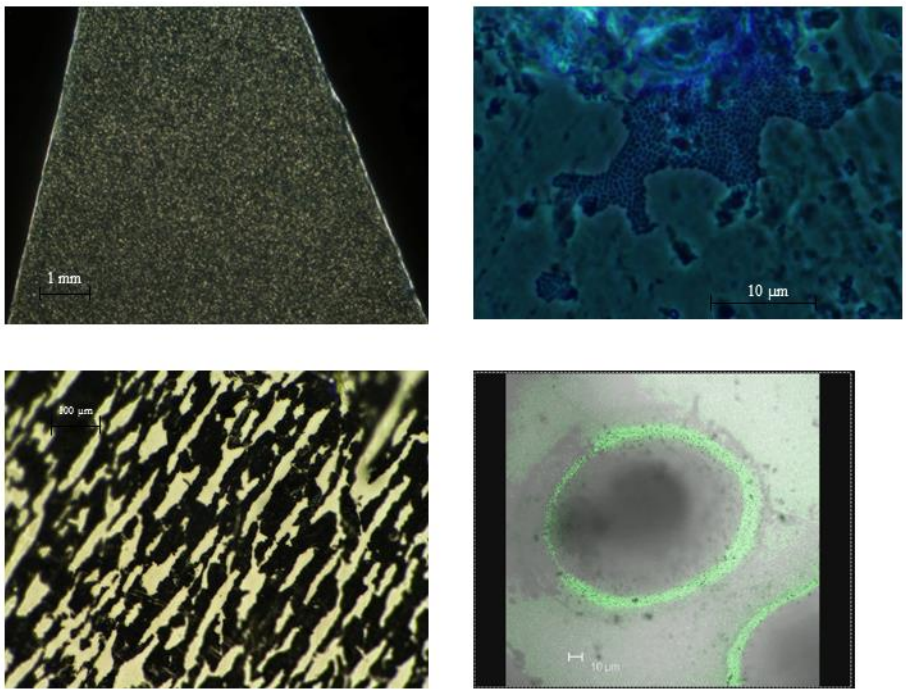

Figure 5 Microscopy images (a) Dark field image of CBnHS showing heavily pitted surface; (b) bright field image of stained CBHS showing microbial colony at edge of pit; (c) bright field image of CBM showing loss of metallic layer; (d) CBHS Combined fluorescent and differential interference contrast images showing microbial presence around pit, using a Leica TCS SP2 confocal laser scanning microscope. Images (a), (b) and (c) courtesy of Prof Francisco Torrella, University of Murcia. Image (d) courtesy of Dr Yue Zhang, University of Southampton

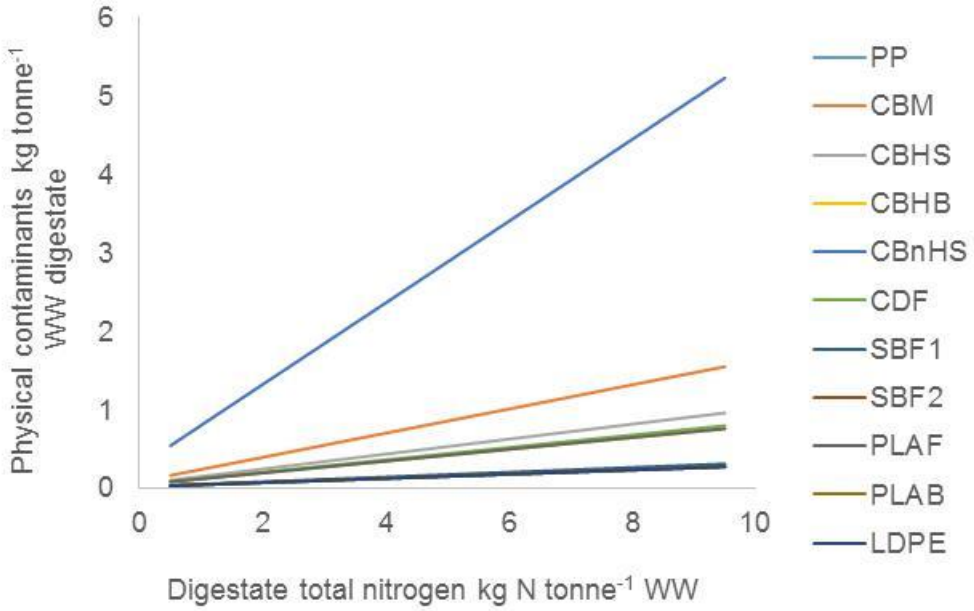

Figure 6 Permissible plastic load for a given nitrogen content in the digester based on modelled bioplastic destruction rates in Table 4.