Report FD 03/29
INVESTIGATION OF THE NATURE
AND EXTENT OF BIODEGRADABLE
POLYMERS USED IN DIRECT FOOD
CONTACT APPLICATIONS

PROJECT INFORMATION

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Author: L Castle

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Sponsor: Food Standards Agency
Aviation House
125 Kingsway
London
WC2 6NH

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Principal Workers: L Castle

Team Leader: L Castle

Distribution:
1. Dr Barnes (FSA) (x5 + disk)
2. CSL Library
3. Dr Dennis (CSL)
4. Prof. Gilbert (CSL)

CSL
Sand Hutton
York
YO41 1LZ

SUMMARY

This project addressed the identification of possible migrants and any testing requirements for biodegradable food contact polymers. This was achieved via a group of 6 linked objectives, which were:

i)   Gather information on the chemical composition of biodegradable polymers intended for food contact.

ii)   Gather information on the conditions of use including the type of foods packaged along with the contact conditions of time and temperature.

iii)   Make estimates of the amount of biodegradable polymers used in the UK per annum.

iv)   Evaluate the migration potential from biodegradables given their composition and conditions of use.

v)   Evaluate the suitability of standard migration test protocols, for example from the sectors of paper and plastics, for use to test biodegradables.

vi)   Make final report on the information gathering exercise along with recommendations for further work, including experimental work, if any is required.

A large number of biodegradable polymers are available or are under development. Nevertheless, the actual market for biodegradable polymers (excluding paper and board) for food contact applications is presently very limited indeed. The only biobased food-packaging materials used commercially on a major scale are based on cellulose. An estimate made in 2003 concluded that of the 2.7 million tonnes per annum polymer market in the UK, less than 0.1% of this production is from bio-based materials. It is not known what fraction of this already small fraction is used for food packaging applications. There is currently no system of coding (e.g. by logo) and no system has yet been set-up in the UK to monitor sales and usage of biodegradable food packaging polymers.

A hydrolysable linkage is a feature common to most polymers that are biodegradable and most of the biodegradable polymers available are polyesters. The source materials can by synthetic (e.g. monomers derived from petroleum) or bio-based (i.e. monomers or polymers derived from crops or other living sources). The nature and the source of the material determine the possible migrants. In general, biodegradable polymers built-up by polymerisation of monomers (from either natural or synthetic sources) have a more defined composition than biodegradable polymers obtained as such from biopolymers. This is because the processes available to purify monomers (e.g. distillation, recrystallisation) are more efficient than the processes available to purify polymers (e.g. washing). The composition and possible contaminants in biodegradable polymers should be limited where needed by compositional and/or migration limits, perhaps coupled with restrictions on source materials and the manufacturing processes used.

The methods of test for migration, using food simulants, are likely to be directly applicable to testing most biodegradable polymers. Since the methods of test are supposed to be directly related to the actual conditions of use in contact with food, and mimic these, then if a biodegradable polymer is suitable for a particular application in contact with food then a correctly specified test procedure should be applicable also. One caveat is that tests for overall migration may not be technically possible for humidity-sensitive materials.

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LIST OF ABBREVIATIONS

CEN   Comité Européen de Normalisation (European Standardisation Body)
EVA   poly(ethylene-co-vinylacetate)
HDPE   high density polyethylene
LDPE   low density polyethylene
LDPP   low density polypropylene

PE   polyethylene
PEG   polyethylene glycol
PET   polyethylene terephthalate
PHA   poly(hydroxyalkanoate)
PHB   poly(hydroxybutyrate)

PHV   poly(hydroxyvalerate)
PLA   polylactic acid
PP   polypropylene
PS   polystyrenes
PVA   polyvinyl alcohol / polyvinyl acetate

PVC   poly(vinyl chloride)
RCF   regenerated cellulose film

1. INTRODUCTION

1.1 Background

Nearly three million tonnes of plastic waste are produced in the UK each year, much of which is packaging (60 per cent). More than half of this packaging is food packaging. Plastic makes up less than one percent of all waste produced in the UK by weight, but more by volume. It is almost all non-degradable and at the end of their life, most (over 80 percent) plastic products are landfilled [1].

The use of biodegradable polymers to make food packaging is beginning to be a practical reality [2]. It may at first seem to be a contradiction - the desire to have a biodegradable packaging material that nevertheless can withstand contact with food and protect that food from external conditions. However, commercial applications are in prospect, especially where the higher cost of biodegradable materials compared to synthetic polymers derived from petroleum can be off-set by a marketing advantage. Sustainability and non-polluting are attributes that are traded on. Also, there is increasing governmental pressure on manufacturers via eco-taxes to reduce the amount of non-degradable plastic packaging.

1.2 Biodegradable – definitions

There are various definitions, technical and legal, of 'biodegradable'.

According to European Standard EN13432, it means materials that are degraded after use into low molecular weight substances by combined action of physico-chemical agents (e.g. sunlight) and microorganisms (e.g. composting), ultimately degrading into carbon dioxide, water and biomass.

Biodegradability is one of a set of degradability attributes. The American Society for Testing and Materials and the International Standards Organization Definitions on Environmentally Degradable Plastics [3] are as follows and they help to place 'biodegradability' into the context of 'degradability' in general:

degradable plastic, a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification.

biodegradable plastic, a degradable plastic in which the degradation results from the action of naturally-occurring micro-organisms such as bacteria, fungi and algae.

photodegradable plastic, a degradable plastic in which the degradation results from the action of natural daylight.

oxidatively degradable plastic, a degradable plastic in which the degradation results from oxidation.

hydrolytically degradable plastic, a degradable plastic in which the degradation results from hydrolysis.

compostable plastic, a plastic that undergoes degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known, compostable materials and leaves no visually distinguishable or toxic residue.

1.3 Earlier projects on biodegradable food packaging materials

Two European projects have been undertaken in this area [4,5]. The EU-funded project 'Food Biopack' [4] aimed to create a network of institutes and companies involved in biopolymers, identify industrial needs to promote biobased food packaging materials, and identify future research needs in relation to quality and safety of foods. Part of the 'Food Biopack' project considered the safety and legislation aspects, in brief, and concluded that "The same safety criteria and test methods should be applied for all materials, regardless of their origin". The project did remark that 'However, due to differences in origin and properties, some undesirable interactions are more relevant for one or the other material' [4]. No concrete recommendations on migration test criteria or test conditions were proposed.

EU project "Bionanopack" [5] had the goals to develop a new biodegradable food packaging material with improved functional properties. The attributes desired included low permeability to oxygen, carbon dioxide, nitrogen and water vapour. These attributes were to be conferred by homogeneously dispersing functionalised layered silicates (clay minerals) in thermoplastic starch via polymer melt processing techniques. This project does not seem to have been finalised and no final report is available at the time of writing.

No project has been reported that specifically addresses the identification of possible migrants and any testing requirements for biodegradable food contact polymers. These were the main aims of this project, which were achieved via a group of 6 linked objectives.

1.4 Objectives of the project

The objectives of this project were as follows.

   1. Gather information on the chemical composition of biodegradable polymers intended for food contact.

   2. Gather information on the conditions of use (food type, time and temperature contact conditions).

   3. Make estimates of the amount (tonnage and contact area) used in the UK per annum, broken down by material type.

   4. Evaluate the migration potential from biodegradables given their composition and conditions of use.

   5. Evaluate the suitability of standard migration test protocols (e.g. from the sectors of paper and plastics) for use to test biodegradables.

6. Make final report on the information gathering exercise along with recommendations for further work, including experimental work, if any is required.

2. MAIN CLASSES OF BIODEGRADABLE PLASTICS

It must be appreciated that 'biodegradable' plastics are defined by their 'biodegradability'. This is a property of the plastic and it does not denote the origin of the source materials. The source material (the feedstock) can be 'natural' or 'synthetic' or a mixture of the two.

2.1 Natural polymers

These plastics are obtained directly from biomass such as starch and polysaccharides. Natural polymers are generally biodegradable. The main classes are:
- Starch
- Cellulose
- Chitin
- Chitosan
- Gluten
- Zein

A number of materials derived from natural sources [6] are listed in the Commission Synoptic Document [7]. In the main they are listed because they are foods or food additives. They are not suitable for use directly as food packaging materials (with the exception of the Biopol copolymer) although they could in principle be components of biodegradable packaging materials.

On the list of 'Starting substances' (monomers list)

Albumin	Cellulose	Glucose
Lactic acid	Lignocellulose	Starch, edible
Sucrose		
3-Hydroxybutanoic acid-3-hydroxypentanoic acid, copolymer (aka Biopol)		

On the list of 'Additives'

Alginic acid	Casein	Cellulose
Cellulose acetate butyrate	Cellulose derivatives, var.	Cellulose, regenerated
Dextrin	Glycerol and various derivs	Gelatin
Hydroxyethyl starch	Hydroxypropylstarch	Lactic acid
Lactic acid, butyl ester	Pectin	1,2-Propyleneglycol alginate
Starch, edible	Starch, hydrolysed	

<u>With no classification</u>

Alginate	Carrageenan	Cellulose acetate
Modified natural cellulose	Chitin	Chitosan
Gluten	1,3-Propyleneglycol alginate	Zein

2.2 Modified natural polymers

These are bioplastics obtained directly from biomass but have then undergone chemical modification to confer improved physical, chemical and/or barrier properties. The main types are:

- Cellulose acetate
- Cellulose acetate butyrate
- Cellulose nitrate
- Cellulose, regenerated
- Hydroxymethyl starch
- Hydroxypropyl starch
- Starch-acetate
- Starch-acrylamide

2.3 Polymers obtained by chemical synthesis, using monomers derived from petrochemical or biobased sources

The synthetic polymers that are subject to biodegradability are typified by the polyesters, polyamides and polyurethanes, since these contain hydrolysable linkages. According to Chiellini [8] and Garde [9] the main types are:

- Polyvinyl alcohol / polyvinyl acetate (PVA)
- Polyaspartic acid
- Polyester urethanes
- Poly(amide-esters)
- Poly(ester-urethanes)
- Polyanhydrides
- Polyethyleneglycol (PEG)
- Polylactic acid (PLA)
- Aliphatic / aromatic polyesters
- Terephthalic acid, succinic acid, butanediol, adipic acid copolymer

2.3.1 Starting substances obtained from non-renewable sources
'Normal' synthetic polymers, such as polyethylene (PE), polypropylene (PP), polystyrenes (PS) and unplasticised poly(vinyl chloride) (PVC), are very stable [10]. Many of the plasticisers used in PVC are biodegradable, albeit slowly, because they are esters (e.g. di(2-ethylhexyl)adipate, epoxidised soybean oil) and this confers some biodegradability onto plasticised PVC. Very low molecular weight fractions of polyethylene may be broken-down and a guideline for biodegradability of linear PE is a molecular weight of less than 1000 [11]. At

this low molecular weight the PE is a hydrocarbon wax and does not constitute a durable packaging material, with some exceptions such as the wax coating on cheese. Branched polyolefins are more resistant to biodegradation so that low-density PE and PP (LDPE and LDPP) are even more resistant than high-density PE (HDPE).

2.3.2 Starting substances obtained from renewable sources

Biodegradable polymers can be made from starting substances obtained from non-petroleum sources. These include amino acids, microbial metabolites from the conversion of glucose and other monosaccharides (e.g., acetic acid, acetone, 2,3-butanediol, butyric acid, isopropanol, propionic acid), lactic acid, ethanol and fatty acids.

For example, a series of biodegradable polymers with different properties and different potential industrial uses were made starting with succinic acid and/or 1,3- propanediol. There were two routes for making the polyester- based materials; the direct ring-opening polymerization of lactones (cyclic esters) synthesized from 1,3-propanediol, and the chain-extension of alpha,omega-dihydroxy-terminated oligomeric polyesters produced by thermal polycondensation of 1,3-propanediol and succinic acid (oligo(propylene succinate)s) [12]. The starting substances, 1,3-propanediol and succinic acid, could be obtained from either a renewable or a non-renewable source.

Amino acids have been used to make biodegradable co-polyamides. These were synthesised by melt polycondensation with the incorporation of alpha-amino acids into adipic acid,/isophorone diamine polyamides [13] or into adipic acid/bis (p-aminocyclohexyl) methane polyamides [14]. These materials represent biodegradable plastics made using starting substances from both renewable and non-renewable sources.

2.4 Polymers obtained from microorganisms or genetically-modified bacteria

Some microorganisms synthesise polymers and store them as an energy source. These polymers may be extracted, isolated, purified and used as plastics.

Polyhydroxyalkonates

The general structure is:

$$-(-O-CHR^1-CH_2-CO-)_x-(O-CHR^2-CH_2-CO-)_y-$$
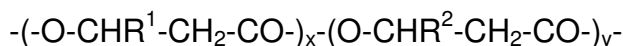
For poly(hydroxybutyrate) (PHB) the two alkyl group R^1 and R^2 are ethyl. PHB resembles PP in its melting point and mechanical properties. For poly(hydroxyvalerate) (PHV) the R^1 alkyl group is methyl and the R^2 group is ethyl. PHV is commonly used as a copolymer with PHB.

Polylactic acid

The structure of PLA is

$$H-(O-CHMe-CO-O-)_n-OH$$
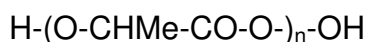
The water vapour barrier properties of PLA resembles LDPE and PLA can be fabricated into many packaging articles that PE is used for presently.

3. LEGISLATION ON THE COMPOSITION OF FOOD CONTACT MATERIALS

It would be quite easy to assume that if polymers are derived from natural sources and/or are biodegradable then they must automatically be safe. It is sobering therefore to consider the very extensive specifications placed on the copolymer 3-hydroxybutanoic acid-3-hydroxypentanoic acid, which is obtained by means of bacterial fermentation and which was the first biodegradable polymer to gain specific EU approval [15]. This microbial polymer is produced as such by the microorganism and it must be extracted, isolated and purified from the bacteria. The extensive specifications necessary, reveal the fact that this purification process can never be as complete for a polymer as it can be for a low molecular weight monomer. Monomers can be purified by highly effective physical processes including distillation or recrystallisation but these procedures cannot be applied at all (distillation) or applied with such effectiveness (recrystallisation) to polymers. It is likely that other biodegradable polymers should also have specifications placed on them to control the possibility of chemical migration to a food in contact.

The general rules applicable to all food contact materials are laid down in Framework Directive 89/109/EEC. The guiding principle is that food contact materials shall neither endanger human health nor contaminate or change the properties of the food [16]. Specific Directives lay down requirements for Ceramics (84/500/EEC), Regenerated Cellulose (2004/14/EC as amended by 2004/14/EC) and Plastics (2002/72/EC as amended by 2004/19/EC, 82/711/EEC, 85/572/EEC).

Plastics, which are covered by Directive 2002/72/EC, are defined in that Directive as organic macromolecular compounds obtained by polymerisation, polycondensation, polyaddition or any other similar process from molecules with a lower molecular weight or by chemical alteration of natural macromolecules. To protect the consumer only toxicologically evaluated starting substances and additives shall be used in the production of plastics. These are included in the list of authorised substances, which also sets restrictions for their use such as specific migration limits. There is a basic requirement that plastic food contact materials should be inert. To this purpose an Overall Migration limit is set at 60mg/kg packaged food. Furthermore the Directive contains rules for the enforcement of the migration limits.

New substances intended for food contact can be authorised according to the following procedure. A petition supplying a dossier has to be sent to the European Food Safety Authority. This dossier has to contain chemical and physical specifications of the substance, the migration behaviour into food simulants and toxicological properties. New materials such as biobased or biodegradable materials would have to comply with the provisions of the Framework Directive and with the requirements of any specific Directives applicable to them. If they fell under the scope of the Plastic Directive they would have to be manufactured using authorised starting substances and additives. If the material included unauthorised substances a petition for authorisation would have to be launched with the European Food Safety Authority.

4. CONDITIONS OF USE

Migration from packaging materials is a diffusion process that is subject to the normal laws of physics. Consequently, the conditions of use of biodegradable polymers will influence the levels of migration that may be expected from them.

Migration increases with:
- increased time of contact
- increased temperature of contact
- intimacy of the contact
- foodstuffs that interact strongly with the packaging and have a high solubility for the migrant(s)

Migration decreases with:
- only indirect contact
- low diffusivity ('inert') packaging materials
- presence of an inert barrier layer

4.1 Natural polymers

Whereas the petrochemical industry has reached a high degree of sophistication in the production of packaging materials, the development of bio-based packaging materials is still at a very early stage. Natural polymers generally are inferior to the petrochemical products in terms of gas barrier and especially moisture permeability. The consequence of this relative poor performance is that biodegradable packaging made from natural polymers are proposed for use almost exclusively for dry foods, for secondary packaging (indirect contact only), or incorporated as the inner layer of multi-layers to provide thickness and rigidity [17]. In all these applications they can be considered as alternatives to paper and paperboard packaging materials.

Starch-based products
The UK starch manufacturing and processing industry used 1.3M tonnes of raw starch in 1999/2000 but very little starch is used for the production of polymers in the UK, or in Europe as a whole. In the UK starch-based moulded and film packaging has not yet reached the market to any significant extent and there has been little development of manufacturing capacity to food industry standards.

A main player is National Starch & Chemical, which has licensed a number of companies for the production of starch based polymeric products for use in the packaging industry. Green Light Products produces loose packaging materials from wheat flour; Ecofoam wrapping materials and loosefill packing are also produced under the National Starch & Chemical banner. National Starch & Chemical has developed the technology for production of starch biopolymers for loosefill and void filling packaging, sheets shapes and blocks for food service & electronics packaging, injection moulding, films & native starch fillers, and children's toys. Starch-based co-polymers ('Mater-Bi') from Novamont are used as moulded tableware and plastic bags.

Potatopack is a UK company producing compostable polymeric compounds from imported potato starch for packaging use by the food industry. Currently this is small operation employing a technology developed elsewhere to produce injection-moulded trays for vegetables.

Apack AF is a European based company developing a range of food grade packaging products. It has one plant based in Belgium utilising wheat starch and a second under development in Thailand, which will produce starch from tapioca. Apack makes vegetable trays and carrier bags. Similarly, Novamont produce bags for vegetables and fruit, and netting for oranges and onions.

Starch-based hot melt adhesives have been proposed as alternatives to those based on synthetic waxes gums and resins [18] but these adhesives, either synthetic or biodegradable, are not intended for direct contact with food. The development of two-ply laminated biodegradable fibre-based trays for high temperature use has been reported [19]. The applications envisaged are similar to those for ovenable paperboard trays.

4.2 Modified natural polymers

Chemical modification of a natural polymer or blending with a synthetic polymer can improve the resistance to water but often at the expense of impaired biodegradability. For example, LDPE can be blended with starches. The blends have properties intermediate between LDPE and starch and a delicate balance has to be struck to give desirable properties (e.g. short-term resistance to water) whilst retaining the attribute of biodegradability.

One of the most common modified natural polymer packaging materials is modified cellulose. Including coated RCF (regenerated cellulose film) a wide range of food contact applications is possible.

Coatings
The functional properties of bio-based polymers can be enhanced by combination with aliphatic polyesters. These are currently derived from petrochemical sources but in the longer term they could be formed from natural oils. Eastman/BASF make aliphatic polyesters used for waterproof coatings on trays. In fact, some sensitivity to moisture can be used to good effect, for example with coated RCF that has controlled moisture barrier/passage properties that help keep pies and pastry products in good condition [20]. These are used as replacements for perforated synthetic polymers since the latter are falling out of favour because of hygienic considerations.

4.3 Polymers obtained by chemical synthesis, using monomers derived from petrochemical or biobased sources

Polylactic acid based products
Polylactic acid materials(e.g. ' NatureWorks' from Cargill Dow Polymers) can be used for a wide range of materials and articles Trials have been conducted using polylactic acid (PLA) to pack fresh orange juice for 14 days at 4ºC and one food producer has tested PLA pots for packing yoghurt in Germany.

Supermarkets are looking to expand their range to PLA pots for orange juice and trays for meat, fish and frozen microwave meals [21]. The actual UK applications of PLA-based products (if any) are not known at present.

Biodegradable hot melt adhesives have been prepared with modified PLA by end-capping with acetic anhydride or by modification with t- butylperoxy benzoate [22]. Similarly, hot melt adhesives based on poly(caprolactone) have been tested as alternatives to the conventional non-biodegradable hot melt adhesive based on poly(ethylene-co-vinylacetate) (EVA) [23]. As noted above, hot melt adhesives are not intended to make direct contact with packaged foods.

4.4 Polymers obtained from microorganisms or genetically-modified bacteria

These polymers are invariably polyesters and as such they can be used for the wide range of food contact applications that synthetic polyesters (e.g. PET) are used for. The uses of poly-beta-hydroxybutyric acid (PHB) include the plastic laminate on the inside of paper cartons for long-life milk and fruit juices. High PHB gives a plastic that has high crystallinity, is strong and stiff. High poly-beta-hydroxy-valerate (PHV) gives a plastic that is flexible and tough. For blowing applications, some hydroxy valerate is incorporated to make a PHB-PHV co-polymer.

5. EXTENT OF USE IN CONTACT WITH FOOD

It has been estimated [24] that there are more than 20 academic centres engaged world-wide on research into bioplastics. Similarly, in 2002 there were more than 130 publications and 100 patents issued on biodegradable polymers, covering petrochemical-derived, natural polymers, modified natural polymers and hybrids. Nevertheless, the actual market for biodegradable polymers (excluding paper and board) for food contact applications is presently very limited indeed. In fact, it has been stated in 2002 [17] that the only biobased food-packaging materials used commercially on a major scale are based on cellulose.

The European polymer market has been estimated at more than 30 million tonnes per annum of which only a small fraction is produced from bio-based materials. An estimate made in 2001 suggested that this fraction was some 25,000 tonnes, <0.5% for Europe. A more recent estimate made in 2003 concluded that of the 2.7 million tonnes per annum polymer market in the UK, less than 0.1% of this production is from bio-based materials [25]. It is not known what fraction of this already small fraction is used for food packaging applications. There is currently no system of coding (e.g. by logo) and no system has yet been set-up in the UK to monitor sales and usage of biodegradable food packaging polymers [26].

PHB is at present the most promising PHA; and BIOPOL, its copolymer with PHV, is already industrially produced (ICI, UK), and used as a food packaging material (WELLA, FRG). The price at present is about 4-5 times that of synthetic polymers (ca. US$4-5 per kg compared to ca. US$1 per kg) although this ratio will fluctuate as production volume increases and as the price of crude oil increases or decreases. One producer is said to have made 60 tonnes for pilot product/process development but has also declared an aim to make 10,000 MT by 2005 [27].   PLA dominated the production figures for bioplastics in 2002 with ca. 180,000 MT of PLA produced [28]. Milk containers are produced from high density polyethylene (HDPE) which is non-compostable. A product with similar properties can be manufactured from polylactic acid but not yet at a competitive price.

There have been trials of potato starch-based replacement of expanded polystyrene, at special events such as outdoors catering [29]. The feasibility of the large-scale commercial use of such packaging made from potato starch is to be evaluated in a study co-funded by the UK Government, The British Potato Council and 11 industry partners [30]. Containers made by Potatopak featured in British Potato Council seminars and were used for catering at the 2001 British Potato event [31]. The packaging is used for some high value foods, notably organic fruit, and for outdoor catering [30]. It does seem likely that applications will, in the near future, be confined to niche areas such as these.

6. MIGRATION POTENTIAL

6.1 Natural polymers

6.1.1 Overall migration
If natural polymers are used in direct contact with moist and aqueous foods, then high migration of the water-soluble polymers can be anticipated.

6.1.2 Specific migration
Of main interest would be the migration of additives used to make the natural polymer function as a food contact material. For example, to overcome the natural brittleness of starch, plasticisers are needed to make materials with usable physical properties. Glycerol, sorbitol, other low molecular weight polyols, polyesters and urea are used. As low molecular weight constituents, these softeners have the potential to migrate. Migration of softeners from an analogous food packaging material, regenerated cellulose film, has been reported [32, 33]. On the other hand, these softeners are polar, water-soluble molecules, and so migration would not be favoured given that the natural biodegradable polymers tend to be used to package dry foods only.

Another topic of interest is to consider if contaminants of the natural polymer source would be removed during manufacture of the finished material or article. Or if, conversely, any contaminant residues might persist with the potential to then migrate. A case study on fumonisins in maize and materials derived therefrom, is presented as Annex 1. The conclusion in that case study was, that if the source material is food-grade then migration of any contaminant residues is likely to be very low if at all.

6.2 Modified natural polymers

6.2.1 Molecules formed during chemical modification
The functional properties of natural polymers are commonly improved by chemical reaction. Examples of these treatments include;
- pre- treatments of jute fibres with sodium hydroxide and then co-polymerisation with acrylonitrile [34];

- using an acrylic acid-grafted polyethylene-octene copolymer as a compatibiliser of corn starch-reinforced metallocene polyethylene-octene elastomer blends [35];

- modifying starch by reaction with acrylamide

Acrylic acid, acrylonitrile and acrylamide are themselves very reactive molecules. The point of concern would be if these treatments of the natural polymer gave rise to oligomers or reaction side products that had a low molecular weight and the potential to migrate. Recent guidance on the safety assessment of a substance to be used in food contact materials prior to its authorisation (2003) notes that '… experimental data show that the migration of oligomers (molecular weight <1000) or reaction products occurs and in some cases high levels were found. Therefore, there is a need for information on the migration of oligomers and reaction products..' [36] Therefore the issue of

oligomers and reaction products has been recognised for 'normal' plastics too and similar information would need to be provided for biodegradables.

6.2.2. Migration of additives

Cellulose acetate (with 53 to 56% acetyl groups) is suitable for thermoplastic processing and with appropriate plasticisers it has usable functional properties. Cellulose acetate with such a degree of substitution is biodegradable, but degradation is very slow. However, it is reported that when common plasticisers are substituted by specific esters and other low molecular components (at least 30% by weight), the plastic then has the same desirable thermoplastic properties but will decompose in soil or water [37]. The migration of these low molecular weight plasticisers could occur if placed in contact with food.

6.3 Polymers obtained by chemical synthesis, using monomers derived from petrochemical or biobased sources

6.3.1 Starting monomers and impurities

These polymers prepared by chemical synthesis do not in principle differ from non-degradable plastics covered already by the Plastics Directive. The level of residual monomer depends on the completeness of polymerisation and any clean-up steps that are used subsequently. Similarly, the purity of the starting monomer should not be a factor whether it was derived from a petroleum source or from a natural source such as a fermentation. The physico-chemical purification processes such as distillation or recrystallisation could still be used.

Taking PLA as an example, lactic acid can be produced by the fermentation of glucose. The sodium salt of lactic acid is then purified, concentrated and isolated using electrodialysis [38]. The monomer composition of PLA depends on the carbon source and the strain of microorganism used. The monomer exists as one of two optical isomers so the resulting polymer has different diastereoisomeric forms (meaning, has different chemical and physical properties). The ratio of D- to L- lactic acid determines the processing temperature, which is in the range of 60 to 125ºC.

Other starting substances obtained from natural sources for the synthesis of biodegradable polymers include castor oil used to make polyurethanes; oils & fats used to make alcohols, amines and esters; 1,3-propan-diol made by fermentation; and 1,4-butan-diol and adipic acid obtained from glucose. The suitability of each of these as starting substances for polymerisation, depends in part on the isolation and purification processes available.

6.3.2 The question of oligomers

Many of the biodegradable polymers are polyesters. They have the potential to form relatively large quantities of (cyclic) oligomers. For example, the 'traditional' plastic PET contains a cyclic trimer at ca. 1% w/w along with other oligomers in lower quantities.

PLA (II) is produced from lactic acid (I) by way of a cyclic intermediate, a cyclic dilactide.

$$\text{HO-CHMe-CO-OH} \quad \text{--->} \quad \text{H-(O-CHMe-CO-O-)}_n\text{-OH}$$

$$(I) \qquad\qquad\qquad\qquad (II)$$

Lactic acid

cyclic dilactide
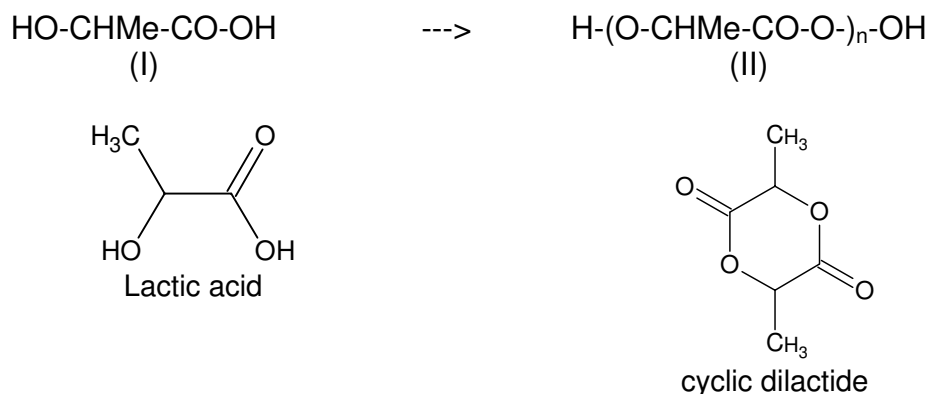
When PLA was tested for migration into 8% ethanol solution and olive oil, under test conditions of 10 days at 43ºC, the overall migration was 0.85 and 0.15 mg/dm^2 into the two simulants, respectively. The migrate comprised lactic acid, lactoyllactic acid (linear dimer), trimer, and lactide (cyclic dimer). The conclusion was that all the migrate was lactic acid after hydrolysis (i.e. *in vivo*) [39.]

In a second study, the overall migration from a PLA film was less than 1 mg/dm^2 into 3% acetic acid solution, 15% ethanol solution, and olive oil, under test conditions of 10 days at 40ºC, and into isooctane under conditions of 30 min at 40ºC.

6.3.3 Migration of additives
Annex 2 presents a case study of photodegradable plastic carrier bags which have a photodegradation catalyst or a degradable additive incorporated into the plastic. It is recognised that plastic carrier bags sometimes find secondary use by consumers, such as for gathering blackberries. For a typical catalyst incorporation of 200 parts per million the migration potential is the range 0.02 to 0.4 mg/kg food. For a typical additive incorporation of 3% by weight the migration potential is the range 8 to 150 mg/kg food.

PLA can be plasticised with monomeric or oligomeric LA, and made into blown films, injection moulded articles, coatings etc [4]. In the tests for overall migration mentioned above, the same authors commented that the choice of plasticiser depended on the end application intended [40]. Annex 3 presents a case study of a PLA sleeve used over a plastic yoghurt pot. In this type of application, migration from the sleeve into the yoghurt is unlikely.

6.3.4 Other breakdown products
Pre-treating films with uv radiation at 290 nm has been proposed as a means to promote subsequent compostability [41]. Irradiation in this way can be expected to break-down polymer chains, introduce oxidised functionalities (e.g. functional groups, C=O, -OH) and lead to an increase in overall migration and in the specific migration of polymer chain fragments.

6.4 Polymers obtained from microorganisms or genetically-modified bacteria

The main interest for migration from this type of biodegradable plastic is a feature shared with polymers that are formed *in situ* such as adhesives and internal coatings for metal cans. The issue is, that the possibilities to remove any impurities, reaction by-products etc are limited. Consequently, there may be a requirement for specifications along with a description of the manufacturing and purification processes used.

The archetypal polymer in this class are the PHAs. The carbon sources used to make PHAs include sugars, ethanol and methanol. In one process, used to make PHB, wastes from sugar cane (bagas) are hydrolysed to liberate free sugars. *Ralstonia eutropha* bacteria then feed on the sugars and transform them into intracellular granules that are polyesters. These are stored as an energy reserve, in the same way that mammals store fat. The PHB granules are extracted from the bacteria using an organic solvent and then made into pellets for production of materials and articles. No information is available on the likely impurities that may arise from this production route to PHB. However, it is informative to look at the specifications placed on another PHB produced by bacterial fermentation [42]. The legal specifications for a PHB/PHP copolymer are given in Annex 4. A specific migration limit is placed on the impurity crotonic acid and a purity requirement was placed on the raw copolymer prior to granulation, encompassing nitrogen, zinc, copper, lead, arsenic and chromium. It must be assumed that these may arise from the source material and/or the fermentation medium.

7. SUITABILITY OF STANDARD MIGRATION EXPOSURE TEST PROTOCOLS

7.1 Background

Migration tests, extraction tests and compositional tests, are used in the packaging sectors of paper, plastics, metals and ceramics. For example, the cornerstone test for plastics intended for room temperature applications is immersion in a liquid food simulant for 10 days. For ceramics it is extraction of the surface using 4% acetic acid in water. For paper and board materials, extraction with hot or cold water is employed or exposure to the dry food simulant modified polyphenylene oxide.

If biodegradable materials fall within the definition of plastics [42] then they should be tested as plastics.

> *"For the purposes of this Directive, 'plastics' shall mean the organic macromolecular compounds obtained by polymerisation, polycondensation, polyaddition or any other similar process from molecules with a lower molecular weight or by chemical alteration of natural macromolecules. Other substances or matter may be added to such macromolecular compounds"*

It is clear then, that each of the three types of biodegradable plastics defined earlier – natural polymers, modified natural polymers, and polymers made by chemical synthesis – fall within the definition of 'plastics' in the Plastics Directive. The Commission 'Practical Guide' also states that 'Biodegradable plastics are included in the field of application ' [43]. Therefore, biodegradable plastics would be required to meet limits on overall migration and on the specific migration of certain substances where appropriate.

Technical Committee 194 (TC194) of CEN (Comité Européen de Normalisation) deals with 'Utensils in contact with food'. In turn, SubCommittee (SC1) deals with Methods of test for plastics materials and articles intended for contact with foodstuffs [44]. CEN TC194/SC1 has a number of working groups and task groups responsible for a series of European Standard Methods, prepared under a mandate given to CEN by the European Commission and the European Free Trade Association. This being the case, the mandate means that there is a strict link between the development of standards and the European Union Directive on plastics.

7.2 Existing test methods

The guiding principle in the EC Directives on plastics, is that migration testing should mimic actual and foreseeable conditions of use, and this includes taking into account the physical state of the packaged food and the nature/extent of the contact [45, 46]. CEN/TC194/SC1 has prepared a series of standards. The EN 1186 series deals with overall migration and the EN 13130 series deals with specific migration. The procedures used to bring and maintain the plastic in contact with the food simulant, procedures used for both overall migration and specific migration, are described in the 1186 series of standards. These are listed in Annex 5.

Consequently, and to a first approximation, if biodegradable food contact materials are suitable for food contact then the test methods for plastics should be applicable to biodegradable too. If for example, during the standard exposure tests the material is found to degrade due to its biodegradability, and this does not occur when used under worst foreseeable conditions in contact with food, then the test conditions applied with food simulants are inappropriate and should be changed.

7.3 Problems with humidity-sensitive materials

Overall migration tests using simulant D (olive oil or its alternatives) are not possible with materials that are very moisture-sensitive. The solution is available already. 'Migration tests using olive oil or substitutes shall not be carried out to check compliance with the overall migration limit in cases where there is conclusive proof that the specified analytical method is technically inapplicable'.

7.4 Other test requirements?

Microbial abuse may occur via damage to materials designed for long shelf life aggressive foodstuffs, and biodegradable materials are prone to digestion by microorganisms. As biobased materials can be made of compounds which can be considered as food source such as starch and proteins, insect and rodent abuse may also have to be consideration for investigation and legislation [47].

7.5 Conclusion

For biodegradable polymers that are classed as plastics, the existing CEN test methods for migration from plastics will be applicable in the main. For biodegradable polymers that are not classed as plastics, it is unlikely that the CEN methods of test for plastics will be directly applicable. So, for example, different test methods are required for cellulosic materials such as paper and board.

8. FUTURE DEVELOPMENTS

At the present time products produced from maize starch are considered not to be acceptable to food retailers because of a perceived risk of the adventitious presence of genetically-modified maize in the imported feedstock. Additionally although the process technology could be adapted for wheat starch, warranted free from any genetically-modified presence, none of the UK plants is currently suitable for the production of food-grade packaging [48].

Perhaps the most significant factor influencing the uptake and usage of biodegradable food packaging polymers, could be the amendment to the RCF EU Directive [49]. New types of RCF are available which have a plastic coating and which are compostable and biodegradable. The new Directive [49] expands the range of functional surface coatings permitted. The Directive recognises that, since the layer in contact with foodstuffs consists of a plastic material, then the rules provided for testing plastics should be applied to these plastic-coated RCF materials too. This includes using the list of food simulants along with the conditions of time and temperature of test. These plastic-coated RCF films have the potential to expand the range of packaging applications for biodegradable RCF beyond the limited uses for dry foods found to date. So RCF may experience a resurgence in use. It may also be significant that existing producers of RCF films, and of the coating plastics that are now permitted, are experienced in the special ramifications of making 'food-grade' materials and this would not be a significant barrier to them entering the marketplace.

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ANNEX 1. CASE STUDY. FUMONISINS

Fumonisins are environmental toxins produced mainly by the moulds Fusarium moniliforme (F. verticillioides), F. proliferatum, and several other Fusarium species that grow on agricultural commodities in the field or during storage [50]. These mycotoxins have been found worldwide, primarily in corn. More than ten types of fumonisins have been isolated and characterized. Of these, fumonisin B1 (FB1), B2 (FB2), and B3 (FB3) are the major fumonisins produced. The most prevalent of these mycotoxins in contaminated corn is FB1, which is believed to be the most toxic [51, 52].

Fumonisins have been shown to cause liver and kidney damage in animals after long-term exposure and it is possible that they could have the same effect on humans. The SCF has recommended that a group TDI of 2 ug/kg bw/day for fumonisins B1, B2 and B3, alone or in combination, could be applied [53]. While there is no limit for fumonisins in food currently, the European Commission (EC) has proposed a limit of 0.5 mg/kg. In a recent survey, the FSA reported that two products of maize meal containing 4.7 and 20.4 mg/kg fumonisins had been withdrawn from sale as a precaution, although there was unlikely to be any immediate risk to health [54].

In a review of 25 surveys conducted worldwide, of food, feed and maize in general trade, there was a high incidence of detectable FB1 [55]. The maximum levels were in the range 0.5 to 330 mg/kg and the mean values were in the range 0.1 to 63 mg/kg. The highest reported samples were associated with observed toxicity effects in man or animals. Fumonisins levels in randomly-selected good quality maize are generally much lower than in maize samples associated with human or animal health problems. For 1,300 samples of US maize collected from 1988-1995 the maxima were 5 to 38 mg/kg and the means were 1 to 3 mg/kg. For other countries, levels up to ca. 10 mg/kg have been reported. Disease symptoms in animals are usually observed at FB1 levels of 5 to 10 mg/kg [55].

Data indicate that this process results in fumonisin- containing fractions in descending order of highest to lowest fumonisin levels: gluten, fibre, germ, and starch [56]. No fumonisins have been detected in the starch fraction obtained from wet milling of fumonisin contaminated corn. The starch fraction is further processed for the production of high fructose corn syrups and other corn sweeteners [56]. Therefore, these types of products do not contain any detectable levels of fumonisins [see Appendix 1 for more details].

Scenario 1
Parameters used
  a) Maize containing 10 mg/kg FB1 with no reduction in processing to produce a biodegradable plastic.
  b) Plastic density = 1
  c) 1kg food in intimate contact with 600 cm^2 of packaging
  d) 100 % migration from a 0.25 mm layer (15 g layer of plastic)
  (Fumonisins are large molecules with a 20-carbon atom chain, and so extensive migration by a diffusion mechanism is unlikely)

- Worst-case migration potential = 10 * 15/1000 = 0.15 mg/kg food.

<u>Scenario 2</u>
Parameters used
  a) Maize containing 10 mg/kg FB1 with no reduction in processing to produce
  a biodegradable material similar to paper and board..
  b) Fibrous material density = 0.5
  c) 1kg food in intimate contact with 600 cm^2 of packaging
  d) 100 % migration from a 1 mm layer (30 g layer of fibrous material)

- Worst-case migration potential = 10 * 30/1000 = 0.30 mg/kg food.

ANNEX 2. CASE STUDY. PHOTODEGRADABLE PLASTIC CARRIER BAGS

When used in food shops and supermarkets, plastic carrier bags are intended for carrying pre-packaged foods and non-packaged foods such as fruit and vegetables (in their skins) along with dry foods especially bread loaves. It is possible however, that these bags may be used in more intimate contact with foodstuffs in the home. Carrier bags claimed to be photodegradable or biodegradable are available for supermarket use.

Scenario 1
Parameters used
  a) a typical plastic carrier bag is 10 g in mass, 32 dm^2 in total area and the plastic film is ca. 35 um thick.
  b) assume that a photodegradation catalyst is incorporated in the plastic at 200 ppm (200 ug/g plastic).
  c) assume that the carrier bag was used for example to gather blackberries, with a mass to contact area ratio of 1 kg to 6 dm^2 (e.g. 2.5 kg fruit, half-filling the bag).
  d) assume that the acidic fruit extracts

  e) 100% of the photodegradation additive
• The migration would be 0.4 mg/kg.

  f) 5% of the photodegradation additive
• The migration would be 0.02 mg/kg.

Scenario 2
One company's literature [57] says that for their degradable carrier bags, patented additives are incorporated to allow time-controlled total degradation of the plastic material leaving only water, a minimal amount of carbon dioxide and biomass. They say that the degradable bags are made from "normal" polyethylene but also contain 3% by weight of a proprietary patented oxo-biodegradation technology material called TDPA (Total Degradable Plastics Additive). Further, that the technology has been independently tested and proven to be environmentally safe, leaving no toxic substances at the end of the degradation process, and has been tested as safe for direct food contact under EU standards (no further details given).

Parameters used
a) the degradation additive is incorporated in the plastic at 3% w/w
b) assume that the carrier bag was used for example to gather blackberries, with a mass to contact area ratio of 1 kg to 6 dm^2 (e.g. 2.5 kg fruit, half-filling the bag).
c) assume that the acidic fruit extracts

d) 100% of the degradation additive
• Then the migration would be 150 mg/kg.

e) 5% of the degradation additive
• Then the migration would be 7.5 mg/kg.

ANNEX 3. CASE STUDY. A PLA SLEEVE OVER A YOGHURT POT

It has been observed that some yoghurt pots come with a polylactic acid (PLA) sleeve. The sleeve carries printing. Migration from the sleeve into the yoghurt is considered to be unlikely because:

a) the pots with their sleeve applied are unlikely to be stacked, and so set-off from the printed surface onto the inner, food contact surface, would not occur;

b) the product has a short shelf life at refrigerated storage temperature

c) the primary packaging, which is polystyrene but which could also be polypropylene, will provide a reasonable barrier to migration under these storage conditions.

ANNEX 4. SPECIFICATIONS FOR A PHB/PHP COPOLYMER

Products obtained by means of bacterial fermentation

Annex iv *
Products obtained by means of bacterial fermentation

Ref. No	CAS No.	Name	Restrictions and/or specifications
(1)	(2)	(3)	(4)
18888	080181-31-3	3-Hydroxybutanoic acid-3-hydroxypentanoic acid, copolymer	SML = 0.05 mg/kg for Crotonic acid (as impurity) and in compliance with the specifications laid down in Annex V

3-Hydroxybutanoic acid-3-hydroxypentanoic acid, copolymer

Definition
The copolymers are produced by the controlled fermentation of Alcaligenes eutrophus cepa using mixtures of glucose and propanoic acid as carbon sources. The organism used has not been genetically engineered and has been derived from a single wild-type organism Alcaligenes eutrophus strain HI6 NCIMB 10442.Master stocks of the organism are stored as freeze-dried ampoules. A submaster/working stock is prepared from the master stock and stored in liquid nitrogen and used to prepare inocula for the fermenter. Fermenter samples will be examined daily both microscopically and for any changes in colonial morphology on a variety of agars at different temperatures. The copolymers are isolated from heat treatment bacteria by controlled digestion of the other cellular components, washing and drying. These copolymers are normally offered as formulated, melt formed granules containing additives such as nucleating agents, plasticisers, fillers, stabilisers and pigments which all conform to the general and individual specifications.

Chemical name. Poly(3-D-hydroxybutanoate-co-3-D-hydroxypentanoate)
CAS number. 80181-31-3
Structural formula. $-[O-CH(CH_3)-CH_2-CO]_m-[O-CH(CH_2CH_3)-CH_2-CO]_n-$
where $0 < n/(m+n) </= 0.25$. i.e. the co-monomer n is less than 25% of the total monomer content (m+n).
Average molecular weight. Not less than 150 000 Daltons (measured by gel permeation chromatography).
Assay. Not less than 98% poly(3-D-hydroxybutanoate-co-3-D-hydoxypentanoate) analysed after hydrolysis as a mixture of 3-D-hydroxybutanoic and 3-D-hydroxypentanoic acids.
Description. White to off-white powder after isolation

Characteristics

Identification tests:

<u>Solubility</u>. Soluble in chlorinated hydrocarbons such as chloroform or dichloromethane but practically insoluble in ethanol, aliphatic alkanes and water.

<u>Migration</u>. The migration of crotonic acid should not exceed 0.05 mg/kg food.

<u>Purity</u>. Prior to granulation the raw material copolymer powder must contain;

Nitrogen Not more than 2500 mg/kg of plastic

Zinc Not more than 100 mg/kg of plastic

Copper Not more than 5 mg/kg of plastic

Lead Not more than 2 mg/kg of plastic

Arsenic Not more than 1 mg/kg of plastic

Chromium Not more than 1 mg/kg of plastic

* Corrigendum to Commission Directive 2002/72/EC of 6 August 2002 relating to plastic materials and articles intended to come into contact with foodstuffs. (Official Journal of the European Communities L 220 of 15 August 2002)

ANNEX 5

Standard methods used to test plastics for migration.

EN 1186 Materials and articles in contact with foodstuffs – Plastics-

Part 1. Guide to the selection of conditions and test methods for overall migration

Part 2. Test methods for overall migration into olive oil by total immersion

Part 3. Test methods for overall migration into aqueous food simulants by total immersion

Part 4. Test methods for overall migration into olive oil by cell

Part 5. Test methods for overall migration into aqueous food simulants by cell

Part 6. Test methods for overall migration into olive oil using a pouch

Part 7. Test methods for overall migration into aqueous food simulants using a pouch

Part 8. Test methods for overall migration into olive oil by article filling

Part 9. Test methods for overall migration into aqueous simulants by article filling

Part 10. Test methods for overall migration into olive oil (modified method for use in cases where incomplete extraction of olive oil occurs)

Part 11. Test methods for overall migration into mixtures of ^{14}C-labelled synthetic triglyceride

Part 12. Test methods for overall migration at low temperatures

Part 13. Test method for overall migration at high temperatures

Part 14. Test methods for 'substitute tests' for overall migration from plastics intended to come into contact with fatty foodstuffs using test media iso-octane and 95 % ethanol

Part 15. Alternative test methods to migration into fatty food simulants by rapid extraction into iso-octane and/or 95% ethanol

APPENDIX 1 (background information for ANNEX 1)

OCCURRENCE OF FUMONISINS IN PROCESSED CORN PRODUCTS

One of the major factors that determines the level of fumonisins in processed corn products is whether a dry- or wet-milling process is used. The whole corn kernel consists of the following major constituents:

- Starch - the most abundant constituent from which corn starches and corn sweeteners are produced
- Germ - located at the bottom of the center of the kernel from which corn oil is produced
- Gluten - contains the majority of the protein found in corn kernel
Hull (Pericarp) - the outer coat of the kernel from which corn bran is produced

Dry milling of whole corn kernel generally results in the production of fractions called bran, flaking grits, grits, meal, and flour. Because the fumonisins are concentrated in the germ and the hull of the whole corn kernel, dry milling results in fractions with different concentrations of fumonisins. For example, dry milled fractions (except for the bran fraction) obtained from degermed corn kernels contain lower levels of fumonisins than dry milled fractions obtained from non- degermed or partially- degermed corn. Industry information indicates that dry-milling results in fumonisin-containing fractions in descending order of highest to lowest fumonisin levels: bran, flour, meal, grits, and flaking grits. Consequently, corn products such as corn bread, corn grits, and corn muffins made from the grits and flour fractions may contain low levels of fumonisins. Ready-to-eat breakfast cereals made from flaking grits, such as corn flakes and puffed type cereals, contain very low levels (non-detectable to 10 parts per billion (ppb)) of fumonisins (Stack and Eppley, 1992).

Data provided by the North American Millers' Association (NAMA) accumulated over two crop years (1997 and 1998) indicate that degermed corn meal in the U. S. has a mean level of total fumonisins of 0.15 parts per million (ppm) (Standard Deviation (SD) = 0.50). The mean levels of total fumonisins in corn meal prepared from partially degermed and whole non-degermed corn were 0.59 ppm (SD = 1.01) and 1.21ppm (SD = 1.71), respectively, according to NAMA data.

Wet milling of whole corn generally results in the production of fractions called starch, germ, gluten, and fiber. Data indicate that this process results in fumonisin- containing fractions in descending order of highest to lowest fumonisin levels: gluten, fiber, germ, and starch (Bennett and Richard, 1996). No fumonisins have been detected in the starch fraction obtained from wet milling of fumonisin contaminated corn. The starch fraction is further processed for the production of high fructose corn syrups and other corn sweeteners (Bennett and Richard, 1996). Therefore, these types of products do not contain any detectable levels of fumonisins. Corn oil, extracted from corn germ and refined, does not contain any detectable levels of fumonisins (Patel et al., 1997). The gluten and fibre fractions from the wet-milling process do contain

fumonisins; however, these fractions are used to produce animal feed, such as corn gluten meal and corn gluten feed.

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