

Degradation Studies of β -Cyclodextrin Polyurethane Polymers using Soil Burial Experiments

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ABSTRACT

Degradation studies of β -cyclodextrin polymers cross-linked with toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI) were carried out by exposing the polymers to different soil types for up to 120 days. The aim of the study was to determine the fate of these novel polymers in the environment. The polymers were either digested with sulphuric acid prior to performing a soil burial test or buried undigested. Results from the study indicate that the β -CD/TDI polymers with aromatic links underwent a greater mass loss during soil burial when first digested in sulphuric acid (ca. 50 % maximum mass loss). The β -CD/HMDI polymers, on the other hand, underwent the same mass loss for both the digested and undigested polymers (ca. 30 % maximum mass loss). Although the Fourier transform infrared (FTIR) spectroscopy data suggested no changes in the overall polymer structures, the scanning electron microscopy (SEM) micrographs revealed changes in the surface morphology of the polymers. Moreover, results of thermogravimetric analysis (TGA) point to polymer degradation under all conditions tested.

KEYWORDS

Degradation, cyclodextrin polyurethanes, scanning electron microscopy, soil burial test, microorganisms.

1. Introduction

Cyclodextrins (CDs) and CD-polymers have been widely used in the pharmaceutical, food and water industries because of their ability to form inclusion complexes.¹ Highly cross-linked β -cyclodextrin polyurethane polymers have been synthesized in our laboratories by polymerizing the cyclodextrin moiety with suitable bifunctional diisocyanate monomers such as hexamethylene diisocyanate (HMDI) and 2,4-toluene diisocyanate (TDI).² After characterization, these water-insoluble polymers were tested for their ability to extract a variety of organic pollutants from water and were found to remove these pollutants efficiently from water to parts-per-billion (ppb) levels. This technology has since been utilized in the removal of geosmin and 2-methylisoborneol from a Rand Water Treatment Plant.³ Additionally, cyclodextrins polymerized with carbon nanotubes were used for the extraction of trichloroethylene (TCE) from water.⁴ It is noteworthy that these polymers can be recycled many times and reused; they have been tested up to 25 cycles with minimal loss in performance.⁵ While we have successfully demonstrated the utilization of β -CD-polymers in the removal of organic contaminants from water, it is also crucial that the same polymers, once they have been used, should be disposed of in an environmentally safe way. Therefore, a need exists to determine the eventual fate of the polymers in the environment. Owing to the rise in global environmental awareness and waste management concerns, it is important to study the biodegradability of these CD-polyurethane polymers.

A biodegradable polymer undergoes significant chemical and physical changes under specific conditions.⁶ Polymers can be degraded by exposure to sunlight (photo-oxidation), microorganisms (bacteria and fungi), chemicals and macroorganisms (invertebrates and insects). Bacteria and fungi that reside in the soil produce enzymes that assist them in breaking down

complicated non-living material (e.g. polymers) into simple compounds, notably organic acids. These organic acids (also called volatile fatty acids) serve as food for the microorganisms, which convert the acids into carbon dioxide, methane, water and mineral salts.⁷ Microbial digestion will undoubtedly lead to a significant change in the chemical structure of the exposed material. When the polymer is extraordinarily resistant to environmental stresses such as heat, light and ultraviolet (UV) radiation, chemical pre-treatment is essential in overcoming this stability. Inorganic acids are usually employed in the chemical degradation of the polymers. This is achieved by simply exposing the polymer to aggressive acid solutions for varying periods (up to 12 weeks). Alternatively, the polymer is pre-digested with the inorganic acid prior to microbial digestion in the soil.⁸

In order to achieve maximum degradation, environmental conditions such as ambient temperature, the presence of nutrient material and humidity are essential.^{9,10} Biodegradation studies are normally carried out in complex biological environments (e.g. soil, sewage and compost) that have a large number and variety of microorganisms.⁷ The American Standard Testing Method (ASTM) and the Organization for Economic Cooperation and Development (OECD) have proposed several test methods for biodegradation studies. These methods include the Sturm test, closed bottle test, petri-dish screen and soil burial test.¹⁰ Due to its common usage and viability in the evaluation of a wide range of soil conditions and degradation environments, the soil burial test has been adopted for this study. As an added advantage, the conditions used for the soil burial biodegradation test are similar to actual conditions of waste disposal.¹¹ The soil burial biodegradation test method involves a simple burial of the material being tested in soil beds; this exposes the material to microorganisms in the soil. In addition to these advantages, soil burial offers the possibility of identifying microorganisms that are capable of accelerating degradation of unusual materials.

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The mechanistic pathway for the degradation of most polymers is not fully understood. It is assumed that microorganisms attack the 'degradable' parts of the surface of the polymer such as polar moieties or defects.¹² This leads to a decrease in the cohesiveness of the polymer while the surface area to volume ratio is increased. The polymer is eventually exposed to permeation of more microorganisms from water and soil leading to further degradation whereby low molecular mass compounds are released into the surrounding area. In addition, it is inevitable that the crystallinity, lamellar thickness and the overall morphology of the polymer are altered.¹³ Herein we report on the biodegradation of recycled β -CD/TDI and β -CD/HMDI polymers (pre-digested with sulphuric acid or undigested). The soil burial test method was employed and the polymers were exposed to a variety of soil types over a four-month time frame.

2. Experimental

2.1. Materials

All chemicals, solvents, and materials were used as received, apart from drying where necessary by using standard procedures. Food-grade cyclodextrins were purchased from Wacker Chemie (Munich, Germany). Diisocyanates were obtained by kind donation from Industrial Urethanes, Johannesburg, as industrial grade materials, or from Sigma-Aldrich (Johannesburg) as CP reagents, and were used interchangeably without any noticeable effects on the products formed. Soils were obtained from a local nursery in Gauteng. All other chemicals and solvents were purchased from Sigma-Aldrich or Merck (Johannesburg) as AR reagents. Columns and fibres for analysis were purchased from Separations, Johannesburg.

2.2. Preparation of Cyclodextrin Polymers

These were prepared according to a previously reported procedure.² Typically the bifunctional linker (8 molar equivalent of either HMDI or TDI) was added dropwise under an inert atmosphere and at room temperature to a solution of β -CD (4.00 g, 3.52 mmol) dissolved in DMF (40 mL). The temperature was raised to ~ 70 °C and the reaction mixture was left stirring under an inert atmosphere for 18–24 h. The polymerization reaction was monitored by IR spectroscopy. The completion of the polymerization was confirmed by the total disappearance of the isocyanate peak at around 2270 cm^{-1} after 18–24 h. Addition of acetone (100 mL) led to the formation of a precipitate. After filtering, the isolated white polymer was washed with copious amounts of acetone ($3 \times 100\text{ mL}$) to remove traces of DMF. The polymer was then dried overnight under vacuum.

2.3. Preparation of Recycled Polymer

Aliquots of *para*-nitrophenol (PNP) (10 ppm, 30 mL) were flushed through the polymers (0.5 g). After each extraction step, ethanol (30 mL) was used to wash off the absorbed PNP from the polymers. This process was used to simulate the use of polymers in the removal of the model pollutant (PNP) from water. It has already been established from circular dichroism experiments that the model pollutant (guest) forms an inclusion complex with the polymer (host).¹⁴ Finally, the polymers were dried under vacuum overnight in preparation for the soil burial tests.

2.4. Preparation of Digested Polymeric Samples

The recycled polymers were soaked overnight in 1 mol L^{-1} H_2SO_4 , filtered and dried under vacuum in preparation for soil burial tests. Digestion of the polymers was carried out with the aim of initiating hydrolysis of the polymers with the hope that this would lead to an increase in the surface area of the polymers.

2.5. Soil Burial Tests

Three different soil types, namely, compost, topsoil, and 'Supermix' (a mixture of topsoil, manure and compost), were obtained. The soil was charged into shallow basins ($30 \times 23\text{ cm}$). The bottoms of these basins have small holes that allow aeration and draining of excess water. The recycled polymers (1 g of each) (pre-digested with acid and undigested) were loaded into clean glass cylinders fitted with sintered glass frits, and buried approximately 10 cm below the surface of the soil. These containers were porous both on top and at the bottom so as to allow the polymers to have contact with air, moisture and microorganisms. The pores also allow easy recovery of the polymeric samples at regular intervals for examination and testing. The basins were then placed in an open area to allow exposure to rain and sunlight. Exposed samples were periodically taken out of the soil after 10, 20, 40, 60 and 119 days for analysis. Mass loss determination, surface morphology, surface area, and thermal analysis were conducted on all samples. The last sampling interval (119 days) was delayed in order to allow further degradation of the polymer. It was not necessary to wash the polymers after they had been removed from the soil because the tightly closed glass containers ensured that the polymer material had no direct contact with the soil. Every polymeric sample recalled from the soil was dried under vacuum for about 5 days to ensure complete dryness prior to analysis.

By using initial degradation studies using the β -CD/TDI polymer, it was established that degradation reached a maximum at about 40 days. Therefore, the samples pre-digested with the acid were buried for 40 days.

2.6. Fourier Transform Infrared (FTIR) Spectroscopy

Polymers buried in 'Supermix', compost and topsoil were analyzed with a Midac FTIR 5000 spectrophotometer. Potassium bromide (KBr) pellets were prepared by mixing 1 part of the sample with 99 parts of KBr. The samples were analysed over a range of $4000\text{--}400\text{ cm}^{-1}$.

2.7. Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used in order to determine the surface morphology of the polymers. Samples were mounted on glass slides and thereafter gold coated using an Emscope SC 500 sputter coater. The gold coating prevents an electrical charge build-up on the surface of the polymers. The samples were then examined under a Jeol JSM-560 scanning electron microscope.

2.8. Brunauer-Emmet-Teller (BET) Measurements

BET was used to determine changes in surface area of the polymers at periodic intervals during the experiment. A Micromeritics Flowprep 060 sample degas system was used to degas the samples for 5 h prior to analysis. Samples (0.2 g) were analysed in a Micromeritics Tristar surface area and porosity analyser.

2.9. Thermogravimetric Analysis (TGA)

A Perkin Elmer Pyris 1 TGA was used to investigate the stability and thermal properties of the polymers. The thermogravimetric analyses were carried out in air up to a temperature of $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ on a 20 mg sample.

3. Results and Discussion

3.1. Mass Loss Analysis

The three different soil types ('Supermix', compost and topsoil) were used in order to compare the effects of different soils and microorganisms on the degradation of the polymers. An experi-

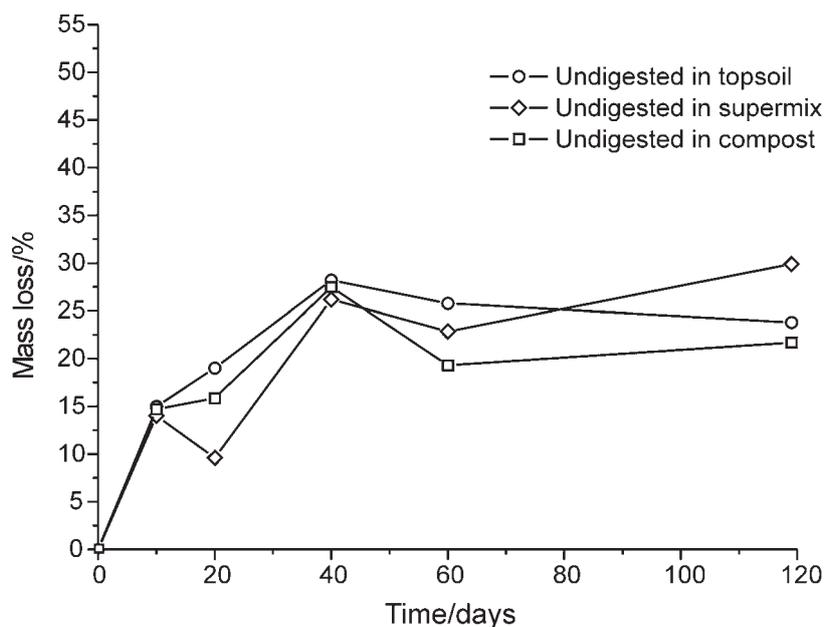


Figure 1 Mass loss of β -CD/TDI (undigested) in the three different soil types.

ment conducted by Kim *et al.*¹⁵ showed that the number of microbial counts in compost soil is greater than that in natural soil because of the nourishment provided by the compost. The soil burials were conducted from the months of October through to January (spring to summer season in the southern hemisphere). Heavy rains and high temperatures (up to 35 °C) were intermittently experienced during this period, but the average daily temperatures (28 °C) and monthly rainfall (96 mm) were considered normal for the area. The percentage mass losses of the as-prepared (undigested) polymers (β -CD/TDI and β -CD/HMDI) after burial in 'Supermix', compost and topsoil are depicted graphically in Figs. 1 and 2. The percentage mass losses of both polymers after digestion in acid and soil burial for 40 days are shown in Tables 1 and 2.

As illustrated in Fig. 1, irrespective of which soil type was used, degradation of the undigested polymers resulted in a mass loss of up to 30 % in 119 days. However, a mass gain after 20 days was unexpectedly observed in all the polymers. This mass gain was

Table 1 Percentage mass loss for β -CD/TDI digested in acid after 40 days.

Soil type	% mass loss
Topsoil	45
Compost	49
Supermix	50

Table 2 Percentage mass loss for β -CD/HMDI digested in acid after 40 days.

Soil type	% mass loss
Topsoil	21
Compost	30
Supermix	23

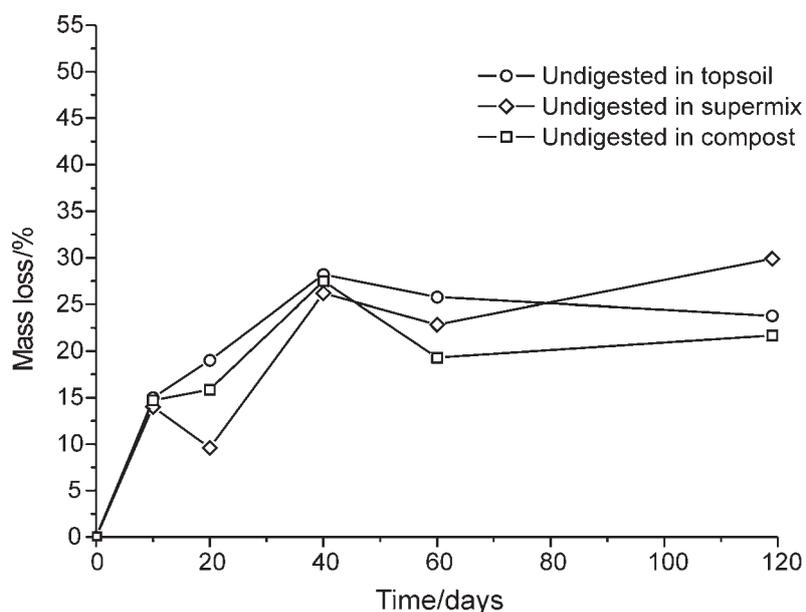


Figure 2 Mass loss of β -CD/HMDI (undigested) in different soil types.



Figure 3 Colonies of fungi on an Ohio agar plate after one week of incubation (β -CD/TDI polymer in 'Supermix').



Figure 4 Colonies of fungi grown on an Ohio agar plate after one week of incubation (β -CD/HMDI polymer in 'Supermix').

much more pronounced when 'Supermix' was used. We suspect that the mass gain is due to growth of microorganisms, which are embedded within the polymer structure.

Evidence for this argument is provided by growth of fungi on an Ohio agar plate after a one week incubation of the β -CD/TDI polymer in 'Supermix' (Fig. 3). The β -CD/TDI polymer buried in 'Supermix' (after 120 days) was grown in this plate and the numerous colonies of fungi give evidence that the 30 % mass loss (shown in Fig. 1) of this polymer was caused by these microbes. Further investigation on the identity of the fungi and the likely mechanism of action is currently underway, however, preliminary evidence indicates that the fungi are sequestering carbon from the polymers.

As expected, for the digested polymer, a fairly high mass loss (e.g. a maximum of 50 % β -CD/TDI) was recorded after a 40-day

period (Table 1).

The mass loss for the HMDI polymers is depicted in Fig. 2. A maximum of 30 % loss in the 'Supermix' was recorded. Similarly, a mass loss of about 30 % for the digested β -CD/HMDI was observed after soil burial for 40 days. Figure 4 shows fungal growth of the β -CD/HMDI polymer buried in 'Supermix' (after 120 days) after one week of incubation. As before, the observed fungal growth accounts for the microbial growth in the polymer hence the 30 % mass loss observed in Fig. 2.

These results suggest that the acid facilitates the degradation of the TDI polymers by initiating hydrolysis. We believe that the acid resulted in morphological variations on the polymer such as the formation of cracks; this assertion is supported by the scanning electron micrographs in Figs. 5b and 5d.

The degradation of both β -CD/HMDI and β -CD/TDI polymers

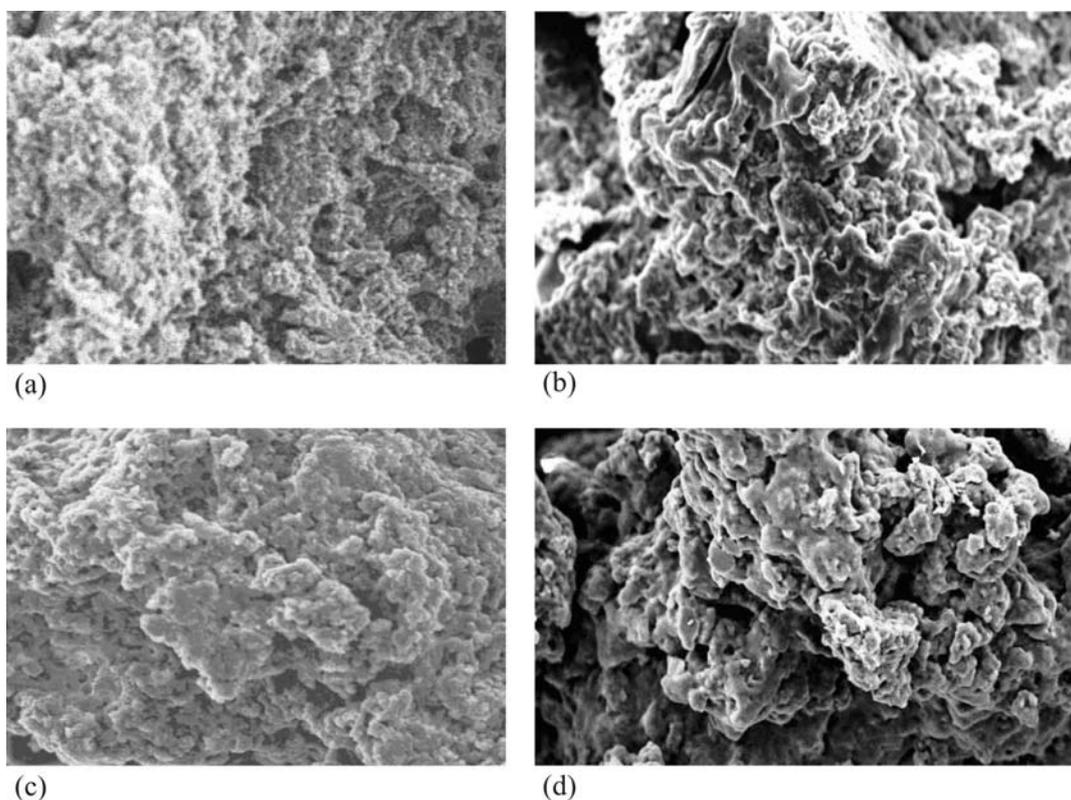


Figure 5 SEM micrographs from β -CD/HMDI (a) undigested before degradation, (b) digested with H_2SO_4 before degradation, (c) undigested and buried in compost after 40 days and (d) digested and buried in compost after 40 days.

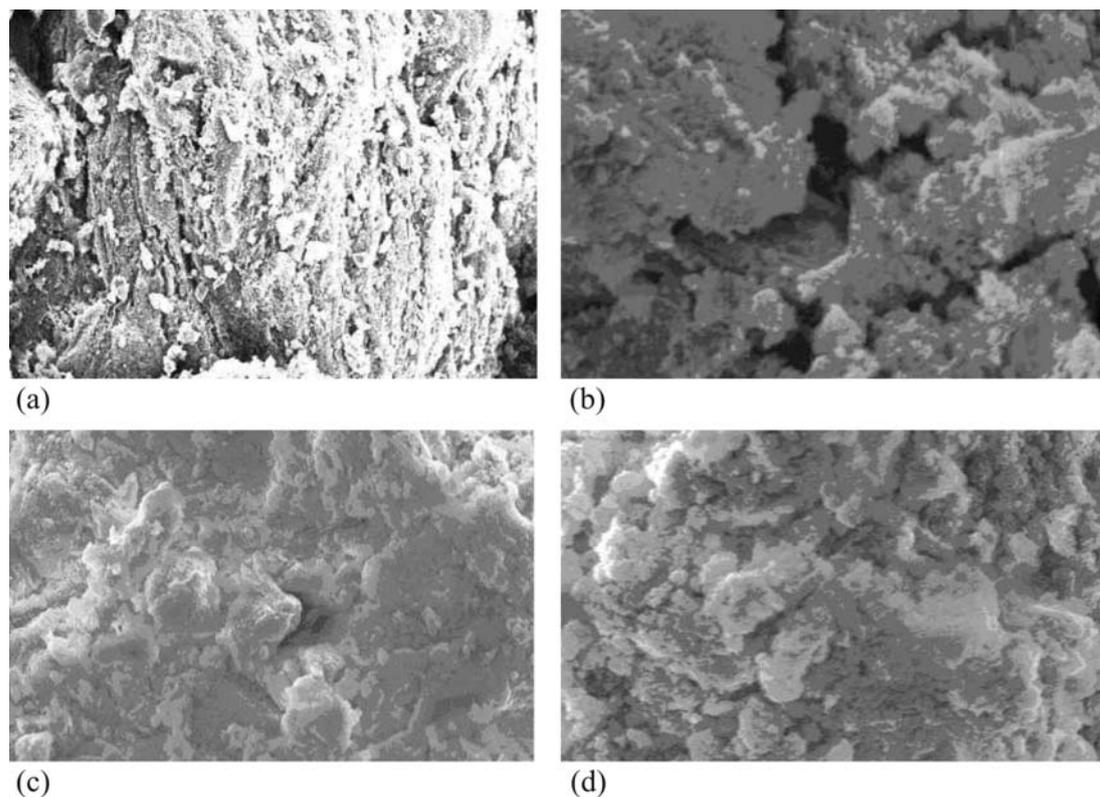


Figure 6 SEM micrographs from β -CD/TDI (a) undigested before degradation, (b) digested with H_2SO_4 before degradation, (c) undigested and buried in compost after 40 days and (d) digested and buried in compost after 40 days.

seems to be much more enhanced in 'Supermix' when compared with the other two soil types. However, it appears that digestion of polymers with the acid only accelerates the mass loss for β -CD/TDI and not for the β -CD/HMDI polymers.

Changes in the polymer morphology are expected to render the polymers more prone to microbial attack, thereby enhancing the degradation. Abastari *et al.*^{16,17} have reported that the mass loss of polyamide 66 (PA 66) increased sharply when acid-induced cracks were observed on the polymer. Therefore, it is likely that the modified surface morphology after acid treatment allowed the β -CD/TDI polymers to degrade faster and hence experience a greater mass loss.

From an environmental standpoint, the mass loss of between 15 % and 50 % in each of the soil types would not be considered sufficient to justify the disposal of the polymers as landfills. On the contrary, the low mass loss seems to suggest that these polymers are resistant to biodegradation.

3.2. Scanning Electron Microscopy (SEM) Analysis

Figures 5a and 5b show SEM micrographs of the undigested and digested β -CD/HMDI polymer, respectively, prior to biodegradation. The micrographs of the corresponding β -CD/HMDI analogue are shown in Figs. 6a and 6b, respectively. An analysis of the SEM micrographs of the polymers before biodegradation (Figs. 5a and 5b, and 6a and 6b) reveals small morphological differences. As evidenced by the formation of cracks and holes on the polymer surfaces (Figs. 5b and 6b), the use of sulphuric acid for digesting the polymers before soil burial affects the surface morphology of the polymers. Generally, all the polymers (both undigested and acid-digested) showed morphological changes after being buried in compost. Micrographs of polymers buried in 'Supermix' and topsoil were comparable. Holes and cracks on the surface of polymers present microorganisms with an opportunity to get into contact with the

polymer chains.¹⁸ When the mass loss and the SEM analysis after 40 days for both polymers (undigested or digested) are taken into account, a correlation between mass loss and the morphological changes of the polymers is observed.

3.3. Fourier Transform Infrared (FTIR) Spectroscopic Analysis

The FTIR spectra shown in Fig. 7 indicate that the overall chemical structure of the undigested polymers (β -CD/TDI) remained largely unaffected by acid treatment or burial in compost soil over a 40-day period. A similar spectral pattern was observed for the other soil types, including samples buried up to 119 days. Also, the original functionalities of the β -CD/HMDI polymer could still be identified in the FTIR spectrum for both undigested and digested β -CD/HMDI after soil burial tests. This seems to suggest an absence of a severe alteration in the core structure of the polymer, although the similarity in functional groups before and after degradation makes it difficult to identify significant changes. While the FTIR analysis is not conclusive, the mass loss analysis appears to indicate some breakage in the long polymer chains. This suggests that the polymers are degrading by breaking into smaller polymers or oligomers, but the overall chemical structure remains fairly unaffected.

3.4. Thermogravimetric Analysis

Thermogravimetric analysis was carried out in order to determine how the biodegradation process affects the thermal stability of the polymers. It is noted in Fig. 8 that all the polymers (undigested or digested) before and after degradation undergo a small water loss below 100 °C. Secondly, the polymers suffered a significant mass loss of 60 % between 200 and 300 °C. The last stage represents the slow charring of the polymer residue (300–600 °C).

The derivative TGA curves (Fig. 9) show noticeably sharper peaks for the undigested polymers compared with the digested

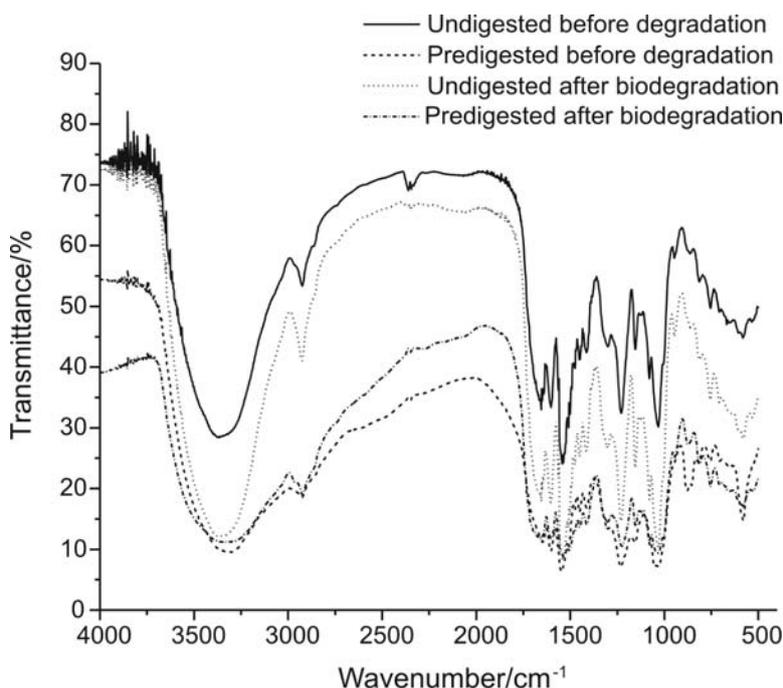


Figure 7 FTIR spectra of β -CD/TDI (undigested and digested) buried in compost soil over 40 days.

analogues. The broadness of the peaks for the digested polymers suggests that the digestion results in fragmentation of the polymers. These newly formed fragments disintegrate at different temperatures when heated, resulting in a slower thermal decomposition. When comparing the undigested polymers before and after degradation, a similar broadening and shift to lower temperatures can be observed. While the difference in this case is much less pronounced, we once again believe that this is a reflection of changes in the polymer structure (such as change in crystallinity or surface cracking). This implies that the buried polymers disintegrated at a slower rate when exposed to heat.

3.5. Absorption Studies Analysis

The polymers that were buried over 40 days were tested for their efficiency in the removal of PNP from water. This was done

Table 3 Absorption of PNP on β -CD/HMDI before and after degradation.

Polymer	Absorption before degradation/%	Absorption after degradation (undigested)/%	Absorption after degradation (digested)/%
β -CD/HMDI	60 ± 2	58 ± 2	52 ± 2

in order to investigate if the polymers were still capable of removing organic compounds after being partly digested and biodegraded.

A small decrease in the absorption efficiency (from 60 % to 52 %) was noted for the polymer that was acid digested and biodegraded (Table 3). This again indicates that there might have been some structural changes that resulted in the decrease in the absorption efficiency of the polymer. The undigested polymer,

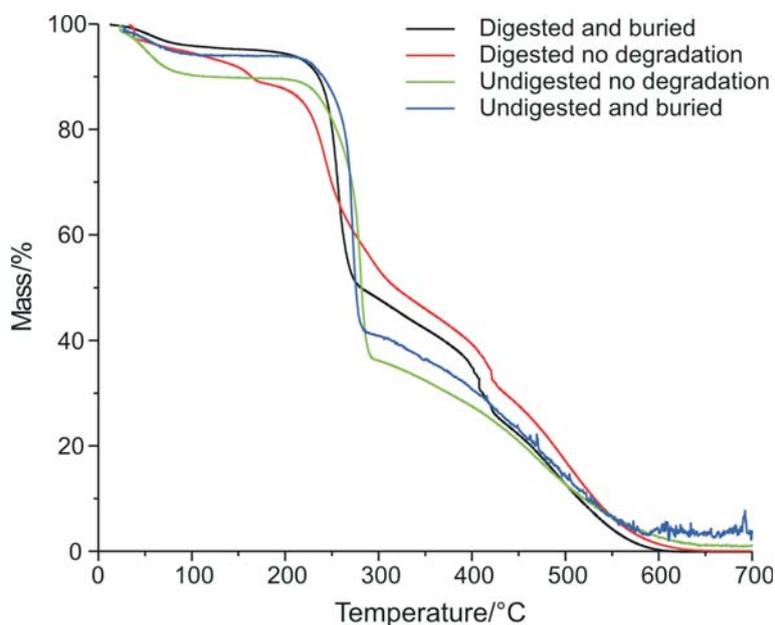


Figure 8 TGA curve of β -CD/TDI (undigested and digested) after 40 days in topsoil.

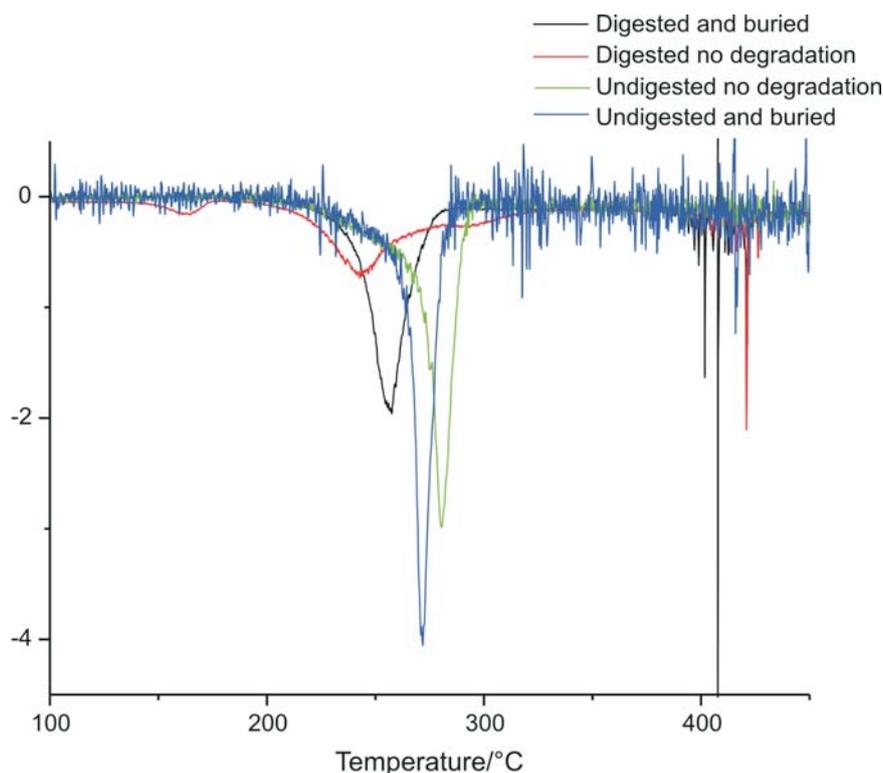


Figure 9 Derivative TGA curves of β -CD/TDI (undigested and digested) after 40 days in topsoil.

Table 4 Surface area of undigested and digested β -CD/TDI before (0 days) and after (40 days) degradation.

Soil type	Surface area/m ² g ⁻¹ (undigested, 0 days)	Surface area/m ² g ⁻¹ (digested, 0 days)	Surface area/m ² g ⁻¹ (undigested, 40 days)	Surface area/m ² g ⁻¹ (digested, 40 days)
Topsoil	20.02 ± 0.75	12.63 ± 0.75	17.63 ± 0.75	13.49 ± 0.75
Supermix	20.02 ± 0.75	12.63 ± 0.75	18.35 ± 0.75	11.09 ± 0.75
Compost	20.02 ± 0.75	12.63 ± 0.75	40.00 ± 0.75	12.66 ± 0.75

Table 5 Surface area of undigested and digested β -CD/HMDI before (0 days) and after (40 days) degradation.

Soil type	Surface area/m ² g ⁻¹ (undigested, 0 days)	Surface area/m ² g ⁻¹ (digested, 0 days)	Surface area/m ² g ⁻¹ (undigested, 40 days)	Surface area/m ² g ⁻¹ (digested, 40 days)
Topsoil	19.7 ± 0.75	1.85 ± 0.75	0.95 ± 0.75	1.69 ± 0.75
Supermix	19.7 ± 0.75	1.85 ± 0.75	1.90 ± 0.75	1.47 ± 0.75
Compost	19.7 ± 0.75	1.85 ± 0.75	1.70 ± 0.75	1.38 ± 0.75

on the other hand, maintained its absorption efficiency even after being buried. This observation further suggests that acid-treated polymers are more prone to structural modification of the key cyclodextrin moieties.

3.6. Brunauer-Emmet-Teller (BET) Analysis

The surface area of the undigested β -CD/TDI polymer showed a significant increase only in the compost-buried sample. After 40 days' burial of the same type of polymer, no such increase was observed (Table 4). It was expected that the surface area of the polymer should increase, since during degradation microorganisms attack and compromise the surface of the polymer. This in turn should reduce the cohesiveness of the polymer and thus increase its surface area. The results in Table 4 also show that there was a drastic decrease in the BET surface area of the digested samples, which was not anticipated. An important factor in the promotion of degradation is a large surface area and

this was not achieved when the polymer was digested in the acid.

A similar effect was noted for β -CD/HMDI, when comparing the surface area before and after digestion. This unexpected decrease in surface area might explain why the β -CD/HMDI polymers did not show any significant increase in biodegradation after acid treatment.

In this case, soil burial of the undigested polymers also resulted in a dramatic decrease in the surface area (Table 5). This once again partly explains the low degradation rate (maximum 30 % over 120 days) of these polymers.

4. Conclusion

β -CD/HMDI and β -CD/TDI polymers, both undigested (as-prepared) and digested (acid-treated) were degraded in compost, 'Supermix' and topsoil over a period of 120 days. The mass loss and changes in surface morphology confirmed that

some structural modification of the polymer material occurred. The use of acid as a digesting solution facilitated the process of degradation to a certain degree, especially in the case of TDI-linked polymers. Also, the presence of microorganisms played a role in the degradation of the polymer. This indicates that the choice of predigestion conditions needs to be carefully matched with the polymer type. For example, hydrogen peroxide might be better as a digesting solution for HMDI, since it is a very strong oxidizing agent. Studies involving the utilization of superheated steam to cleave the urethane bonds are also in progress. Identification of the fungi that grew on the Ohio plates is under investigation in order to determine if these fungi could be used in an enhanced degradation bioreactor.

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