MICROFIBRE POLLUTION – WHAT'S THE STORY FOR WOOL?

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ABSTRACT

Contamination of the environment with fibres and fibre fragments is a serious concern facing the textile industry. We studied the comparative marine biodegradation of three wool types and four synthetic fibres with which wool competes commercially, via a method based on a standard biodegradability test. We confirmed that wool readily biodegrades in sea water, consistent with earlier findings relating to soil biodegradation. Wool biodegradation appears to progress through phases relating to its composition and microstructure. We are now investigating the effect of standard chemical finishes used on wool fabrics, and the correlation between accelerated laboratory methods and 'real world' biodegradation.

Key Words: MICROFIBRE POLLUTION; BIODEGRADATION; WOOL; MARINE

1. INTRODUCTION

The contamination of our environment with fibres and fibre fragments from textiles is one of the greatest concerns currently facing the textile industry. While it is not totally certain what the environmental impact of these fibres is, it is certainly concerning that they now seem to be ubiquitous, having been found in such everyday products as tap water, beer and sea salt [1]. The high aspect-ratio of fibres means that they have the potential to penetrate and entangle with organisms to a greater degree than other plastic fragments. Even fibres that one would assume are biodegradable, such as cellulosic materials, have been found to persist in deep sea sediments [2]. Most research has focused on where fibres are found in the environment and their relative abundance (for example [3]) and measuring the extent to which they are shed during laundering (for example [4]). In our research we have set these issues aside, to focus on the ultimate fate of fibres in the aquatic environment.

Literature relevant to the biodegradation of wool in terrestrial environments is plentiful (for example, wool carpets [5], apparel [6] and geotextiles [7]), but far less is known of its behaviour in aquatic environments. A study by Brown [8] showed that wool 'knops' (intended for use as oil sorbents in the ocean) biodegraded in the natural marine environment (Lyttleton Harbour, New Zealand), but this work was largely qualitative rather than quantitative, and did not compare with other fibre types. It also examined the behaviour of wool fibres in a structure (i.e. wool knops) that is not a typical source of microfibre pollution (i.e. apparel). However, it demonstrated clearly that there are microorganisms in the ocean that readily biodegrade wool keratin.

In a more recent study [9] that included biodegradation in an aqueous environment, wool was compared to polylactic acid (PLA) and cotton fibres, with biodegradation assessed by weight loss and strength reduction. The trial conditions were designed to be favourable for aerobic microbial activity: elevated temperature (35°C), light excluded, with aeration, for a period of 42 days. Wool had a rate of mass loss between that of cotton and PLA, and a strength loss comparable to that of cotton. Overall, wool and cotton biodegraded readily under these conditions. By comparison, in water-logged archaeological deposits human hair and wool textiles can be relatively well preserved because microbial activity is reduced [10]. However,

these conditions are not at all typical of aquatic environments such as lakes, rivers and oceans, as light and oxygen are reduced or excluded.

In our work we adapted an internationally-accepted methodology for the measurement of biodegradability of plastics in the marine environment [11] in order to measure the biodegradability of two deconstructed apparel fabrics and five fibre samples collected from tufted carpets. Our aim was to understand the relative rate of biodegradation of wool and fibres with which it competes in commercial applications, and to observe the changes to the fibres caused by marine biodegradation.

In the case of the apparel fabrics, the likely route by which fibres would enter the marine environment would be through shedding during laundering (during product lifetime) and through migration (e.g. wind, water run-off) from landfill (after end-of-life disposal). Fibres from the carpets would enter the marine environment through disposal of water residues (to domestic or commercial drain) after wet-cleaning (during product lifetime), or through migration from landfill (either at end-of-life, or during lifetime due to disposal of vacuuming residues). In both cases smaller amounts of fibre would also be lost to the environment, some ultimately migrating to the oceans, through normal wear and tear.

2. MATERIALS AND METHODS

2.1 Fibre Samples and Preparation

Six commercial products were selected for this comparison: two apparel products (one merino wool, one polyester) and four interior textile products (tufted carpets in wool, nylon, polypropylene, and a partly bio-based polyester: Triexta). One further non-commercial sample was included: a wool carpet lacking any of the chemical finishes that are present in the commercial products. The products were not identical in construction, but are equivalent in terms of their intended end-use. These are described in Table 1.

A positive control was included in the study: microcrystalline cellulose powder. This has been used in previous marine biodegradation studies [12] and is one of the positive control options provided in the standard test method (see Section 2.2).

Table 1. Description of samples.

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Sample ID	Fibre/fabric type	Sample mass*				
A1	Merino wool knit fleece	22 g				
A2	Polyester knit fleece	16 g				
C1	Wool carpet pile – non-commercial	23 g				
C2	Wool carpet pile – commercial	23 g				
СЗ	Nylon carpet pile – commercial	16 g				
C4	Triexta carpet pile – commercial	16 g				
C5	Polypropylene carpet pile – commercial	12 g				
Control	Microcrystalline cellulose	23 g				

^{*} To give 10 g carbon; see Section 2.2.

Samples were deconstructed before biodegradation testing, in order to minimise the influence of textile structure. The apparel samples were deconstructed by shredding, which was done

twice to reduce them to fragments of fibre, yarn and fabric with at least one dimension no larger than one centimetre. For the carpet samples only the pile fibres were of interest as these are most likely to be lost from the product. These were simply shorn off the carpet backing using heavy duty animal hair clippers, producing a loose 'fluff' of short fibres. The shredder and clippers were carefully cleaned between samples to avoid cross-contamination of fibres.

2.2 Test Method

The biodegradation test was carried out using a method closely based on ASTM D6691 – 09 [11]. This method is used to measure the amount and rate of marine biodegradation of plastic materials in either natural or 'synthesised' sea water, under aerobic conditions. We used a natural sea water inoculum, collected outside the tidal influence zone in the Bay of Plenty, New Zealand. The principle of the test is to measure the CO_2 evolved by the samples as they biodegrade, i.e. as the material carbon (wool or other fibre polymer) is converted into CO_2 by decomposition. Three replicates of each material were tested, and the test was carried out with the vessels in a water bath at $30\pm2^{\circ}C$. The position of the vessels in the water bath was randomised. As well as the positive control, three 'blanks' with just the sea water and no sample were included. The only agitation of the samples was shaking of the vessels at weekly intervals, thus conditions were generally static.

One notable variation to the standard method was the larger size of the sample. We used sample sizes providing 10 g of carbon (see Table 1), in a 1.5 L seawater inoculum. This was to suit the design of the biodegradation test facility, but also improved accuracy of CO₂ detection.

3. RESULTS AND DISCUSSION

3.1 Extent of biodegradation

The extent of biodegradation (i.e. the percentage of material carbon converted to CO₂) after 90 days is given in Table 2.

Table 2. Extent of biodegradation (mean of three samples \pm 95% confidence interval).

Sample ID	Fibre/fabric type	Biodegradation (%)		
A1	Merino wool	22.9 ± 5.3		
A2	Polyester	1.3 ± 1.1		
C1	Wool – non-commercial	16.2 ± 2.1		
C2	Wool – commercial	20.7 ± 1.7		
C3	Nylon	1.1 ± 1.3		
C4	Triexta	1.0 ± 0.5		
C5	Polypropylene	-0.3 ± 0.4		
Control	Cellulose	10.2 ± 12.5		

It is very clear that wool samples (A1, C1 and C2) showed substantial biodegradation, of between 16 and 23%, compared to negligible levels for the synthetic fibres. The wool also had greater biodegradation than the positive control. The very large variability in the latter should be noted; this suggests that microcrystalline cellulose was not entirely suitable as a control. The untreated wool from sample C1 showed lower biodegradation than its commercial equivalent C2. We expected that the reverse would be true, as the commercial wool carpet contains

dyestuff and an insect resist agent (i.e. a mothproofing treatment), which may have been antimicrobial in character, as observed in our earlier soil biodegradation study [6]. Perhaps the process of dyeing the fibre (typically done in water, at the boil for up to an hour) caused sufficient fibre damage to accelerate the commercial sample's biodegradation.

The progression of biodegradation over the 90 days is shown for the three replicates from each of the two apparel samples in Figure 1.

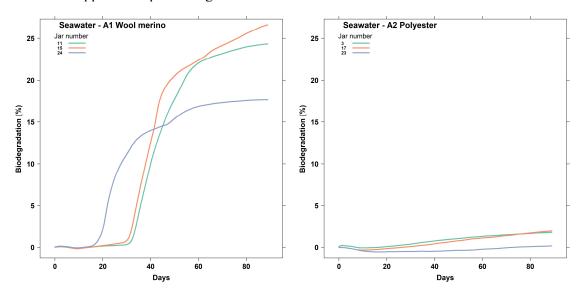


Figure 1. Progression of biodegradation over 90 days for merino wool and polyester apparel fabrics.

The wool sample shows an initial lag in biodegradation, before a rapid escalation and then slowing, although biodegradation was still continuing at the 90-day endpoint. Wool and synthetic carpet fibre samples showed similar behaviour, respectively.

3.2 Analysis of residues

At the conclusion of the 90 day test the residual sea-water inoculum for each replicate of each sample was analysed, and the fibre residues were imaged using scanning electron microscopy.

3.2.1 Residual seawater inoculum

Results for the seawater residues are provided in Table 3. The slightly acidic pH of the blank, control and non-wool samples was probably due to the microbial nutrients (0.5 g/L NH₄Cl; 0.1 g/L KH₂PO₄) that were used to prevent nutrient limitations (as required by the standard method). Interestingly it seems that the biodegradation of wool has had the effect of neutralising this, returning the pH of these samples to close to 7. The wool samples also had far higher dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) levels, indicating that the seawater residues contained partially biodegraded keratin that had not yet evolved all CO₂.

Sample ID	Fibre/fabric type	рН	DOC¹ (mg/L)	DIC ² (mg/L)
A1	Merino wool	7.2 ± 0.3	83.3 ± 2.03	8.4 ± 5.9
A2	Polyester	5.5 ± 0.3	29.3 ± 8.5	0.2 ± 0.1
C1	Wool – non-commercial	7.0 ± 0.1	110.9 ± 13.4	4.8 ± 1.5
C2	Wool – commercial	7.2 ± 0.1	14.3 ± 30.8	6.5 ± 0.7
C3	Nylon	5.8 ± 0.2	40.5 ± 3.3	0.2 ± 0.1
C4	Triexta	5.5 ± 0.3	26.9 ± 7.5	0.0 ± 0.1
C5	Polypropylene	5.8 ± 0.1	47.9 ± 5.6	0.3 ± 0.1
Control	Cellulose	5.4 ± 0.0	103 ± 95.1	0.5 ± 0.5
Blank	None	5.5 ± 0.2	21.0 ± 4.0	0.0 ± 0.1

Table 3. Analysis of residual seawater after 90 day test (mean of three samples \pm 95% confidence interval).

3.2.2 Residual fibres

Scanning electron images of the untreated wool carpet fibre (C1) and Triexta carpet fibre (C4) after the 90 day test are provided in Figure 2. Other wool and synthetic samples showed similar results, respectively.

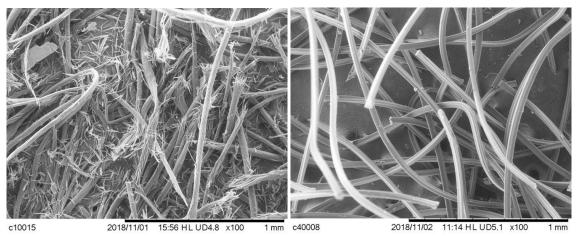


Figure 2. Wool (left) and Triexta (right) fibres after 90 days biodegradation.

It is clear that the wool fibres are substantially degraded. Some intact fibres are visible but there are broken ends showing cortical cells, as well as fully separated cortical cells. In some regions fibres are intact but cuticle is completely absent. By comparison the Triexta fibres are entirely intact and unaltered by the biodegradation test.

4. CONCLUSIONS

The wool samples tested biodegraded readily under the conditions used in an accepted standard laboratory test for measuring biodegradation of materials in seawater. The synthetic fibres did not biodegrade to any obvious extent under the same conditions. On this basis we expect wool would only persist in the marine environment for months, whereas synthetic fibres would be likely to be present for many years, if not decades.

^{1.} Dissolved organic carbon.

^{2.} Dissolved inorganic carbon.

Although the conditions used in this study were suitable for our purpose, they did not include all parameters that can effect biodegradation. In the real world, other factors would also be present. For example, light and UV acting on fibres high in the water column would further accelerate the degradation of wool (which is susceptible to UV and light degradation), having less effect on synthetic fibres. The lower mechanical strength of wool compared to synthetics would encourage rapid physical degradation (i.e. fibre breakage), which would then accelerate biodegradation. With the exception of polypropylene, all of the fibre types evaluated here are more dense than water so would eventually sink, meaning that over time light and oxygen levels would be reduced, and the rate of biodegradation might reduce.

In our ongoing work we are examining how biodegradation of wool is affected by standard chemical finishes used on wool apparel fabrics, and comparing with a wider range of synthetic apparel fibre types. We are also planning to compare the results from laboratory biodegradation testing with real world marine biodegradation.

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