An inventory of fibres to classify their potential hazard and risk

Prepared by the **Health and Safety Laboratory**
for the Health and Safety Executive 2006

RESEARCH REPORT 503

HSE
Health & Safety Executive

An inventory of fibres to classify their potential hazard and risk

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Although there is considerable knowledge of the hazards and risks of asbestos and machine made vitreous fibres (MMVF), there are many other fibre types in production and use. These include: synthetic, some semi-synthetic fibres (eg cellulosic fibres) which are sometimes referred to as machine-made (or man-made) organic fibres (MMOFs) and also a range of other non-organic fibres and whiskers and specialist technical fibres including various types of carbon fibres and nanofibres. This project was designed to carry out an audit of these "other" fibres based either on available data or by making a series of measurements of their physical dimensions, properties and behaviour. This included bench scale assessments of the solubility and dustiness, if the fibres were found to be small enough to be inhalable.

The data generated was used to identify fibres that may potentially be hazardous or give rise to a risk and merit further investigation. Available published information on the toxicity of specific fibres was also collected and organised along with the physical and descriptive data in a Microsoft Access database. This report summarises the types of fibres in use or close to market, the manufacturing processes and the methods used for data collection and physical characterisation.

It was found that the new technologies which allow the production of much finer conventional fibres that can be used on existing textile machinery, along and the many high performance technical fibres and textiles in production, are of concern.

This report and the work it describes were funded by the Health and Safety Executive (HSE). Its contents, including any opinions and/or conclusions expressed, are those of the authors alone and do not necessarily reflect HSE policy.

HSE BOOKS

First published 2006

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EXECUTIVE SUMMARY

OBJECTIVES

a) Gather data on current fibre types in production and their use.

b) To establish a test strategy and operating procedures to measure the relevant physical characteristics, on selected fibre types where data is lacking.

c) To make an initial indicative assessment of the likely hazard or risk based on suppliers / manufacturers information and published data / reviews.

d) To generate new data using the methods in 2) for fibres about which little is known.

e) To produce an inventory of fibres in the form of a database and an internal report to summarise there potential hazard or risk.

MAIN FINDINGS

Overall the worldwide production of fibres is continuing to increase. The production and use of synthetic (oil based) fibres continues to expand rapidly and has overtaken the production of natural animal and plant fibres. Semi-synthetic fibre made from processing natural materials has also expanded but the development of speciality fibres and processes offer new materials and new hazards.

The perception of textiles of consisting of relatively large fibres with little health risk from the fibres themselves is still largely valid for natural fibres and many familiar synthetic fibres. This is due to the fibre sizes that can be handled by conventional textile machinery are typically above 10 µm diameter and cannot readily penetrate into the pulmonary regions of the lung.

One exception appears to be during flock manufacture of synthetic fibres using worn rotary cutters or potentially during the recycling of the fibres, where slivers of the fibres of finer widths are produced and may enter the lung and produce interstitial fibrosis.

In the development of more silk-like, smooth, soft textiles, ever-finer fibres are being produced and due to their low density and aerodynamic behaviour are respirable at diameters larger than traditionally considered respirable.

The development of bi-component fibres where a textile-sized fibre is produced but consists of many smaller fibrils bonded together, allows finer fibres to be processed in the conventional way to manufacture textiles. The finished article is then chemically or mechanically treated to separate the fibrils from the fibres, which creates a softer smoother surface but means the fibres are now readily respirable, should they be released to the air due to secondary manufacturing processes, recycling or use.

Nonwoven products do not have a size limitation for processing and increasingly use respirable diameter fibres. The production of filter media is one area where direct production of fine fibres by meltblowing and now electrospinning, is likely to be widely used. The fibres are still long

which will limit their respirability but any processing or secondary use that will break the fibres, will increase their potential become respirable.

Technical textiles, smart fibres and medical fibres represents a group of specialised products which are enhanced by the addition of specialist coatings or cores that contain a wide range of added materials other than the fibre polymer to enhance properties. These may also affect the toxicity of the fibres.

The development and production of nanofibres and nanotubes represents a significant increased in the potential of fibres to reach the lung and other organs.

The mechanical grinding test carried out showed that a significant number, 15 of the 68 synthetic fibres (and some natural fibres) tested, had an ability to fibrillate and break down into fine respirable fibres.

The dustiness test is a more suitable test to estimate the risk of release of fine fibres. The medium value for respirable fibre release during dustiness testing for the polyacrylonitrile flock was a surprise and many of the fibres looked like slithers shaved off the fibre. It is unlikely this could be due to tumbling in the drum and must have been present in the flock. The Kevlar pulp and metal fibres also gave low levels of respirable fibre release.

The solubility test showed that the fibres tested had very limited solubility in modified Gamble's solution and had a potential to remain in the lung. However, the biosolubility of some of these fibres in the lung may be substantially different and the solubility test should be regarded as an initial assessment and whether in-vivo assessment is required.

The database collates available information and provides a useful resource to determine the known health hazards associated with a range of existing fibres.

The test data is aimed at identifying the dimensions, durability/solubility, dose and dustiness, which are useful predictors of lung related health hazards and risks. However, the processes of fibre carcinogenicity are still not well-defined and the hazard and risk may also be modified by the surface chemistry, surface structure and chemical composition.

RECOMMENDATIONS

The current advances in technology reviewed in this report show that there is a continued need to monitor the new fibre technologies as they are introducing fine respirable, non-soluble fibres into many new and traditional products. As these fibres are often made or based on existing fibre types these would not be notified or tested under the Notification of New Substances Regulations.

1 INTRODUCTION

1.1 AIM

The aim was to identify the main types of fibres that are currently in use or in development, and by using available data or measurements of their physical characteristics, to rank their potential hazard and risk.

1.2 METHOD AND OBJECTIVES

The project as conceived, was to apply the knowledge base from the considerable experimental work carried out to investigate and explain the epidemiology and toxicology of asbestos and man-made vitreous fibres (MMVF), to other fibres types. This would take the form of an audit of the physical dimensions, properties and behaviour of other fibre types to generate a database that would help identify fibres that may potentially be hazardous or give rise to a risk and may be worthy of further investigation. Available published information on the toxicity of specific fibres would also be collected and placed on the database.

The initial starting objective was to carry out a product and literature search of the fibres types currently manufactured or in use and for any information on the product in terms of physical characteristics and health effects/ hazard classification. The other main objectives were:

- To establish a test strategy and operating procedures to measure the relevant physical characteristics on selected fibre types where data is lacking.
- To make an initial indicative assessment of the likely hazard or risk based on suppliers / manufacturers information and published data / reviews.
- To generate new data using the methods for fibres about which little is known.
- To produce an inventory of fibres in the form of a database and an internal report to summarise their potential hazard or risk.

1.3 SCOPE

There are many fibres in use and it was well beyond the funding given to this project to consider all fibres and the industries where they are used. Of particular concern are fibres with diameters of <3 µm, which can reach the pulmonary regions of the lung (respirable fibres). Although fibres (up to 20 µm diameter) can theoretically deposit in the thoracic region of the lung and may potentially be of concern, it is the finer diameter respirable fibres that are generally acknowledged to be most important predictor of hazard and risk for cancers of the lung.

It was not intended to further review the knowledge base for mineral and MMVF's as these have already been subject to detailed assessment and classified by various agencies and systems e.g. EU, US EPA, IARC, WHO for their potential carcinogenicity. Also a substantial amount is also known about the health risks from working with traditional natural plant and animal fibres.

In this audit we wanted to focus on the potential for carcinogenic and fibrogenic hazards and risks from other machine-made (or man-made) fibres (MMFs). These include: synthetic, some semi-synthetic fibres (e.g. cellulosic fibres) which are sometimes referred to as machine- made (or man-made) organic fibres (MMOFs) and also a range of other non-organic fibres and whiskers and specialist technical fibres including various types of carbon fibres and nanofibres. The report also reviews and horizon scans the recent advances and trends towards the production of finer MMFs with an aim to locating where problems may arise.

2 BACKGROUND

2.1 DEVELOPMENT OF MMFS

The early development and production of machine made fibres can be divided into three main types, based on the starting materials: silicate minerals, cellulose and oil.

The possible production of MMFs was first described in 1665 by Robert Hooke in his book " Micrographia or some physiological descriptions of minute bodies" where he described the idea of producing artificial silk from a gelatinous mass.

The mid 19th century saw the development of glass mineral fibres and by 1842 Louis Schwabe, a Manchester based woven silk fabric manufacturer, exhibited glass yarns and woven glass yarn fabrics at the British Association in Manchester. Schwabe produced his yarns by pressing molten glass through the fine orifices of a kind of spinneret. This technique has been the principle method for MMF production and only recently have significant changes or advances to the basic spinneret design and manufacture been made.

The practicalities of producing synthetic “silk” fibres started with Schönbein’s experiments in Basel in 1846, with cotton treated with nitric and sulphuric acid, inventing nitrocellulose, which he called gun cotton. In 1848 he treated the gun cotton with alcohol and ether, putting it into solution producing the substance with which he later spun the first artificial silk. Chardonnet started trials in 1878 for producing artificial silk from dissolved nitrocellulose and Joseph Swan injected dissolved nitrocellulose into an alcohol bath to produce monofil yarns and patented his process (Brit. Patent No. 5978 of 31.12. 1883). Swan was the first to succeed in denitrifying nitro-yarns, thereby eliminating their explosive tendency, and exhibited a number of small tablecloths and napkins crocheted from his artificial silk fibres at the London Exhibition of Inventions in 1885. Count Chardonnet submitted the description of a process for producing artificial nitro-silk to the Academy of Sciences in 1884 and was granted the first of his 48 artificial silk patents. At the World Exhibition in Paris (1889) Chardonnet introduced the first artificial silk spinning machine and the first fabrics from artificial nitro-silk.

Slightly later but rather more rapidly, the technology to produce semi-synthetic fibres based on cellulose was being developed. In 1862 Ozanam, describes the production of cellulose fibres by means of spinnerets and in 1875 Mitscherlich invented the sulphite cellulose process. The Lönsberger Hütte cellulose factory started production in 1879.

2.2 CLASSIFICATION OF FIBRES

2.2.1 Classification by type and chemistry

There are many fibre classifications systems that have been published (e.g. see figure 1). The variations are usually due to the interest of the industry, group or person applying the classification and the use of slightly different terminology. The development and production of new fibre types is also a driver for reclassification. As this is report is primarily concerned with the potential health effects of fibres, the International Agency for Research on Cancer (IARC) classification has been used in this report, although it has been adapted and updated to take account of some of the newer fibres developed since its publication. IARC is clearly focussed on the carcinogenic hazards and risks of fibres (mortality) rather the morbidity effects such as coughs, fevers, allergic reactions, reduction in lung functions, asthma etc.

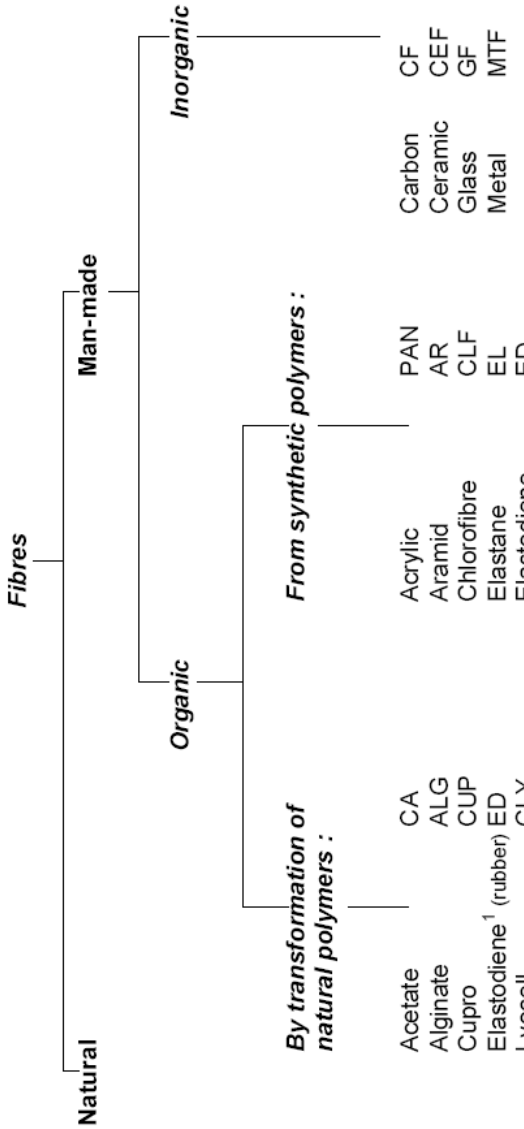


Figure 1: Example of fibre classification and common abbreviations for production fibres.

2.2.2 Modified IARC classification

The listings below are essentially an extension of the International Agency for Research on Cancer (IARC) listings for fibres. The IARC classifications group has also been given. Group 1 is carcinogenic to humans. Group 2 is used when it is found to be carcinogenic in animal experiments (the number of species and type of in-vivo test will decide whether it is 2A) probably carcinogenic to humans or 2B) possibly carcinogenic to humans). Group 3 are not classifiable as to their carcinogenicity to humans. IARC (see various IARC references) has only reviewed a small number of the fibres listed. A forthcoming workshop in September 2005 is to look at a number of fibres for assessment (or mainly reassessment). An asterisk identifies these fibres; high priorities for assessment have been given two asterisks. The classification where assigned has been given in brackets.

NATURAL FIBRES

I(i) Mineral fibres:

- Asbestos fibre (chrysotile, amosite, crocidolite, anthophyllite, tremolite, actinolite(Group 1)
- Other amphibole fibres occurring in the asbestos habit (e.g. Richterite, edenite etc.)
- Wollastonite (columnar structure; can be reduced to acidular particles – Group 3)
- Palygorskite (attapulgite**): hydrated magnesium aluminium silicate (fibres > 5µm length: Group 2B and fibres < 5 µm length: Group 3)
- Sepiolite: hydrated magnesium silicate (Group 3)
- Halloysite
- Sericite mica (partially fibrous)
- Erionite*: fibrous component of some zeolite deposits (Group 1)

I(ii) Plant fibres:

- Jute, hemp, sisal, bamboo, cotton, flax, etc.

I(iii) Animal fibres:

- Wool, angora, silk etc.

II SEMI-SYNTHETIC FIBRES

II(i) Inorganic material based:

Continuous glass filament fibres (Group 3 with exception):

- AR glass fibres: Mg, Na, Ti, Zr
- A glass: soda lime glass high silica content
- C glass: high silica chemically resistant
- E glass: borosilicate (Group 2B)
- ‘475’ glass fibres (Group 2B)
- S glass: high silica + high Al2O3-Fe2O3

Mineral wool fibres (Group 3):**
- Glasswools , slagwools, rockwools

Ceramic or refractory fibres (Group 2B):**
- fibres based on silicon, alumina, zirconia and boron
- fibres based on Ca, Mg, Al, and silica
- alumino silicate fibres
- pure alumina or pure zirconia
- silica fibres
- boron fibres
- Silicon carbide fibres and whiskers*
- potassium titanate fibres*
- aluminium oxide fibres
- alumina boria silica fibres (Nextel)
- boron fibres
- magnesium sulphate*.

Alkaline earth silicate refractory fibres **(Group 3):

- high temperature fibres with limited biopersistence due to greater amounts of Mg and Ca in glass networks with compositions similar to Wollastonite.

Metallic fibres:
- steel*, ductile iron, Cu wool fibres and various other pure metals and metal alloys.

II(ii) Natural polymer based:

Regenerated cellulose derivatives:
- Viscose / rayon
- Cuprocellulose
- Cellulose acetate
- Cellulose triacetate

Regenerated Protien fibres
- Peanut
- Corn
- Soyabean
- Milk

III SYNTHETHIC FIBRES (Based on petrochemical polymers)
(including common trade name and fibre polymer abbreviation and composition)

III(i) Synthetic polymer fibre:

Polyamide:
aliphatic:
- PA6 (Perlon)
- PA6.6 (Nylon: $(-NH-CO-(CH_2)_4-CO-NH-(CH_2)_5-)_n$)

- PA11 (Rilsan)

*wholly aromatic Aramid** and Para-aramid**:*
- Poly(p-phenyleneterephtalamide) (Kevlar, Twaron: (-NH-Ar-CO-Ar-CO-)$_n$) (Group 3)
- Poly(m-phenylenediphenyletherephtalamide) (Nomex)
- Copoly(p-phenylenediphenyletherterephtalamide) (Technora)

aliphatic-aromatic / aromatic heterocyclic polyamides

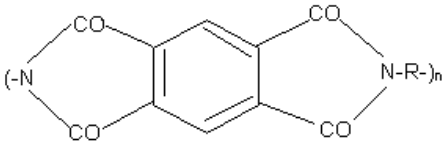
Polyester:
- Polyethyleneterephtalate (PET) (Trevira, Diolen: (-O-CO-Ar-CO-O-(CH_2)$_2$-)$_n$)
- Polytrimethyleneterephtalate (PTT or PTMT)
- Vectran (*aromatic polyester*)

Polyolefine:
- Polyethylene** (Spectra, Trofil: (-CH_2-CH_2-)$_n$)
- Polypropylene** (PP) (Herculon: (-CH(CH_3)-CH_2-)$_n$)
- ES (bicomponent of polyethylene + polypropylene)

Polyvinyl:
- Polyacrylonitril (PAN) (Orlon, Dralon: (-CH(CN)-CH_2-)$_n$)
- Polyvinylchloride** (PVC) (Fibravyl, Leavil: (-CH(Cl)-CH_2-)n)
- Polyvinylalcohol **(PVA) (Kuralon: (-CH(OH)-CH_2-)n)

Polyurethane:
- (Lycra, Dorlastan: (-NH-R_1-NH-CO-O-R_2-OCO-)$_n$)

Polyimide:
aliphatic-aromatic / wholly aromatic / heterocyclic



- polyimide 2080
- polybenzimidazolimide

Polyimidazole:
- Polybenzimidazole:

aliphatic
wholly aromatic:
- poly(2,2'-m-phenyllene-5,5'-benzimidazole) (PBI)

Polythiazole:
- polybenzobisthiazole (PBT)

Polyoxazole:
- polybenzobisoxazole (PBO)

- AB type polybenzoxazole (AB PBO)

Polyhydrazide
(-(NHNH-CO-Ar-CO-))
(-(NHNH-Ar_1-NHNH-CO-Ar_2-CO-))

Polyazomethine
(=(N-Ar_1-N=CH-Ar_2-CH)=)

III(ii) Carbon fibres

Over 99% pure carbon produced by pyrolysis
- PAN-based carbon fibres (Magnamite, Celilon)
- Pitch-based carbon fibres (Thonel)
- Rayon-based carbon fibres
- Graphite fibres

IV NANO FIBRES (Sub-micrometre fibres)

Carbon nanotubes
Carbon nanofibres
Vapour grown carbon fibres

V TRANSGENIC BIOENGINEERED FIBRES

Transgenic spider's silk fibres (Nexia Biosteel and Protexi)

2.2.3 Classification by use

Traditional textile apparel and fibres for use in tyre and carpets represent a large proportion of the market for the MMFs produced. However the development of fibre technology is such that whole new areas of use and markets have opened up. A general term "technical textiles" has been applied to the new types and uses for fibres and the industry groups involved have applied a system of classification by use. Although these are essentially for marketing, it is useful to talk about the industry sectors, which are driving advances in fibre design and development in specific directions.

The fibres produced and used for technical textiles may be based on common MMF fibres but may be treated or enhanced to give new properties and uses. Often the technical textiles are used in high performance materials and clothing and smart fibre technologies.

The sectors in current use for technical textiles by TechTextil Gmbh are:

Agrotech	Hometech	Oekotech
Buildtech	Indutech	Packtech
Clothtech	Medtech	Protech
Geotech	Mobiltech	Sporttech

2.3 NOMENCLATURE AND UNITS OF MEASUREMENT

The number of fibre types and the various origins of the industry, mean that the nomenclature can be quite difficult and varies between industries and countries. Publications of Dictionaries on the WWW (Celanese Acetate, 2001) are helpful in finding the way around the terminology used by different industry sectors.

The nomenclature used for the length of the fibres, increases from flock to staple fibres to filaments. Flock is defined as "very short fibres intentionally produced for other purposes than spinning"; staples as "a textile fibre of limited but spinnable length" and a filament as "a fibre of very great length considered as continuous". Yarn is used as a general term for one or more long textile strands and tow is used for a large strand of continuous manufactured fibre filaments without definite twist, collected in loose, rope-like form, usually held together by crimp.

One of the more difficult areas for terminology is the units of measurement of the fibres as the industries still uses a range of traditional and metric units. From the health perspective the diameter of the fibres in micrometres (10^{-6} m) is the main unit of concern but this is rarely used. However, the width and length of fibres are important for their commercial and industrial use.

A tex is the metric unit for expressing linear density, equal to the weight in grammes of 1 KM length of yarn, filament, fibre or other textile strand.

A decitex = 0.1 tex (or the weight in grammes of 10 KM length of yarn, filament, fibre or other textile strand).

A kilotex = 1000 tex (or the weight in grammes per metre)

1tex = 1000 Nm (where Nm = metres/g)

1 tex = 9 denier = 11.284 um diameter filament with a density of 1000 kg/m3

Animal, plant and mineral fibres had to be a few centimetres long to be able to be manufactured into woven textiles by carding, spinning and weaving, although non-woven processes were also used for the production of felts. The introduction of semi synthetic and synthetic fibres produced by a spinneret meant that the product was essentially continuous fibres and yarns so the units of measurement (or titre) used were based the weight per length or linear density. Different parts of the industry use different titres and the attempt to impose a single metric unit (tex) have not been successful.

EU filament yarn manufacturers use decitex and tow manufacturers (many yarns gathered together) use kilotex. However, manufacturers of staple fibres (cut yarns and tows usually a few cm long) and spun yarns use the metric number (Nm), which indicates the length of the yarn in metres per gram.

However, the US, a number of non-EU countries and many manufacturers use the Dernier system. Denier is a direct numbering system in which the lower numbers represent the finer sizes and the higher numbers the coarser sizes. In the U.S., the denier system is used for numbering filament yarns (except glass), manufactured fibre staple (but not spun yarns), and tow.

US measurements and terms

DENIER: the number of unit weights of 0.05 grams per 450-meter length.
(This is numerically equal to the weight in grams of 9,000 m of the material i.e. 0.9 dtex).

Denier per Filament (dpf): The denier of an individual continuous filament or an individual staple fibre if it were continuous. In filament yarns, it is the yarn denier divided by the number of filaments.
Yard Denier: The denier of a filament yarn. It is the product of the denier per filament and the number of filaments in the yarn.
Denier per Filament (dpf): The denier of an individual continuous filament or an individual staple fibre if it were continuous. In filament yarns, it is the yarn denier divided by the number of filaments.
Yard Denier: The denier of a filament yarn. It is the product of the denier per filament and the number of filaments in the yarn.
Total Denier: The denier of a tow before it is crimped. It is the product of the denier per filament and the number of filaments in the tow. The total denier after crimping (called crimped total denier) is higher because of the resultant increase in weight per unit length.
Denier variation: Usually variation in diameter, or other cross-sectional dimension, along the length of a filament or bundle of filaments. It is caused by malfunction or lack of process control in fibre manufacturing and degrades resulting fabric appearance or performance.

As the units of measurement are based on the linear density of the fibre this does not make clear what is the actual diameter of the fibre. This will depend on the density of the final fibre and the finishing processes that have taken place. To potentially add to the confusion a number of terms to describe the fineness of the fibres have been adopted by different sections of the industry and the approximate micrometre equivalents are given below:

Ultrafine fibres are ≤ 0.3 denier or 0.33 dtex diameter (about ≤ 7µm diameter).
Micro fibres are 1 to 0.3 denier diameter or 1.1 to 0.33 dtex (about 10 to 8 µm diameter).
Fine fibres are 2.2 to 1 denier diameter or 2.4 dtex to 1.1 dtex (about 13 to 10 µm diameter).
Regular fibres are 6.3 to 2.2 denier diameter or 7.0 to 2.4 dtex (about 25 to 13 µm diameter).
Coarse fibres are > 6.3 denier or 7.0 dtex diameter (about >25 µm diameter)

micro-sized (1-10 µm
nano-sized (<1 µm)

To make an exact conversion the density of the filament/fibre is required:

$$\text{Diameter of filament } (\mu m) = 2.\sqrt{100\,.\,\text{titre in dtex.}\,\text{density}/\pi}$$

2.4 PRODUCTION, USE AND TRENDS

In 2003, the world-production of man-made fibres was 35.1 million tons compared to 22.6 million tons of cotton, wool and silk fibre. The production of cellulosic man-made fibres was 2.8 million tons, that of synthetic man-made fibres 32.3 million tons. The Far East is the dominant producer with a 73% share in world-production. The USA has a share of 12%, Japan 4% and Western Europe 11%. In Western Europe, the man-made fibre production was about 3.5 million tons. In 2004 there was a 6.7 % increase in world fibre production to a total of 67 million tonnes of which 37.9 million tonnes (56%) was MMFs, 24.1 million tonnes (36%) was cotton, wool and silk, the remaining 5 million tonnes (8%) being other natural fibres including 3.2 million tonnes of cellulosic fibre. The end of trade quotas from the beginning of 2005 has open the world market to increased competition and MMF production, especially from China, where new plant is being installed and may saturate some areas of the market.

The principle uses by percentage of fibres in 2003 is given in table 2. Technical textiles are increasing their share of the market and high cost producers are turning to these innovative niche markets because of competition for conventional fibres. It is already estimated that in Japan, technical textiles account for over half of all the MMFs produced (DTI, 2004).

Table 2: Principle market for main fibre types (%)

Use	Synthetic	Cellulosic	Cotton	Wool
Apparel	42.6	10.9	32.9	13.9
Carpets	84.7	0.5	1.4	13.4
Domestic	42.1	12.3	42.2	3.4
Technical / Industrial	55.6	21.9	21.3	1.1
Tyres	39.4	59.3	1.3	0.0

3 HEALTH EFFECTS OF FIBRES

The hazard *(i.e. the potential for harm arising from an intrinsic property or disposition of something to cause detriment),* and risk (i.e. *the chance that someone or something that is valued will be adversely affected in a stipulated way by the hazard)* have been well-documented for a small number of fibres (e.g. asbestos and MMVFs). Other than para-aramids (e.g. Kevlar) relatively few types of MMFs have been studied in detail. Recent reviews of health effects (e.g. ECETOC, Warheit et al., 2001, Vu et al., 1996, Fishwick, 2003 and various IARC monographs) generally emphasise the limited data available.

There are a number of hazards / health effects from exposures to fibres. These can be broadly divided into:

- Mechanical irritant effects of the eyes, nose and skin.
- Dermatitis (atopic eczma)
- Endotoxin induced effects
- Obstructive lung disease (e.g. asthma, bronchitis)
- Other chronic effect (cough, dyspnoea, loss of lung function)
- Interstitial lung diseases (e.g. follicular bronchiolitis)
- Fibrosis of the lung (e.g. asbestosis)
- Cancers of the lung (e.g. lung cancer and mesothelioma)

This report is focussed on the physical properties of the fibres and their potential to cause diseases of the lungs and respiratory system and in particular the likelihood of fatal diseases (mortalities) such as lung cancers and fibrosis will occur, rather than the other non-fatal (morbidity) lung changes. However, the database does include references to health effects.

3.1 HUMAN EXPERIENCE

Many naturally occurring organic plant and animal fibres have been used for a long time and evidence of their health effects and morbidity have been widely documented (e.g. Fishwick et al., 2003). These fibres do not induce cancers or fibrosis and their ill-health effects are due to toxic or allergenic proteins or other substances of bacterial, vegetable or fungal origin. Some natural organic fibres have particular fatal hazards associated with their use (e.g. anthrax with wool and byssinosis from water soluble aminoglycocides on cotton, flax and hemp) but are not per se, a direct result of the fibres or their physical properties.

Lung cancers, mesothelioma (cancer of the pleural and peritoneal linings of the lung) and asbestosis are life-threatening diseases associated with human exposure to some naturally occurring silicate mineral fibres (e.g. asbestos and erionite fibres). Currently HSE considers that there are at least 3500 deaths per year in the UK from asbestos related lung cancers and mesothelioma. There are also over 600 cases a year for disablement compensation for asbestosis and over 400 for diffuse pleural thickening. Other more benign lung changes are also produced (e.g. pleural plaques). These mineral fibres may also enter the digestive system (e.g. after their removal from the bronchus via the mucocillary escalator) but have not conclusively been shown to produce excess cancers elsewhere.

The health effects of asbestos and other silicate fibres were established over the last century and due to the long latency between exposure and disease were not adequately controlled, giving rise to a very high risk of developing disease. Not surprisingly similar effects from the newer

man made silicate fibres (also known as vitreous fibres due to the production technology) were thought possible. Early epidemiological studies of the MMVF industry did find excess respiratory cancers but in later larger European and US studies the effect was diminished (Marsh et al., 1990 & 1996, Hughes et al., 1993, Boeffetta et al. 1997).

Cortez-Pimentel et al. 1975 looked at 7 cases of Synthetic fibre workers and found interstitial fibrosis and other effects, Hillerdal et al., 1990 described 3 cases of diffuse pulmonary fibrosis persons involved in cutting various MMOFs. Mortality studies have mostly looked at effects that are not lung related or fibre related (ECETOC, 1996).

3.2 ANIMAL STUDIES

Animal studies with respirable sized man made vitreous fibres have also shown that they can cause cancer and some types were regulated due to their carcinogenic hazard. Other non-organic MMFs (e.g. Potassium octatitanite fibres and silicon carbide whiskers have also shown to readily result in lung carcinomas in animal experiments (Stanton & Layard 1978, Lee at al., 1981, Davies et al., 1996, Vaughan and Trentley, 1996). Though produced in much greater amounts, most man made organic fibres MMOFs have had had relatively little experimental work carried out on them to identify if they present a hazard. This may be due in part because it is assumed that most of these fibres have too large a fibre diameter (and length) to enter the lung but the absence of tests can offer little reassurance on the safety of MMOFs.

The para-aramid fibres are by far the most studied type of MMOFs partly because they have an ability to fibrillate into fine (usually 0.3 – 0.7 µm wide) fibres. Although Kevlar pulp fibres when used in in-vivo experiments have resulted in lung changes in rats but have been classified as proliferative Keratin cysts (Carlton, 1994) and do not necessarily progress to squamous cell carcinomas and are not regarded as carcinogenic. The low hazard from these fibres appears due to their low biopersistence in the lung as they are readily broken down and shortened by lung fluid and enzymes (Warheit et al., 2001, 2002).

Carbon fibres have generally shown relatively few effects (Holt and Horne, 1978; Owen et al. 1986, Warheit et al. 1994). When other MMOF materials tested (e.g. such as pulverized nylon and polyacrylonitrile by Cortez Pimentel et al., (1975), the experiments were very limited.

3.3 FACTORS AFFECTING THE CARCINOGENIC AND FIBROGENIC EFFECTS OF FIBRES

The carcinogenic and fibrogenic effects of asbestos and MMVFs have been extensively studied in –vitro and in-vivo to the point where a series of standard in-vivo assays are used by the EU for the assessment and classification of MMVF fibres (EU commission report, 1997., EUR 18748 EN 1999.).

The main physical factors known to influence the carcinogenic and fibrogenic hazard in a specific way are the:

- Dimensions
- Durability (or biopersistence) in the lung.

Other factors such as fibre surface effects and chemistry (e.g. Fenton chemistry and activated oxygen species are also thought to be important but a strong relationship and mechanism has yet to be established to be incorporated in a usable model).

The risk is influenced by the Dose (or exposure) which is dependent on the:

- Dustiness of the material;
- Disturbance type:
- Duration of exposure, and the
- Design and use of control systems and PPE.

3.3.1 Dimensions

The dimension, shape and density of particles will determine their aerodynamic behaviour in air and their probability of entering and depositing in the lung. The entry of particles into the lung is largely based on the falling speed or aerodynamic diameter of the particle, which is defined as the diameter of a unit density (1000 kg/m^3) sphere (with the same falling speed in air as the particle of concern). Models of particle entry and deposition into the lung are based on the aerodynamic behaviour of the particles and ISO/CEN conventions for particle deposition in the lung have been developed (ISO/CEN).

Figure 1: CEN/ISO SAMPLING CONVENTIONS

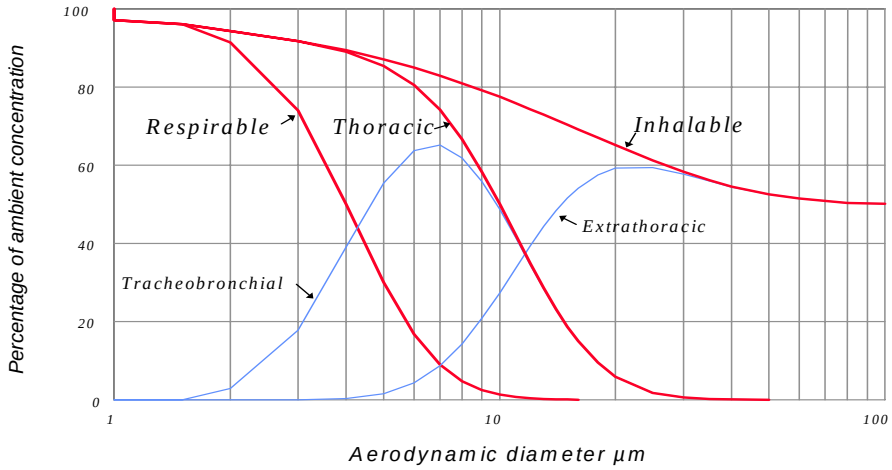


Figure 2: ISO/CEN sampling convention for particles

The shape and density of the fibres are important modifiers of the aerodynamic behaviour. Increasing particle density (>1000 kg/m^3) will increase the aerodynamic diameter, so the maximum diameter that can penetrate into the respirable region of the lung is reduced (e.g. from

7 µm to 3 µm for silicate fibres with densities of ~ 3 000 kg/m^3). The aerodynamic diameter of fibres is relatively little affected by the fibre length and in principle it would be expected that most MMOFs which have a density of 1100 – 1300 kg/m^3 will limit fibres >6 µm diameter reaching the lung.

Work with asbestos has shown that only fibres below about 3 µm in diameter and 100 µm long (Timbrell, 1983) can penetrate past the bronchioles into the pulmonary (air exchange region of the lung). The later MMVF animal data showed that fibres > 1 µm are rarely found to enter the rat lung and a relatively small percentage of >1 µm diameter fibres are found in human lung tissue samples. When evaluating human exposure levels the fibre concentration of "respirable" fibres is based on counts of particles > 5µm long with an aspect ratio of >3:1 and a maimum width of 3 µm, which are visible by phase contrast light microscopy (PCM) at X500 magnification (HSG 238 and WHO). For some synthetic fibres with low density this may be an underestimate of the respirable fibre concentration. For hazard assessment of MMOFs the presence of <6 µm diameter fibres may be important to include bronchial exposure which is essentially the thoracic exposure. For risk assessment given the low probability that larger diameter fibres will reach the pulmonary region of lung it is both practical and reasonable in the light of animal inhalation and human lung experience to continue to count only fibres of <3 µm diameter as a measure of the respirable fibres

The length will play an important role in how far the fibre can penetrate into the lung and where it will deposit. Clearly for continuous filaments even if they have very fine diameters, will not be respirable unless broken into shorter lengths. Long fibres of small enough diameter to enter into the thoracic regions of the lung will preferentially deposit at the bifucations of the bronchioles, due to the processes of interception and impaction. It is at these bifurcations that asbestos related lung cancers commonly occur (Lippmann, 1988) and it may be that long fibres are not effectively removed by the cilliated cells / mucocillary escalator from these sites. In a similar way fibres which are longer than ~ 15 µm are longer than macrophages in the pulmonary lung and cannot be removed rapidly by macrophage mediated clearance.

Not all the particles inhaled will deposit in the lung and for spherical particles a minimum deposition rate occurs at 0.1µm diameter. In MMVF rat studies a deposition rate of 11% at 0.1 µm diameter was found.

3.3.2 Durability/solubility

A fibre settling on the surface of the pulmonary lung is thought to be subject to dissolution in lung fluid, which has a pH of 7.4 and forms a thin layer over the lung surface. The exact composition of the lung fluid and its simulated equivalent is a matter of some debate but essentially the simulated versions are made up from about 12 different chemicals and consist primarily of sodium, calcium and magnesium salts in water. A second model for dissolution is based on the phagatosis of fibres by macrophages which engulf the entire fibre if <15 µm long or may engulf only one end or part of the fibre if longer. The macrophage may move shorter fibres from the lung surface to the mucocillary escalator to eject them from the lung or to the lymph nodes, longer fibres cannot be moved and stay in place. Fibres are also dissolved while engulfed by lung macrophage cells where a more complex chemical reaction takes place at pH = 4.6. The effect of dissolution is to weaken the fibre and essentially break it into smaller fibres, which can then be engulfed and physically transported out of the lung.

These two different solubility process may take place together on the same fibre making the model for in-vitro fibre testing somewhat more complex than measuring the solubility at two pH's.

The measurement of in-vitro solubility (K_{dis}) has been carried out using both static and flow through methods. As problems of super saturation and decreased solubility may arise in static experiments the constant flow methods have generally been favoured. The rate of dissolution of elements from a fibre will depend on its size and surface area. To overcome the variability, the flow (F) to surface area (A) ratio is kept at a constant by adjusting the mass of the fibre in the cell. This means that the surface area of the test fibre must be determined prior to the experiment. The purity of the fibre is also important as if it has been crushed small fragments may be present and if it has been prepared without sedimentation up to about 30% by mass may be large non-fibrous material.

The measured mass (M) dissolution rate from fibres and is generally assumed to be in direct proportion to their surface area (A) and independent of time (t) as shown by equation 1 below:

$$\frac{dM}{dt} = -k\,A \qquad (1)$$

Assuming cylindrical shaped fibres and that the dissolution is based only on the diameter the model can be written as:

$$D_t = d_o - \frac{2kt}{\rho} \qquad (2)$$

Various methods have been used to measure and calculate K_{dis} reflecting some of the assumptions being made; these include mass lost (e.g. Leinweber, 1984), effluent analysis (e.g. Potter and Matterson, 1991; Matterson, 1994,) and diameter reduction. Due to the range of materials effluent analysis was not used and a relatively simple mass loss experiment was conducted. No size reduction measurements have been published to date. The commonly expressed units for K_{dis} are ng/cm2 /h and may vary from about 0.1 - 1000 for various types of MMVF's.

The durability of fibres inside a biological system (biopersistence) is more complicated than simple solubility, as shown by the effect of enzymes on the biopersistence of Kevlar pulp (Warheit et al., 2002). Therefore solubility should only be seen as a first indication that the fibre may persist in the lung and a range of in-vivo testing should be carried out using EU approved methods (EUR 18748 EN 1999).

3.3.3 Dose

The numbers of fibres that can reach the target organ is a critical determinant of the likelihood of disease. Experience with asbestos has shown that often the primary production and manufacturing process incorporates a number of controls that limit the exposure of workers to airborne fibres and the risk of developing a fibre related disease is much reduced. Secondary manufacturing and other users may have much less controls and safeguards in place and use procedures, which preferentially release respirable fibres in poorly ventilated conditions. The

duration of exposures to a particular fibre will, in a first analysis be related to the amount of fibre produced.

3.3.4 Dustiness

As it is not feasible to take on large scale monitoring of airborne fibre levels and a “dustiness” test (a measure of the propensity of the material to release airborne ‘respirable’ fibres) is the best way of assessing the likely exposures from working with different fibre types of fibres. There is no single dustiness test but if the same procedure is used for all fibres it gives a relative ranking of the fibres released. The dustiness will be affected by any further processing of the fibres.

3.4 OTHER CONSIDERATIONS

Although the production and release of fibres of reparable size is the logical starting point for an assessment, there is evidence that even large diameter continuous fibres when subject to secondary treatments or processing can cause health problems. Production and finishing processes use a wide range of chemicals, which may also cause health effect and a number of epidemiological studies for cancers in the textile manufacturing industry have been reported (IARC, 1990) but are outside the scope of this work. Finishing, secondary manufacturing and other production treatments may result in finer material and fibres being produced than expected. There are a number of examples of this. This makes it important to have some understanding of the production procedures to determine which methods and procedures have the capability to produce (whether intentionally or inadvertently) respirable fibres. A brief oversight of the MMF industry is given in the next chapter

3.4.1 Flock workers disease

Reports by Lougheed at al. 1995 and subsequently by Kern et al. (1997, 1998, 2000) have reported some 24 cases of workers in the nylon flocking industry to be at markedly increased risk of a chronic interstitial lung disease after working between 1 and 30 years at two North American manufacturing plants, or their downstream operations. In all these cases the workers were exposed to rotary-cut nylon flock. The lung changes are characterized by bronchiolocentric nodular and diffuse lymphocytic interstitial infiltrates, a lymphocytic bronchiolitis, and variable interstitial fibrosis. The HRCT scans in more exposed cases showed a striking ground-glass opacity, assuming a macronodular appearance in some areas, and prominent subpleural interlobular septa.

The two North American flock manufacturers, cut nylon tow with rotary cutters, which generates fibres of less-precisely defined length, termed *random-cut flock*. In this process, which is much faster than that using guillotine cutters, tow is dyed, finished, cut, dried, screened, and bagged in one continuous operation. However, as rotary-cutter blades become dull, it is difficult to detect a tone change; increasing friction results in rising blade temperatures, and nylon tow may be cut uncleanly, melted, or both. Nylon flock produced under such conditions is more likely to have tiny protuberances, which during subsequent processing may be released as respirable-sized particles (aerodynamic diameter 10 μm). Quality-control inspectors have described such protuberances on flock fibres, and investigators from the National Institute for Occupational Safety and Health (NIOSH) have demonstrated their presence both in bulk samples of rotary-cut flock and as respirable-sized particles in work-room air (Burkhart et al. 1999). Notably, recent intratracheal instillation studies in rats have suggested that respirable sized nylon particles have substantial pulmonary toxicity (Porter et al. 1999).

Animal experiments have shown similar reactions to nylon flock in rats and this and other evidence was reviewed (Eschenbacher et al., 1999) in a special NIOSH workshop was found to support the existence of chronic interstitial pneumonitis associated with nylon flock processing. The workshop participants recommended surveillance for early identification of affected workers and their removal from further workplace exposure.

More recently reported Case studies have shown that similar effects from exposures to polyethylene (Barroso et al., 2002) and polypropylene (Atis et al., 2005) flocks processed by rotary cutting can also occur. This shows that a number of fibres previously thought unable to release respirable fibres can become a hazard and a risk to process workers if inappropriately treated (e.g. during cutting of flock and recycling of MMFs).

There are a number of limitations to the current knowledge base. The case studies do not provide any mechanistic insights into the lung damage that is associated with flock exposure or provide insights into susceptibility factors or biomarkers of exposure. Additionally, the case series is small and is subject to the biases of retrospective descriptive research. For instance, there is only limited information about other potential respirable exposures that were experienced by these blue-collar workers. There is no analysis of a possible dose-response relationship that might strengthen the association between exposure and morbidity. Finally, there is very limited experimental exposure data to strengthen the causal link between flock exposure and interstitial lung disease.

4 REVIEW OF BULK SYNTHETIC AND SEMI-SYNTHETIC TEXTILE FIBRE PRODUCTION

4.1 MANUFACTURE OF TEXTILES FROM MMFS

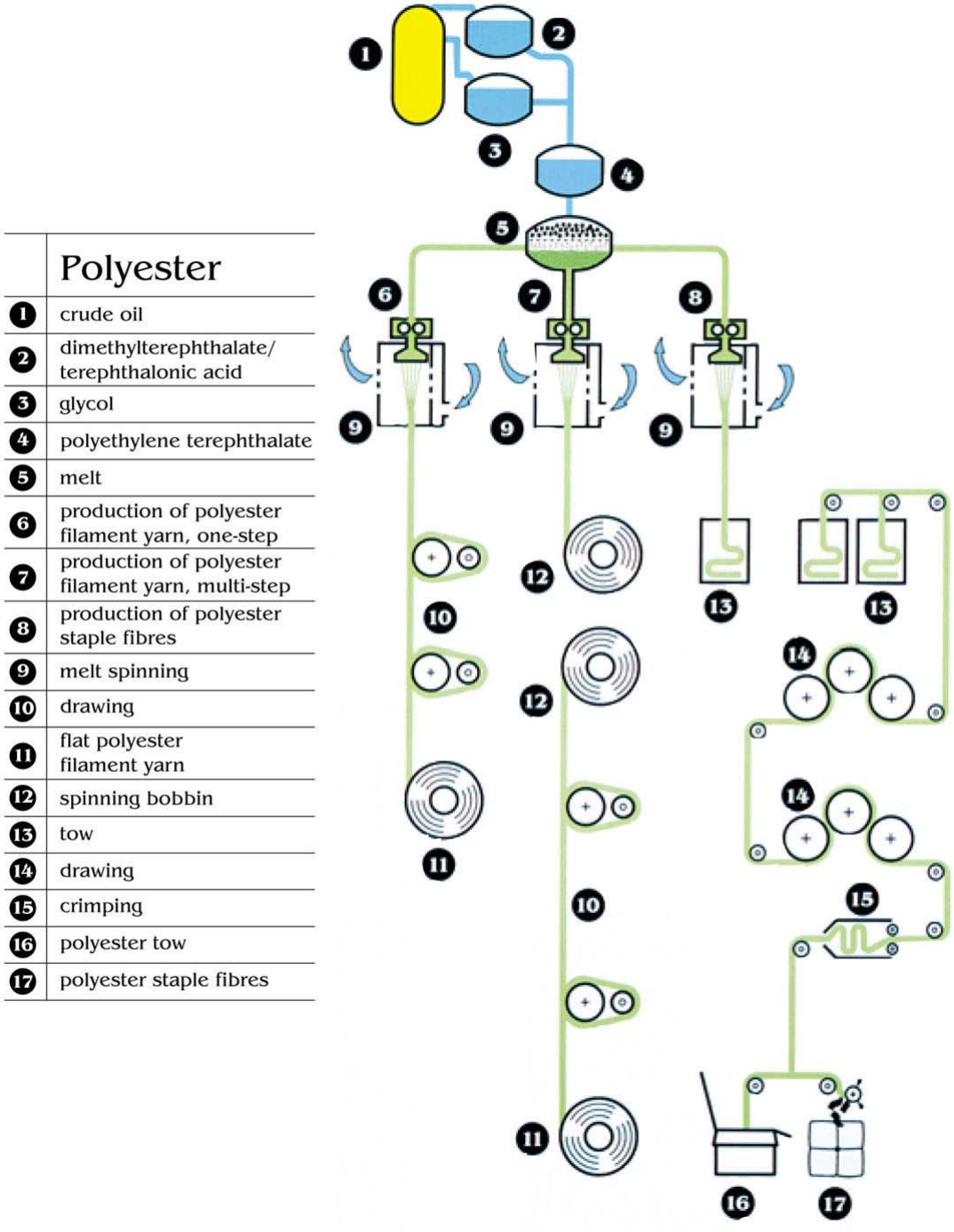
Textile manufacture can be separated into woven and non-woven. Woven is generally used to refer to fabric composed of two sets of yarns, warp and filling, that is formed weaving, which is the interlacing of these sets of yarns. Nonwovens are defined by ISO 9092:1988 and (CEN) - EN 29092, as a manufactured sheet, web or batt of directionally or randomly orientated fibres, bonded by friction, and/or cohesion and/or adhesion, excluding paper and products which are woven, knitted, tufted, stitch-bonded incorporating binding yarns or filaments, or felted by wet-milling, whether or not additionally needled. The fibres may be of natural or man-made origin. They may be staple or continuous filaments or be formed in-situ.

4.2 TYPICAL MANUFACTURING PROCEDURES FOR WOVENS

The production and processing of bulk fibres into manufactured goods is explained briefly below. This is an overview of the main processes and which from a Health and Safety perspective can be used to determine where respirable fibres may be produced and released into the air. It should be noted that it is often found in occupational hygiene investigations that the control and safeguards applied to the production of fibres are less likely to be present among secondary users and manufacturers and the risks to the downstream users can be underestimated.

A typical manufacturing process for bulk synthetic fibre (e.g. Polyester) is illustrated in figure 2.

Figure 2: Typical manufacturing process for synthetic MMF's (courtesy, VCI)



4.3 PRODUCTION

4.3.1 Principles of Synthetic and Cellulosic fibre production

For bulk synthetic fibre production three processes are commonly used, which are based on the formation of long chain polymers (macromolecules) from polymerisation, polyaddition or polycondensation.

Polymerisation: requires that the single molecules have a double bond between the carbon atoms $CH_2=CH_2$ which can be broken to form long continuous carbon chains. $–CH_2-CH_2-CH_2-$. This is achieved by the use of a catalyst to break the bonds and form the long carbon chains. The chain length can be controlled by the additions of other molecules which do not promote interlinking hence a customised chain length can be produced. Polymerisation is used for the production of polyamide 6, polyvinyl chloride, acrylic and polypropylene fibre.

Polycondensation: requires that the single (linking) molecules have reactive groups each end which can react with the reactive groups at the end of other molecules. For example if one of the reactive ends is an alcohol and the other a carboxylic acid this will link to form an ester with the elimination of water molecules. This method is used in the production of polyamide 6,6 and polyester.

Polyaddition: requires the use of two different molecules, which react together to link up and form a macromolecule. Instead of splitting off by-products an alternating dislocation of the hydrogen molecule takes place. This method is used in the production of Elastane.

4.3.2 Fibre formation

All man made fibres start with a spin mass, which is the basic raw materials with the required polymers (or other materials) to be dissolved in a liquid or melted to form a viscous mass. To form fibres the spin mass must be passed through a small hole to produce a continuous filament. Many of these can be formed at the same time using a spinneret (see fig 3 & 4) and gathered to a filament yarn and spooled or joined to form a tow (see fig. 5) consisting of many tens of thousands of such fibres.

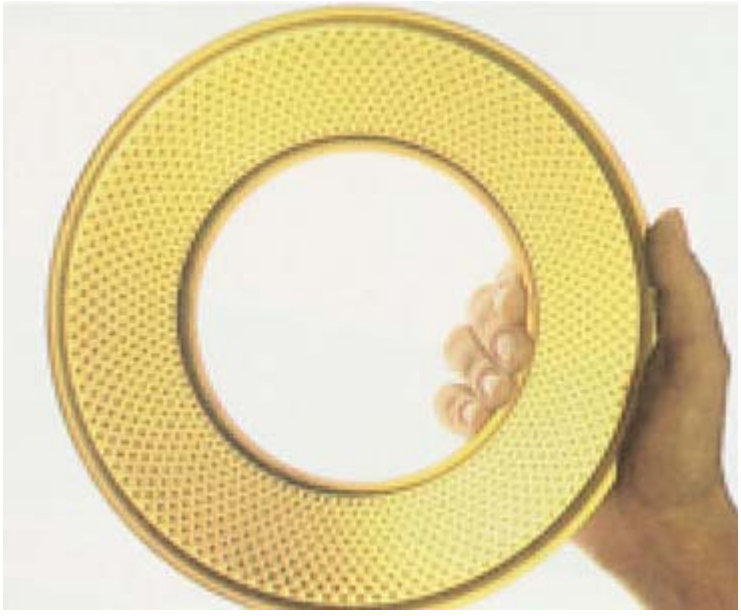


Figure 3: Example of a spinneret

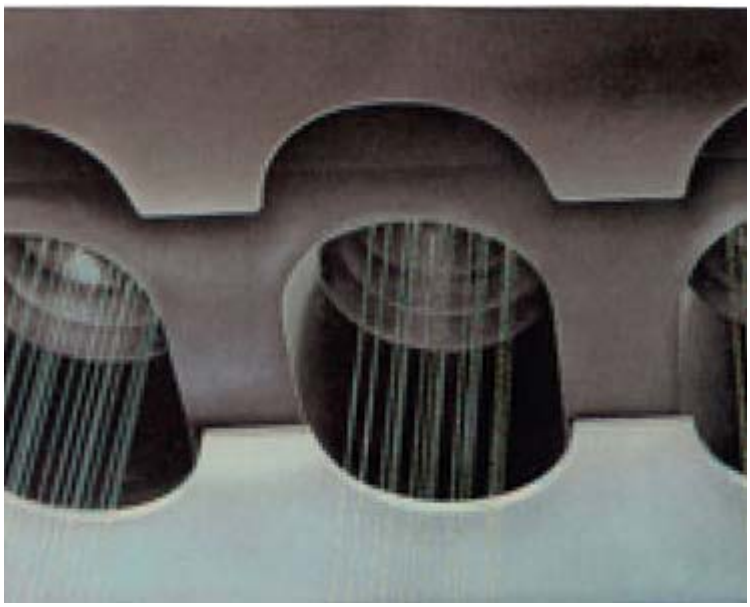


Figure 4: Fibres emerging from a spinneret

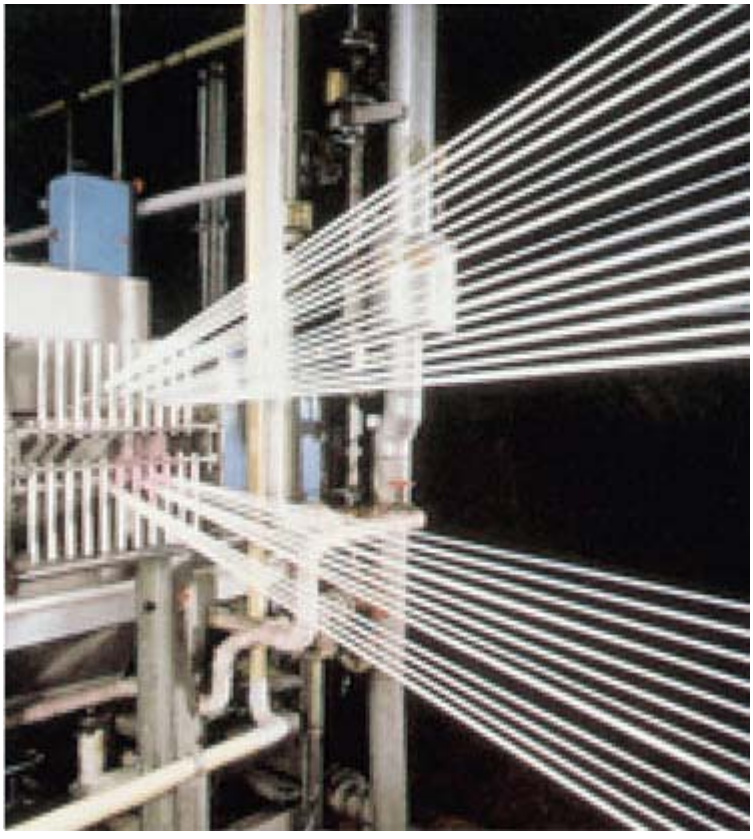
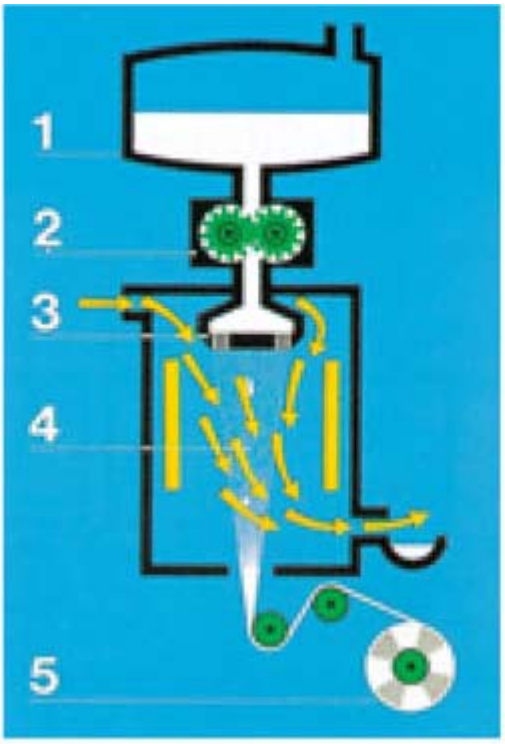


Figure 5: Individual filaments being gathered to form a tow

4.3.3 Spinning

The basic process for spinning is described in figure 6. The medium which the filament can be formed are: warm air (dry spinning) or in liquid coagulating bath (wet spinning). For melted materials such as glass wool and rock wool the molten fibres are dry spun into air (melt spinning).



The spinning processes consist of common basic processes which can be seen in the illustrations: the container holding the spin mass (1) – the spin pump for dosing the spin mass (2) – the spinneret (3) – a medium in which the filament is formed (4) – the device used for gathering and spooling the filament (5).

Figure 6: Basic spinning process

4.3.4 Drawing and texturing

Although the long chain molecules are partially aligned the process can be further optimised by drawing the fibres so the long chained molecules lie parallel to each other and the forces between the fibres are increased resulting in improved tenacity. The shape of the spinneret holes can also influence the appearance of the yarn, which can be shaped by heat are also able to be textured by a variety of processes: e.g. false twist, stuffer box and air jet texturing which will change the appearance and texture of the yarn (see figures 7 & 8)_.

4.3.5 Cutting

Monofilaments and yarns used for spinning and weaving will be many tens of metres or kilometres long although for some products shorter fibres are required. The filaments are usually gathered into a tow where they can be cut to a standard length using a guillotine to give staple fibres of the same length. These are then pressed into bales for shipping. Downstream manufacturers may also carry out this process on the tow using a converter to cut or tear the

fibres into staple fibres. For some process other fibre lengths are required e.g. flock. The various types of process and fibres sizes are summarised in figure 9.

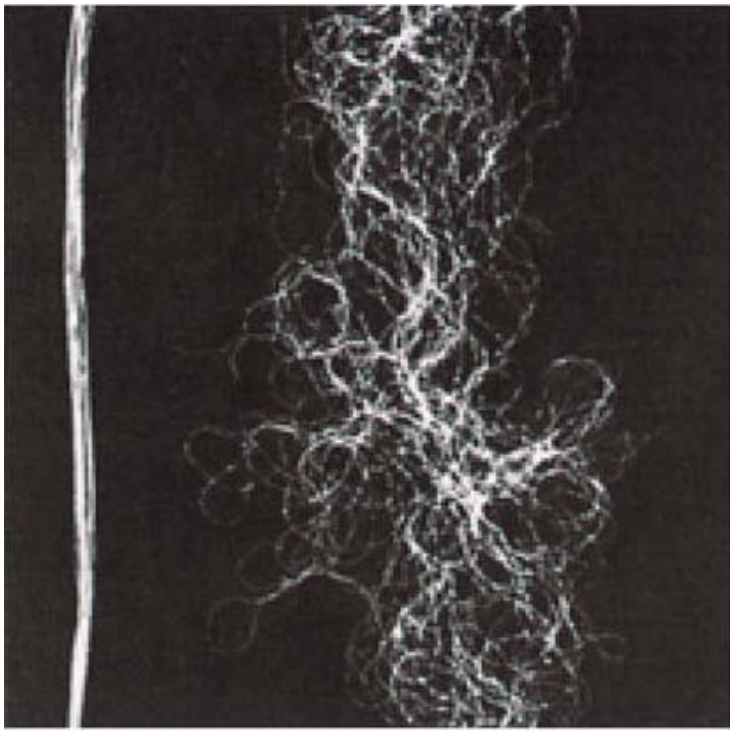


Figure 7: Example of a yarn before and after texturing

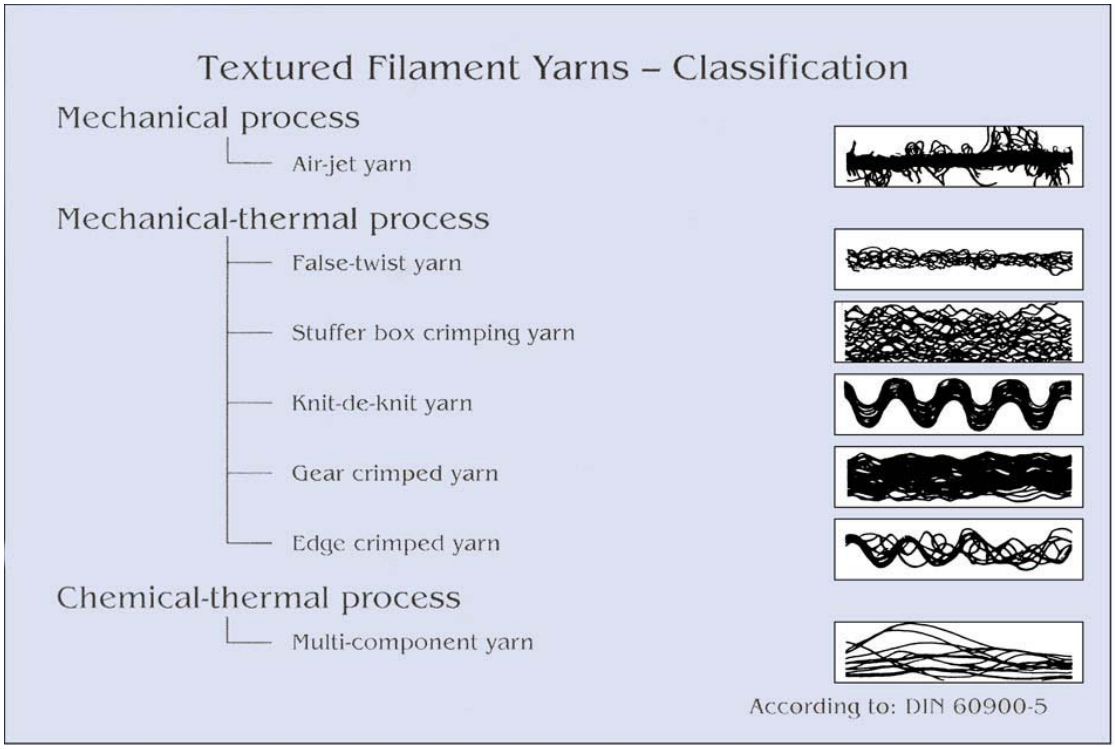


Figure 8: Examples of various texturing processes

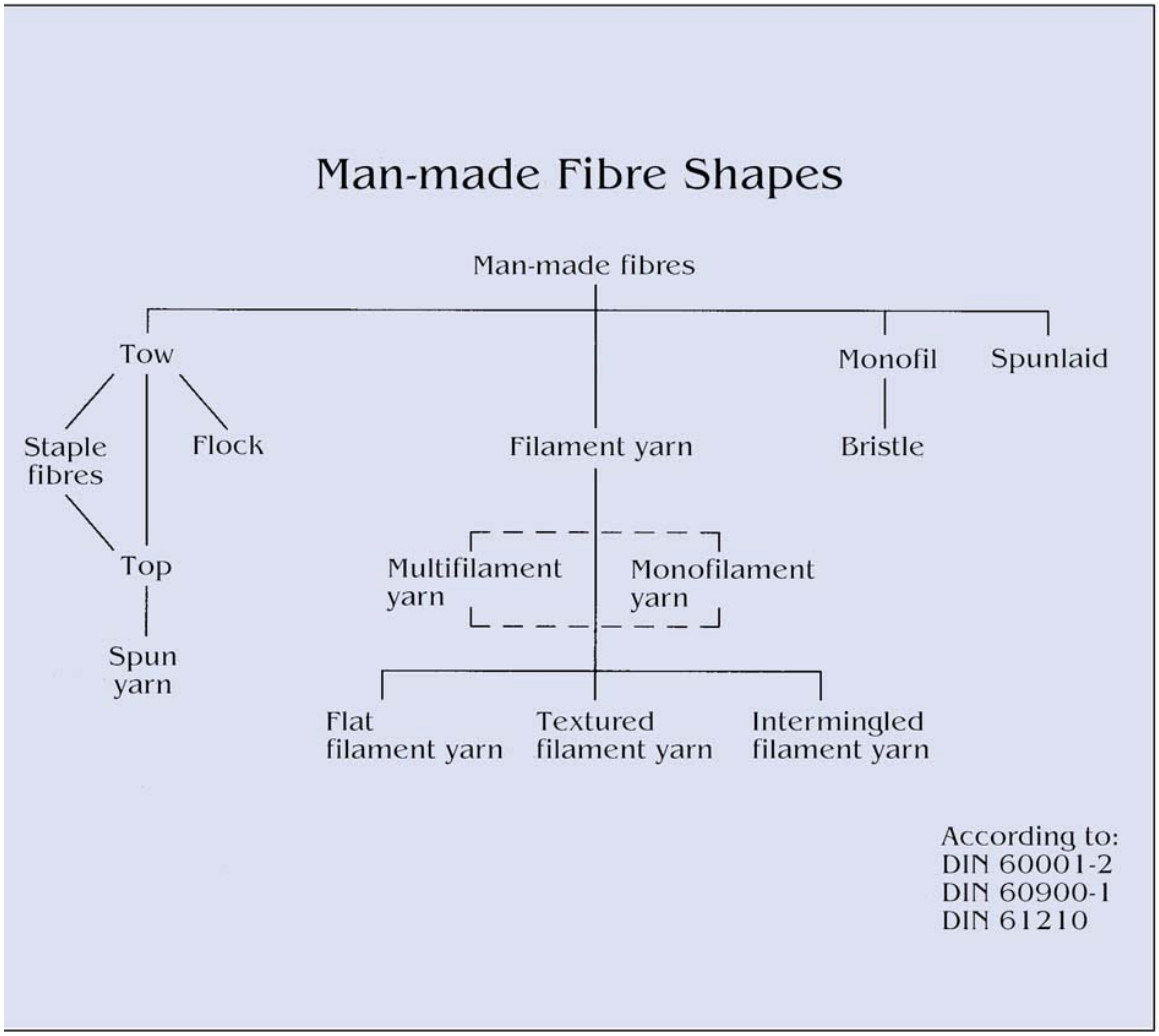


Figure 9: Types of MMFs shapes

4.4 TYPICAL MANUFACTURING PROCEDURES FOR NON-WOVENS

Nonwovens developed from the textile, paper, plastic and leather industries and a separate, specialist MMF industry has evolved. The production of nonwovens takes place in three stages, although modern technology allows an overlapping of the stages, and in some cases all three stages can take place at the same time. The opportunity to combine different raw materials and different techniques accounts for the diversity of the industry and its products. This diversity is enhanced by the ability to engineer nonwovens to have specific properties and to perform specific tasks.

The three stages are:

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4.4.1 Web Formation

Nonwoven manufacture starts by the arrangement of fibres in a sheet or web. The fibres can be staple fibres packed in bales, or filaments extruded from molten polymer granules. Four basic methods are used to form a web, and nonwovens are usually referred to by one of these methods: spunlaid, drylaid, wetlaid and other techniques.

4.4.1.1 Spunlaid

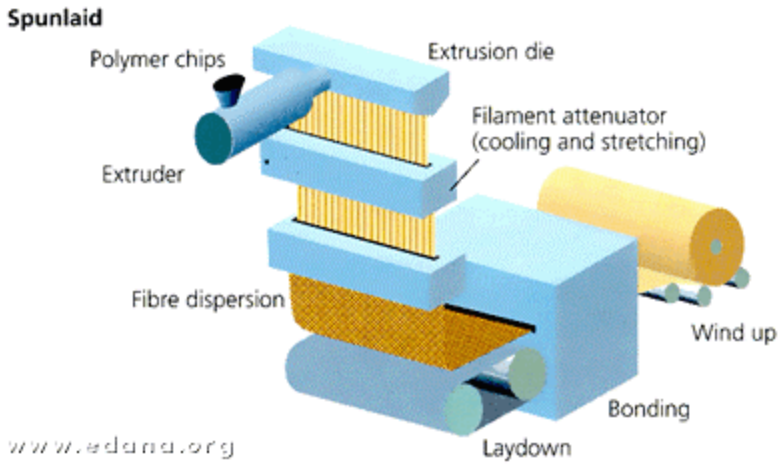


Figure 10: Schematic diagram of the spunlaid process

Spunlaid manufacturing involves both fibre production and forming the end product in a single process. In this process polymer granules are melted and molten polymer is extruded through spinnerets. The continuous filaments are cooled and deposited on to a conveyor to form a uniform web. Some remaining temperature can cause filaments to adhere to one another, but this cannot be regarded as the principal method of bonding. The spunlaid process (sometimes known as spunbonded) has the advantage of giving nonwovens greater strength, but raw

material flexibility is more restricted. Co-extrusion of second components is used in several spunlaid processes, usually to provide extra properties or bonding capabilities.

4.4.1.2 Drylaid

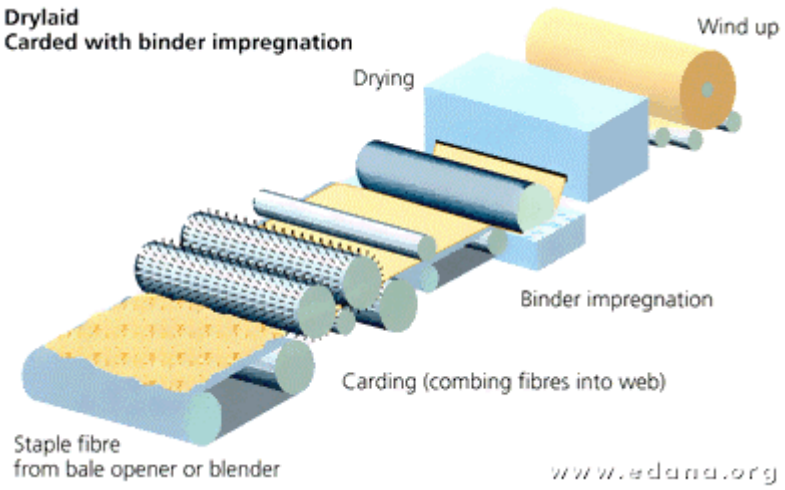


Figure 11: Schematic diagram of the drylaid process

There are two methods of drylaying-carding and airlaying.

Carding is a mechanical process that starts with the opening of bales of fibres, which are blended and conveyed to the next stage by air transport. They are then combed into a web by a carding machine, which is a rotating drum or series of drums covered in fine wires or teeth. The precise configuration of cards will depend on the fabric weight and fibre orientation required. The web can be parallel-laid, where most of the fibres are laid in the direction of the web travel, or they can be random-laid. Typical parallel-laid carded webs result in good tensile strength, low elongation and low tear strength in the machine direction and the reverse in the cross direction. Relative speeds and web composition can be varied to produce a wide range of properties.

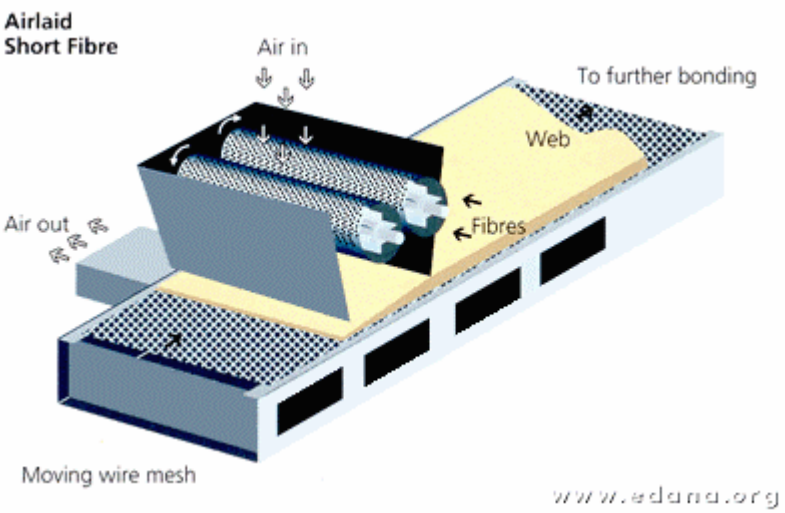


Figure 12: Schematic diagram of the airlaid process

In airlaying, the fibres, which can be very short, are fed into an air stream and from there to a moving belt or perforated drum, where they form a randomly oriented web. Compared with carded webs, airlaid webs have a lower density, a greater softness and an absence of laminar structure. Airlaid webs offer great versatility in terms of the fibres and fibre blends that can be used.

4.4.1.3 Wetlaid

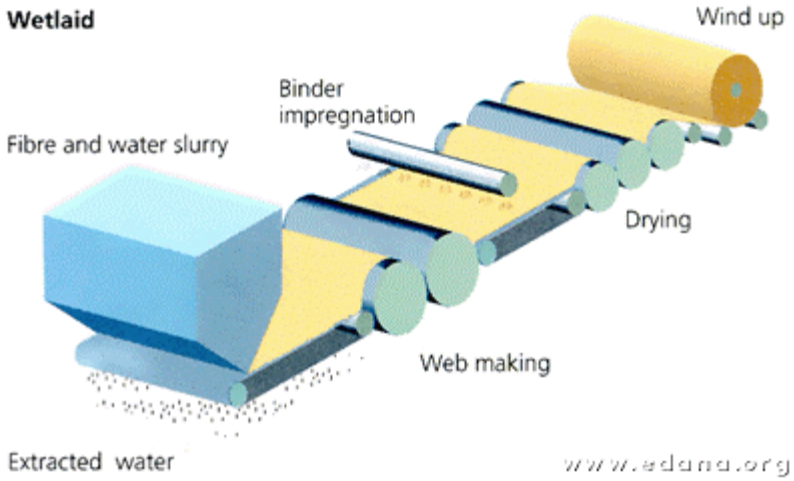


Figure 13: Schematic diagram of the wetlaid process

A dilute slurry of water and fibres is deposited on a moving wire screen and drained to form a web. The web is further dewatered, consolidated, by pressing between rollers, and dried. Impregnation with binders is often included in a later stage of the process.

Wetlaid web-forming allows a wide range of fibre orientations ranging from near random to near parallel. The strength of the random oriented web is rather similar in all directions in the plane of the fabric. A wide range of natural, mineral, synthetic and man-made fibres of varying lengths can be used.

4.4.1.4 Other techniques

This includes a group of specialised technologies, in which the fibre production, web structure and bonding usually occur at the same time and in the same place.

In melt blown web formation, low viscosity polymers are extruded into a high velocity air stream on leaving the spinneret. This scatters the melt, solidifies it and breaks it up into a fibrous web.

Flash spun webs are made by dissolving a polymer in a suitable solvent and then spraying it into a vessel held at reduced pressure. The solvent evaporates, or flashes off, leaving a cloud of fibres, which are collected and bonded. Other variants of web forming techniques include different methods of fibrillation and the use of complex rotating dies.

Processes are emerging where two or more web forming techniques are used in tandem. The spunlaid/meltblown process is an example, where one or more meltblown webs and spunlaid webs are combined.

4.4.2 Web Bonding

Webs, other than spunlaid, have little strength in their unbonded form. The web must therefore be consolidated in some way. This is affected by bonding, a vital step in the production of nonwovens. The choice of method is at least as important to ultimate functional properties as the type of fibre in the web.

There are three basic types of bonding:

- Chemical (adhesion)
- Thermal (cohesion)
- Mechanical (friction)

4.4.2.1 Chemical bonding (adhesion bonding)

Chemical bonding mainly refers to the application of a liquid based bonding agent to the web. Three groups of materials are commonly used as binders-acrylate polymers and copolymers, styrene-butadiene copolymers and vinyl acetate ethylene copolymers. Water based binder systems are the most widely used but powdered adhesives, foam and in some cases organic solvent solutions are also found.

There are many ways of applying the binder. It can be applied uniformly by impregnating, coating or spraying or intermittently, as in print bonding. Print bonding is used when specific patterns are required and where it is necessary to have the majority of fibres free of binder for functional reasons.

4.4.2.2 Thermal bonding (cohesion bonding)

This method uses the thermoplastic properties of certain synthetic fibres to form bonds under controlled heating. In some cases the web fibre itself can be used, but more often a low melt fibre or bicomponent fibre is introduced at the web formation stage to perform the binding function later in the process. There are several thermal bonding systems in use:

Calendering uses heat and high pressure applied through rollers to weld the fibre webs together at speed.

Through-air thermal bonding makes bulkier products by the overall bonding of a web containing low melting fibres. This takes place in a carefully controlled hot air stream.

Drum and blanket systems apply pressure and heat to make products of average bulk.

Sonic bonding takes place when the molecules of the fibres held under a patterned roller are excited by high frequency energy that produces internal heating and softening of the fibres.

4.4.2.3 Mechanical bonding (friction bonding)

In mechanical bonding the strengthening of the web is achieved by inter-fibre friction as a result

of the physical entanglement of the fibres. There are two types of mechanical bonding - needlepunching and hydroentanglement. Needlepunching can be used on most fibre types. Specially designed needles are pushed and pulled through the web to entangle the fibres. Webs of different characteristics can be needled together to produce a gradation of properties difficult to achieve by other means. Hydroentanglement is mainly applied to carded or wetlaid webs and uses fine, high pressure jets of water to cause the fibres to interlace. Hydroentanglement is sometimes known as spunlacing, as the arrangement of jets can give a wide variety of aesthetically pleasing effects. The water jet pressure used has a direct bearing on the strength of the web, but system design also plays a part.

4.4.3 Finishing Treatments

There is an opportunity to meet the needs of the customer even more precisely by modifying or adding to existing properties. A variety of different chemical substances can be employed before or after binding, or various mechanical processes can be applied to the nonwoven material after binding (e.g. cutting, folding, sewing or heat sealing). In this way, the quality, properties and size of the converted nonwoven products can be further tailored to the precise needs of the customer/product.

5 MANUFACTURING PROCESSES THAT PRODUCE RESPIRABLE SIZED FIBRES

The woven and non-woven industry is mainly focussed on production of continuous filaments of a titre that are unlikely to cause any health problems unless the fibres are damaged and finer slivers and fibres are produced during aggressive processing. The problems and health effects from rotary cutting of nylon to produce flock were reviewed in section 3. There are likely to be other examples of mechanical abrasive release (e.g. textile reprocessing industry) that have yet to come to light.

Poor control of the production may result in thinner fibre being produced (dernier variance) but the wide use of extrusion through a spinneret mean that fibres of a uniform diameter are usually produced. Fibre dimension down to about 7 um can be produced with conventional spinneret production. The exception to this is the melt blown process where the molten feedstock is blown away from the spinneret, allowing the still molten material to draw out into longer and finer strands. Melt blown procedures are common for MMVFs and a much wider range of diameters are produced. It is also worth noting that the air layering process used to form MMVF blankets from the extruded fibres is the most suitable nonwoven process for handling short fibres.

For conventional textile manufacture the finest filament diameter that can be handled by the production machinery is much larger than respirable sized fibres (usually > 15 um filament is used). However, for the apparel industry the thinner the fibre the more soft to the touch is the fabric and its ability to fold or hug the body. This has long been a desirable characteristic and the search for artificial silk was the driving force for the start of the MMF industry.

There is also a range of technical textiles that would benefit from access to thinner fibres (e.g. filtration, reinforcement, insulation etc). A number of improvements and new process have recently been brought into effective production to produce thinner fibres. These include:

- Spinneret development
- Melt-blown techniques
- Electro-spinning
- Multi - component fibres
- Nanofibre production

Although some of these processes have been available for a considerable time, it is a combination of these technologies that is now making economic production feasible due to the large increase in production rates. At the start of this project the conventional capabilities of the main production methods would have been as follows in table 2.

Table 2: Main production processes for fine fibres available at start of the project					
Manufacturing process	Fibre description	Cross – section shape	Fibre diameter (µm)	Fibre surface area (m^2/g)	Production rate (g/min/fibre)
Staple or homopolymer Spunbond	One denier homopolymer fibre	round	10.1	0.3	0.67
Meltblown	2 µm fibre	round	2	1.4	0.5
Electrospun	Various	round	0.3	9.5	0.02

5.1 SPINNERET DEVELOPMENT

This production of meltblown glass fibres saw the first use of the spinneret technology that has been the main production method of MMFs for over 100 years. The need for efficient production of fine fibres for filtration has seen the technical development of this process so that fibres diameters down to about 2 um diameter can be routinely produced in large quantities.

Spinnerets have historically been manufactured by conventional methods such as milling, drilling, etc. However, the introduction of new techniques similar to printed circuit board technology has allowed smaller holes and very accurately distribution of polymers in the extremely small area available in the spinneret (extrusion die). These improvements have recently led to many innovations using multi-component polymers, which are economical and practical for production of sub-micron fibres and products.

5.2 MELT BLOWN PRODUCTION

Meltblowing has been the primary source for micro-filtration fibres. Considerable research has gone into production of smaller diameter meltblown fibres. The smallest routine commercial fibres are generally between 1 -5 µm and can be produced at relatively high rates ~0.5 grms/hole/minute. Recent enhancement of the melt blown procedure by the ‘Nanoval’ process which uses a supersonic sheathe of air around the melt fibre as it is extruded to draw the fibre in a laminar flow to ever finer diameters (Gerking, 2005). The high velocity and coldness of the air causes the outside of the fibre to rapidly cool in relation to its core and causes the fibre to burst open and form a multitude of finer filaments, which solidify and can be collected as nonwoven web or yarn. The resulting microfilaments are continuous and quite different from all known meltblown systems. Higher melt temperatures and higher flow rates of the sheathe air produce finer fibres. Current diameters from 0.7 µm upwards are produced from this system and tests have shown that most of the current synthetic fibres can be produced by this new technology.

The improvements in spinneret design have allowed a number of core sheath and segmented fibre types to be produced with smaller fibre diameters and a variety of polymers.

5.3 ELECTRO SPINNING PRODUCTION

Electrospinning is a process that spins fibres of diameters ranging from ten to a thousand nanometres (nm). This method has been known since 1934 when the first patent on electrospinning was filed. A schematic diagram of the principle of electrospinning is as shown in Figure 14. The process makes use of electrostatic and mechanical force to spin fibres from the tip of a fine orifice or spinneret. The spinneret is maintained at positive or negative charge by a DC power supply. When the electrostatic repelling force overcomes the surface tension force of the polymer solution, the liquid spills out of the spinneret and forms an extremely fine continuous filament. It has the misleading appearance of forming multiple filaments from one spinneret nozzle, but current theory is that the filaments do not split. These filaments are collected onto a rotating or stationary collector with an electrode beneath of the opposite charge to that of the spinneret. These are usually allowed to accumulate together to form a nonwoven nanofibre fabric but continuous fibre production has been recently developed Smit (2005).

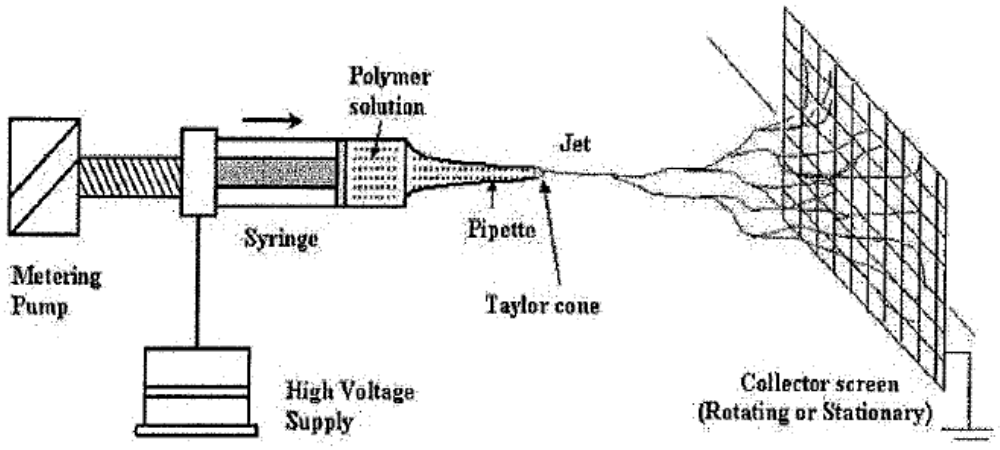


Figure 14. Schematic representation of electrospinning process.

The distance between the spinneret nozzle and the collector generally varies from 15-30 cm. The process can be carried out at room temperature unless heat is required to keep the polymer in liquid state. During electrospinning the electrodriven jet undergoes a set of dynamic instabilities. The whipping instability causes the jet to bend and stretch, ultimately producing superfine fibres that have a broad lognormal size distribution. The resulting morphology and physical properties of the fibre depend on the fluid material properties: conductivity, dielectric permeability, dynamic viscosity, surface tension and density and several operating parameters: flow rate, external electric field, electric current and DCD (distance between nozzle and collector). A considerable amount of research has gone into understanding and improving the technology (Rutledge and Warner, 2002).

At present the production rate of this process is low typically a few grams/hole/hour (~0.03 grms/hole/minute). The fibres are not drawn so lack the strength of conventional fibres and are mainly used as a thin layer in filtration media supported by other fibres. Even so by 2002 the

Donaldson Company was reporting production rates of nonwoven material of >10,000 m^2 per day (Luzhansky, 2002) and the difficulties of production and quality control have been largely addressed.

5.3.1 Polymer-Solvents used in ELECTROSPINNING.

The polymer is usually dissolved in suitable solvent and spun from solution. Fibres in the range of 10 to 2000 nm diameters can be achieved by choosing the appropriate polymer solvent system [5]. Table 3 gives list of some of polymer solvent systems used in electrospinning.

Table 3: Examples of Polymers and solvents used in electrospinning

Polymer	Solvents
Nylon 6 and nylon 66	Formic Acid
Polyacrylonitrile	Dimethyl formaldehyde
PET	Trifluoroacetic acid/Dimethyl chloride
PVA	Water
Polystyrene	DMF/Toluene
Nylon-6-co-polyamide	Formic acid
Polybenzimidazole	Dimethyl acetamide
Polyramide	Sulfuric acid
Polyimides	Phenol

5.4 MULTICOMPONENT FIBRES

The problem of producing fine fibres but which can be processed on conventional textile machinery has been solved by the development of multi-component fibres. These fibres are of the conventional size for used on textile machinery but are really a bundle of finer fibres held together in a matrix. Once the fabric or item of apparel is manufactured it is then chemically or mechanically treated to remove the matrix but leaving a material composed of much finer fibres. Interestingly silk is nature's example of a multicomponent fibre.

Modern melt spinning distribution system technology has recently demonstrated the capability to produce fibres with smaller size and better consistency than either of the two above techniques. In addition, micro-sized (1-10 µm) and nano-sized (<1 µm) multi-component fibres can be produced with improved production rates, economics and physical properties over the other systems, and with even broader polymer choice capabilities. Multi-component fibres sizes of ~0.04 microns (~40 nanometres) have now been demonstrated at commercially attractive production rates. Multi-component fibre production is available in staple, continuous filament, spunbond, and meltblown processes.

By far the most common type of multi-component fibres are bicomponent fibres. The major types include:

- Sheath/Core fibres, most commonly used as binder fibres.
- Side by side fibres, most commonly used to produce bulky, self-crimping fibres.
- Tipped products, most commonly used in limited specialty products.
- Segmented products, where by chemical, thermal and/or mechanical methods, the segments split into small individual fibres.
- Islands-in-a-Sea products, where the sea is normally dissolved away to leave only the very small islands. Various mixes of two or more fibre types to make such specialised products as yarns or fabrics having multiple cross-sections.

5.4.1 Sheath/Core and side –by-side fibres

A concentric sheath core system is typically used in binder fibres with a low-melting sheath around a higher-melting core. A nonwoven fabric is made with these fibres, and then heated to melt the sheath, which bonds the fabric together upon cooling. The concentric sheath/core can also be used to deliver an outer layer of a high value (and/or low strength) polymer around a lower cost, yet stronger core. Non-symmetric combinations (e.g. eccentric sheath core and side-by-side) of polymers are used to introduce either curl or crimp into the fibre.

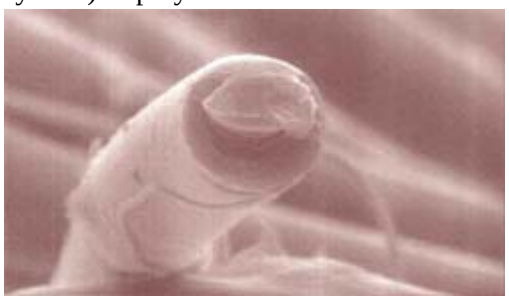


Figure 15: SEM photograph of a sheath core fibre

5.4.2 Pie/Wedge fibres

Pie/Wedge fibres may have a round cross section made of typically 8 to 16 adjacent wedges, similar to slices of pie. Each wedge of polymer A has a wedge of polymer B on either side, for a total of 8 wedges of each polymer. These fibres are designed to be split into the component wedges by mechanical agitation yielding microfibres of 0.1 to 0.2 denier in the final fabric. A combination of core fibres and pie fibres prevents the inner tips of the wedges from joining; thus making splitting easier and produces a more even cross section fibre. Further development has seen pies of 32 wedges being produced.

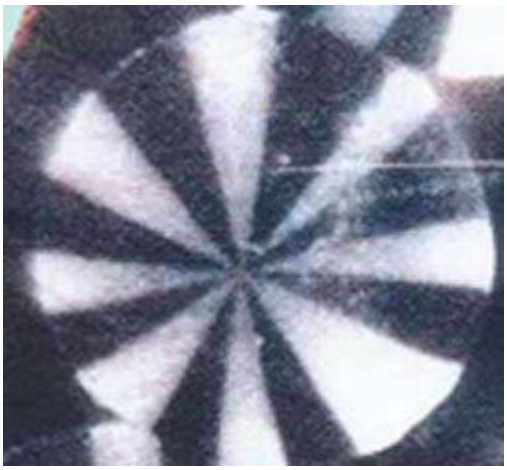


Figure 16: End view of a Pie wedge fibre

The conventional purpose of making a fibre like this is to form a card web of typically 3 denier per filament fibres, and to then pass the web under hydroentangling jets which simultaneously split the fibres into individual wedges, and entangle the fibres to give the fabric strength and integrity. As a result, the fabric contains fibres down to 0.2 denier per filament, but most of the throughput and processing advantages of a 3-denier fibre are maintained.
These fibres commercially available today are made from a mixture of nylon and polyester polymers. They are most often used in making synthetic suede and synthetic leather. In the case of synthetic leathers, a subsequent step introduces coagulated polyurethane into the fabric, and may also include a top coating. Another end-use that has elicited interest in pie wedge fibres is in technical wipes, where the small fibres are useful for picking up smaller pieces of dust. Finally, the fibres are also being evaluated for use in filtration. This application is somewhat limited by the fact that commercial splitting processes have so far been limited to hydroentanglement.

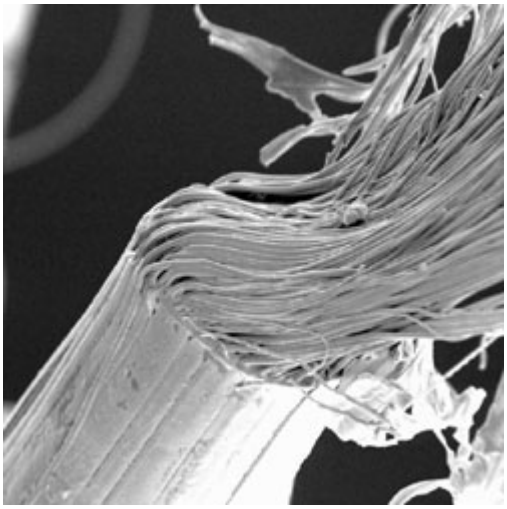
The best reason to use nylon and polyester (PET) for these fibres is that the two polymers have sufficiently little adhesion to each other that the wedges will actually split apart during hydroentanglement. They are also widely available, the PET is relatively inexpensive, and there is a wide body of knowledge about the fibre spinning characteristics of both polymers. However these two polymers have problems for use in fabrics as different dyes have to be used and they will fade at different rates. Ideally, bicomponent fibres should be manufactured from two types of near identical polyester. Significant advances are being made and split table all polypropylene fibres have been produced. Similarly the combination of dissimilar polymers can enhance the performance characteristic of the technical performance of the fibres. For example the polypropylene (PP) and PAN (acrylic fibres) have different chemical resistance and are on opposite ends of a triboelectric series. This means that when they are rubbed against each other, as in needlepunching, they develop opposite charges. As both polymers are good at holding these charges over long periods these have the potential for efficient electrostatic filtration materials.

Other fibre cross sections shapes are produced, partly to help splitting, but they may not be so easy to card or can come apart during carding causing handling difficulties.

Figure 16: SEM photograph of Pie wedge fibres in wipes after hydroentaglement separation.

5.4.2 ISLAND IN THE SEA TECHNOLOGY

This was an extension of the sheath core technology; originally the core would be dissolved away or filled with a cheaper or stronger fibre. However, it was also possible to produce fibre with several cores and by dissolving away the outside smaller fibres would be left. This



technology has rapidly developed over the last 3 years and has progressed from 3 cores to 3000.

Figure 17: SEM micrograph of island-in-the-sea fibres

These islands are of very uniform diameters compared with the much broader fibre size distribution of meltblown fibres. As the main fibre produced is around one denier a 600 islands fibre has islands ~0.3 um (300 nanometres) in diameter.

Hollow islands can also be made and a hollow islands remaining from a one denier, 600 islands-in-a-sea fibre have a wall thickness of only ~0.04 microns (40 nanometres). These are Nanotubes.

Figure 18: Nanotubes produced by Islands-in-the-sea fibres (Courtesy of Hills Inc.)

These micro or nano-sized fibres have excellent tensile properties (similar to conventional staple and spunbond fibres). This is because these tiny fibres are crystallised and oriented in the same manner as in processing conventional fibres. Meltblown and electrospun fibres on the other hand are low in crystallinity and orientation and are therefore very weak. These latter fibres are

so weak that they are often only used in composites with larger and stronger fibres. The bicomponent fibres can much more often be used without the need for larger, stronger fibres to create fabric strength. Alternatively, with modern technology, multi-component meltblown, staple, filament, or spunbond dies can be designed so that the right number and size of nanofibres are simultaneously produced in combination with just the right number and size of larger fibres to achieve the desired custom properties.

Compared to conventional meltblown and electrospun fibres, multi-component fibres can be produced more economically, stronger, more consistently, with broader polymer selection, and without practical restraint on size or shape.

Newer tri-component fibres are increasing the possibilities of this technology by producing even smaller and also a new generation of smart fibres that can adapt to their environment (e.g. fibres for use in a MEMS device (micro electromechanical system) will contract to act as a micro-actuator and is being used to develop self-cleaning or variable area filters (or membrane) by changing the pore sizes via changes in voltage applied to the fibres.

5.5 METAL FIBRES

Metal fibres can be made from pure metals, alloys or metalloid. It is also possible to coat / metallise many other fibre types. The main production methods are mechanical (wire drawing, bundle wire drawing, cutting production) or thermal (melt spinning and melt extraction). Bundle drawing can be used to produce fibres between 1 - 100 µm in diameter but thermal production methods produce fibre diameters of 50 –500 µm (Mac, et al., 2004).

5.6 CARBON NANOTUBES AND VAPOUR GROWN CARBON FIBRES

In the purest form single–walled carbon nanotube (SWCNTs) is a single layer of carbon atoms in a cylindrical arrangement some 0.0015 µm in diameter (1.5 nm) and a millimetre or more in length. These can also form several concentric layers of larger width. Production can take place by several methods but relies on a transitional particle as a catalyst in the presence of atomic carbon at high temperature and/or pressure. Laser ablation of a carbon plug containing Fe and Ni catalyst produces fibres that are collected on a cold finger trap. The HiPCO process introduces ultrafine Fe and NI catalyst into a high pressure and high temperature CO gas stream and the product collected on a filter. These particles group together and are difficult to separate into individual fibres.

Vapour grown carbon fibres (VGCF's) have much lower production costs but offer a range of carbon fibre diameters from 10 – 100,000 nm diameter and up to a few centimetres long. There are a number of production methods. A two stage method is commonly used. The first stage relies on an Fe catalyst particle which when exposed to hydrocarbon gas at 1000 ^{0}C produces a long slender partially graphited filament 10 –200 nm in diameter. A small fraction of these filaments grow to macroscopic lengths when exposed to a low carbursing potential gas while maintaining there filament diameter. Growth rates of 1 mm length per minute have been achieved. In the second stage the filament is thickened due to deposition of pyrolytic carbon.

A single stage method where the catalytic material is incorporated in the feedstock is a compromise between thickening and lengthening, which means that residence time in the reactive hydrocarbon gas is limited and fibre lengths are typically <100 µm and diameters <200nm making them highly respirable. The conditions of formation and further graphitisation at temperatures over 2600 ^{0}C means that these fibres can have a range of structural and surface properties (Van Hattum et al., 1999).

5.7 BIOENGINEERED TRANSGENIC FIBRES

A whole new production technology for fibres based on bioengineering is also being developed. This has seen the production of spider's webs from goat udders (Lazaris, 2002) and the strengthing of silk by bioengineering silkworm cocoons to produce spider-silk (DTI, 2004). Although not in production, it is expected that many types of fine fibres could be produced by bioengineering.

5.8 COMPLEMENTARY PROCESSES

Although it is not possible to go into any depth, a number of new possibilities are already being produced with the new fibre types:

- The addition of nanoparticles and nanotubes to give enhanced structural properties to other fibres.
- The application of coatings to change surface properties.
- The additional of metals to form new conducting structures.
- The additional of bactericides and metals (silver) to form wound dressings.

Variations in the numbers of polymers used to produce shape memory polymers (SMP).

6 USES OF THE TECHNOLOGY

It is too large a subject to cover the current and developing use of MMFs and technical textile fibres. Two different types of production (nonwovens and electrospinning) have been used to illustrated the current importance of synthetic fibres are filling and some of the advances in fine fibre production that will be produced in the next few years.

6.1 MAIN USES OF NON-WOVENS

Some of the current uses of nonwovens are listed in table 4.

Table 4: An A-Z of uses of non-woven products in various sectors.	
Agriculture	Crop covers, seed blankets, weed control fabrics, greenhouse shading, root bags, biodegradable plant pots, capillary matting
Automotive	Boot liners, parcel shelves Heat shields, shelf trim, moulded bonnet liners, boot floor covering, oil filters, headliners, rear parcel shelves, cabin air filters, decorative fabrics, airbags, silencer pads, insulation materials, car covers, underpadding, car mats, tapes, backing for tufted carpets, seat covers, door trim.
Building	Roofing and tile underlay, underslating, thermal and noise insulation, house wrap, facings for plaster board, pipe wrap, concrete moulding layers, foundations and ground stabilisation, vertical drainage.
Clothing	Interlinings clothing insulation and protection, handbag components, shoe components, belt liners, fire protection suits, high visibility garments, industrial headwear /footwear, disposable workwear, clothing and shoe bags, chemical defence suits
Geotextiles	Asphalt overlay, soil stabilisation, drainage, sedimentation and erosion control, pond liners, impregnation base, drainage channel liners.
Healthcare	Surgical: (disposable caps, gowns, masks, shoe covers), drapes, wraps and packs; sponges, dressings, wipes, bed linen, contamination control gowns, examination gowns, shrouds, underpads, procedure packs, heat packs, ostomy bag liners, fixation tapes, Incubator mattress
Home	Wipes / mops, washing pouches, fabric softener, vacuum cleaner bags, washcloths, kitchen and fan filters, tea and coffee bags,

	coffee filters, napkins and tablecloths, clothing and shoe bags, dusters, stain removers, kettle descaler bags, food wrap
Industrial	Coated fabrics, electronics – floppy disc liners, filters - air, liquid, and gases, satellite dishes, clothing Surfacing tissues / veils, cable insulation, insulation tapes, abrasives, conveyor belts, reinforced plastics, PVC substrates, flame barriers, artificial leather, noise absorbent layers, air conditioning, battery separators, alkaline cells, acid systems, rechargeable, anti-slip matting
Filtration	HEVAC / HEPA / ULPA filters, Liquid - oil, beer, milk, liquid coolants, fruit juices etc. Activated carbon
Furniture	Furniture construction, bedding construction window curtains, all coverings, Carpet backings, lampshades
Leisure and travel	Sleeping bags, tents, luggage, handbags, shopping bags, food delivery bags i.e. pizza, airline headrests, CD protection, pillowcases, surf boards, beer can widgets, sandwich packaging
Personal care and hygiene	Baby diapers, Feminine hygiene products, Adult incontinence products, Dry and wet wipes, Training pants, Cosmetic removal pads, Nursing pads, Nasal strips, Adhesive for dental plates, Disposable underwear
Office	Book covers, mailing envelopes, maps, signs and pennants, towels, bank notes
Wipes	Industrial wipes

6.2 DEVELOPMENT AND USES OF ELECTROSPUN FIBRES

Over the last 5 years interest in electrospinning has greatly increased due to interest in biotechnology and materials engineering at the nanoscale. The recognition of electrospun fibres morphologies in biology, and that the surface area associated with electrospun textiles can be a platform from which nanoscale chemical and biological processes can operate, has driven the explosion of interest and potential uses for the fibres. Some of the uses being exploited are due to the ease with which nanometre diameter fibres can be produced from a range of natural and synthetic polymers. The list of electrospun materials includes synthetic polymers with a broad range of conducting properties from non-conducting polyurethane (Demir et al., 2002) to highly conducting polyaniline (Norris et al., 2000), and natural polymers such as collagen (Mathews et al., 2002) and silkworm silk (Jin et al., 2002). The potential applications of such small fibres are numerous and diverse. Their small diameter offers advantages for filtration (Tsai et al., 2002) and composite materials (Kim et al., 1999). Their high surface area makes nanofibres

attractive as catalyst supports (Jia, 2002) and in targeted drug delivery (Kenawry et al., 2002). Electrospinning polymer solution with added carbon nanotubes results in super strong composite nanofibre (Ko et al., 2001). In addition, fibres electrospun from polymers can serve as carbon nanomaterials after pyrolysis (Wang et al., 2002). Non-woven fabrics electrospun from biocompatible materials are being developed for biomedical uses such as wound dressings and artificial tissue scaffolds (Lee et al., 2002). Electrospun conducting polymers have been used to fabricate nanowires (Mac Diamid et al., 2001) and to act as a host for a variety of meal doped products to produce by using palladium and are currently being investigated (Gaddy et al. 2003) for micro optical electronics purposes. The feasibility of incorporation of sized-sized particulates into fibres has made electrospinning even more attractive for the production of composite fibres [Wang et al., 2004a]. Orientation of the filler particles within the fibres during processing creates the possibility for manipulation of nanoparticles through appropriate handling of the fibres in which they are embedded and oriented. The critical material parameters for manufacturing such composite fibres include the type and geometry of the fillers, and the extent of homogeneous dispersion of filler within the polymer solution. Fong and co-workers first demonstrated the electrospinning of layered silicate nanocomposite into fibres [Fong et al., 2002].

7 LITERATURE SEARCH AND SAMPLE SOURCING

The first project objective was to: carry out a product and literature search of the fibres types currently manufactured or in use and for any information on the product in terms of physical characteristics and health effects/ hazard classification. Marketing / sales sections of manufacturers and suppliers were contacted for normal product information and samples of the product were requested.

The product and literature search was conducted using lists and contact addresses of the main fibre manufacturers from the textile yearbooks and similar resources. Most manufacturers also had web sites where some product information and contact information was available.

This proved to be much more problematic than anticipated. We have had very little response from the manufacturers when requesting samples and product information was often limited. This was a surprise and we concluded that mentioning our reasons for the request did not promote a positive response. Although we have tried several times keeping safety as minimal as possible there was a poor response rate in supplying samples via letter and e-mail requests.

Going to trade shows and requesting samples in face-to-face meetings used an alternative approach. The N. American technical textiles meeting was attended in 2004 and did produce much better results. The unexpected difficulties in obtaining samples for testing was a considerable problem, as it took much longer than originally anticipated.

The original impression when the project was devised (some years prior to receiving funding) was that there were a considerable number of synthetic fibres around but few of these textile fibres would present a problem because of their large diameter and other specialist inorganic fibres would be the main focus. However, the literature search showed new technologies have been developed over the last 5 years and are being introduced into synthetic and semi-synthetic fibre production. Although these have not had widespread market production yet, they will soon become commonplace. Similarly, the substantial growth of the technical textiles and levels of research funding in the areas of nanotechnology and biotechnology have added significantly to the ability to engineer fine fibres capable of entering the lung.

A list of MMF fibres identified from the literature search that would be of most interest is listed in appendix 1.

8 TEST STRATEGY AND METHODS FOR IDENTIFYING A POTENTIAL HAZARDOUS FIBRE

8.1 TEST STRATEGY

The test strategy was originally envisaged as follows:

- Microscopical examination of fibres to look for presence of fine fibres <6 µm diameter or evidence of splitting into finer fibres.
- Further microscopical examination after a standard challenge, to measure the propensity of the fibres to produce fibrils.
- If < 6 µm fibres produced measure the length weighted geometric mean diameter using established procedures.
- If presence of <6 µm diameter fibres or evidence of splitting into finer fibres, carry out dustiness test to measure number concentration and size of respirable (<3 µm width) fibres released.
- If significant number of respirable fibres released check solubility using mass loss in simulated lung fluid (static environment, 14 day test).
- If low mass loss, carry out further flow through testing of individual fibres for fibre diameter changes with time.

The principle factor is the presence of respirable fibres in the product or the ability to create finer fibres by some abrasion. Samples that contained or would produce fine fibres when abraded would be tested for their solubility in simulated lung fluid. The dustiness of the product and its ability to release respirable fibres was also tested on a selection of products.

8.2 FIBRE SIZE

Optical microscopy at X500 was used to view the fibre samples and to identify if respirable sized fibres were present and/or there was evidence of fibrils. The samples showing that fibrils could be present were then sized more accurately on the SEM. The fibres were first sized before testing by mounting the fibres onto an aluminium SEM stub using conductive double-sided mounts. The fibres were gold coated to decrease charging effects and to give a good image for SEM sizing. A small increase in the diameter would be produced due to the gold coating. After the fibrillation test samples were prepared and mounted in the same way.

Detailed sizing was carried out using scanning electron microscopy (SEM) to measure the fibre diameters at X5000 magnification (a magnification of X7000 was used for the fibrillated samples). As samples consisted of very long fibres in respect to the diameters, a length weighted diameter was measured. The length weighting is carried out by placing a line on the SEM screen. Only the diameters of fibres that cross the line are sized. The probability that the fibre will cross the line is related to the length of the fibre and therefore corrects for the bias due to

the fibre length. The sizing method was originally developed by HSL for the characterisation of meltblown MMVF fibres and has been adopted as a standard method across the EU. The arithmetic mean and standard deviation, median and the geometric mean and standard deviation were all calculated based on measurements of a minimum of 300 fibres. Also as used previously the length weighted geometric mean diameter – two standard errors was also calculated. This gives a value lower than the geometric mean, which represents the lower 95% confidence limit that other sub-samples sized in the same way, will not be below this value. The method / steps to calculate the geometric statistics are summarised in table 5. The arithmetic statistic and the median were calculated using the standard statistical package in Microsoft Excel.

Table 5: Calculation method used for the Length weighted geometric mean statistics.

1	Measure the diameter of n fibres	$(d_1 .... d_n)$
2	Calculate natural log for each fibre diameter:	$\ln(d_{1....}.... d_n)$
3	Calculate the average (mean) for the logged data:	$x_{ln} = (\Sigma(\ln(d_{1....}... d_n)) \div n$
4	Calculate the standard deviation of the logged data:	$\sigma_{ln} = (\Sigma(\ln(d_1) - x_{ln})) \div (n-1)$
5	Calculate the standard error of the logged data:	$\varepsilon_{ln} = \sigma_{ln} \div n^{½}$
6	Calculate lower 95% confidence limit of logged data:	$x_{ln} - 2 \times \varepsilon_{ln}$
7	Calculate the exponential of the 95% lower confidence interval of the logged data to give LWGM-2SE:	$\text{Exp}\ (x_{ln} - 2 \times \varepsilon_{ln})$

8.3 FIBRILLATION

A number of methods to assess the tendency of the fibres to fibrillate were considered and tested. There are at least two types of fibrillation that can occur:

- the production of fine swarf like fibres from the surface and cut ends of larger fibres during cutting the tow for staple and flock fibre, and
- the main fibres being constructed of smaller fibres usually longitudinally arrayed along the length of the fibre.

As reviewed there are a number of production processes (e.g. carding, cutting, needling, hydroentanglement) where the fibres may be subject to mechanical forces that will promote the fibrillation of the fibres. Fibres will also be abraded during use and again during any fabric reprocessing and reuse. The appropriate test is subjective and a number of methods were evaluated, using para–aramid fibres as the control, as it is known to have an ability to fibrillate.

A test method based on 1 minute of wet grinding in a ceramic pestle and mortar using very gentle pressure was found to be the best of the methods tested for promoting and assessing the ability of fibres to fibrillate.

8.4 DURABILITY / SOLUBILITY

The time and money available for this project only allowed for a limited solubility test to be carried out. A simple static test was used where approximately 500 mg of fibres was dispersed in 200ml of simulated lung fluid based on Gambles solution. The following quantities of chemical (see table 6) were used to make up the simulated lung solution.

Table 6: Chemicals used for modified Gambles Soln.

Chemical	Weight added (g) to 45l of Nanopure water (to make one carboy full)
Sodium Chloride	297
Sodium Hydrogen Carbonate	121.6
Calcium Chloride	0.1
Sodium hydrogen phosphate	16.1
Sodium Sulphate	3.6
Magnesium Chloride	9.5
Glycine	5.3
Sodium Citrate	6.9
Sodium tartrate	8.1
Formaldehyde	90
Pyruvic acid sodium salt	7.7
D - Lactic acid sodium salt	7.9

The solution had a pH = 7.1 at the start of the test as measured by an electronic hand held pH meter, which had been, calibrate against commercial standards.

The test fibres were weighed directly into tared 250 ml polythene bottles. Four similar weights were prepared for each sample. Two hundred millilitres of simulated lung fluid was added to each bottle and then it was capped and placed in an incubator and maintained at 37 ^{o}C. The bottle was shaken for 30 seconds at the beginning of the test and this was repeated twice per day for each test sample (not at weekends). Samples were left for 7,14, 21 and 28 days before filtering the fibre from the bottle onto 47 mm diameter pre-weighed Whatman GFA filters. The filter were placed in open tins and left for a minimum of two days to dry and equilibrate in the weighing room before reweighing. Although there was no pH control in this experiment the pH was measured at the end of the 28-day samples.

The weight difference for each fibre sample was calculated and plotted v time of test to determine the behaviour of the fibres in lung fluid. The surface area of the fibres was not measured.

A number of the more the bulky high surface area fibres were also tested at 50 mg weight to help handling of the samples.

8.5 DUSTINESS

Dustiness testing has been developed and used by HSL for a number of years (MDHS 81) for powders and granular or pellet materials. It has also been applied to a number of asbestos and MMVFs.

8.5.1 Description of the rotating drum test apparatus

The Mk 1 HSE rotating drum dustiness tester has an internal volume of 38 litres and consists of three sections: a main drum and two end pieces (see figure 19). The drum is 30 cm diameter x 46 cm long and has six internal vanes ~2 cm high (see figure 20), which lift and rotate any object inside. The two end pieces are used to direct the airflow into the drum through a P3 respirator type filter and to collect air from the drum using a 25-mm diameter conductive cowl cassette. The drum is mounted on a set of rollers that are driven by an electric motor to rotate at a constant speed. The cowled cassette is attached to the drum outlet using a plastic push fit seal and contained a standard Millipore 25mm 0.8µm pore filter and backing pads and meets the requirements in MDHS 39/4 and MDHS 59. However the end connector has been modified to allow the cassette to rotate but the pipe connecting the cassette to the pump to stay still. The pipe was connected to a battery driven flow controlled sampling pump.

The pumps used were a Casella Vortex 2 (xra10238) and a Casella Vortex Ultra (xra10244). Flow rate was measured using a calibrated bubble flow meter (Gilibrator xra9851).

Figure 19: HSL Mk1 Drum showing cowled cassette attached on the left side and inlet filter on the right.

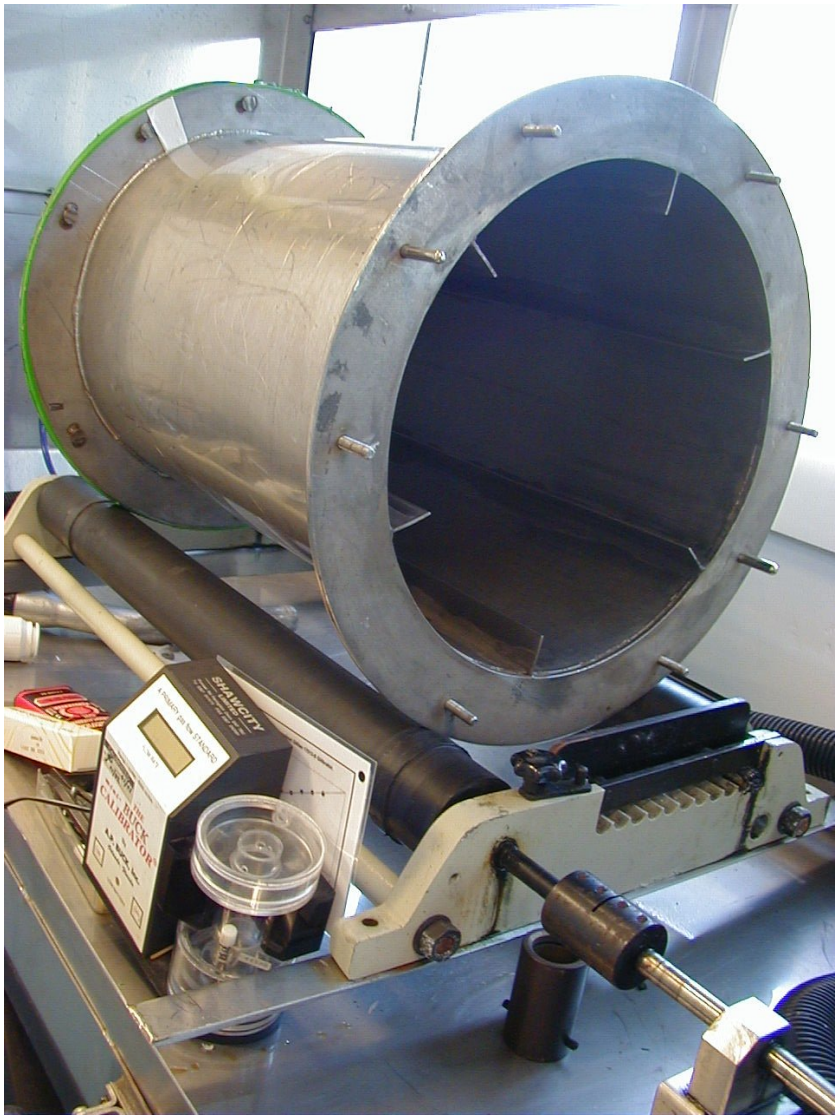


Figure 20: View inside the Mk 1 Drum showing the lifting vanes.

8.5.2 Test conditions

The apparatus allows three main parameters to be varied: rotation speed, flow rate and time of test/sampling. The tests were carried out at a drum rotation speed of 48 revs/minute and a sampling flow rate of 4 litres per minute (L/min.) for periods of 10 minutes. As fibres had different volumes and surface area a standard weight of each material was tested (12g). For powders a standard volume is usually measured but there was not easy way to do this for fibres.

Before the first test and after each subsequent test the drum was thoroughly cleaned using water and dried, to eliminate cross contamination. Before each material was tested a 10-minute blank was run (no material in the drum) to measure any background/residual levels of particulates in the system. The exact flow rate was measured using a calibrated bubble flow meter after the 10 minute blank, based on the average of 3 measurements.

8.5.3 PCM & PLM sample preparation and analysis

Each filter was first cut in half with a scalpel blade and a half filter mounted on a glass slide for optical microscopy using the method detailed in MDHS59 and HSG 248. The remaining half filter was retained for further analysis. The mounted filters were examined at X500 magnification by phase contrast microscopy (PCM) as detailed in MDHS59, to count all fibres (particles > 5µm long, <3µm wide and with an aspect ratio >3:1 (not attached to > 3 µm particles)). A minimum of 200 Walton-Becket graticule areas was normally examined for fibres. The concentration of 'regulatory fibres' meeting the above size range was calculated from the sampling and counting data. The samples tested for dustiness were also examined in RI liquids using polarised light microscopy (PLM) to check that the RI of the fibres was > than the mount (~1.51) so they would be visible. Only one sample was found to have an RI similar to or below the mount and this was etched and a temporary mount formed with water (RI ~ 1.3) as detailed in MDHS 59.

It should be noted that a count of 20 fibres or 40 fibre ends, is used as the limit of quantification for PCM fibre counting analysis due to possible background interferences. As low volumes of air were sampled for the rotating drum test the actual fibre counts and calculated concentration have been given, along with the calculated lower limit of quantification.

8.5.4 Test calculations

The results were all normalised based on the stated test conditions 12g of material, a flow rate of 4 L/min and a sampling time of 10 minutes to calculate the f/ml/g of material released.

9 RESULTS AND DISCUSSION

9.1 OPTICAL MICROSCOPY ASSESSMENT

The results from the optical microscopy of the fibre diameters and whether they showed evidence of containing a proportion of respirable fibres are given in table 7.

Table 7: Optical microscopy evaluation

Fibre category	Sample number	Diameter (μm) measured by PLM (magnification x 500)
Acrylic / PAN fibres	08353/03	~ 20-25
	08262/04	~ 15-17
Pre-oxidised acrylic fibres	08333/03	~15
Para-aramid fibres	08334/03	~ 25 to 3-5 or less
	08293/04	~ 12-13 + few fine fibres < 3
	08340/03 (pulp)	Fibrils
Aramid fibres	08440/04	~ 10-15
Meta-aramid fibres	08296/04	~ 12-15
Polyamide fibres	08439/04 (nylon 6.6)	~ 30
	08348/03 (nylon 6)	~ 20-25
	08349/04 (nylon 6.6)	~ 20
	08260/04	~ 25-35
Copper coated nylon	08540/04	~ 20-22
Cured phenol-aldehyde fibres	08274/04	~ 18
Polyurethane fibres	08342/03 (elastane)	~ 80-150+
Liquid crystal polymer fibres	08441/04	~ 10-40 + few <3
Liquid crystal polester fibres	08345/03	~ 25 + few fine fibres of 3 or < 3
	08402/04	~ 25-35
Melamine fibres	08449/04	~ 5-25
PIPD fibres	08275/04	~ 12 + few fibres < 3
Polybenzobisoxazole (PBO) fibres	08266/04	~10-13 + few fine fibres of 5-3 or <3
PTFE fibres	08332/03	~ 30 + few fibres < 3
Polyester fibres	08401/04	~ 8 to 12
	08424/04	~ 12-15 + few fibres < 3
	08291/04 to 08295/04	~ 15 to 20
Copper coated polester	08541/04	~ 25
Polyetheretherketone (PEEK) fibres	08268/04	~ 15-20
Polylactic acid fibres	08347/03	~ 35
Polyphenylene sulphide (PPS) fibres	08429/04; 08428/04	~ 10 to 20 + fine fibres down to ~ 3
Polyethylene fibres	08336/03	~ 15-20
	08453/04	~ 5-15 with fibres splitting to < 3
Polypropylene fibres	08433/04	10-25 few fibres ≤ 5
	08344/03	~ 45-55

	08259/04	~ 30-50
	08258/04	~ 150-600
	08343/03	~ 20-25
Polyvinylalcohol fibres	08399/04	~ 15-20
Polyvinyl chloride fibres	08442/04	~ 15-20
Polyvinylidenechloride fibres (PVDC)	08448/04	~ 30-35
Calcium alginate fibres	08331/03	~ 10-15
Solubilised cellulose derivative fibre	08460/04	~ 10-12
Cellulose fibres	08452/04	~ 5-20
Viscose fibres	08339/03; 08338/03	~ 10-15
	08257/04	~ 12-17
Soybean fibres	08400/04	~ 13-17
Cotton fibres	08261/04	~ 7-25
Flax fibres	08272/04	~ 10-20
	08271/04	~ 6-30
Hemp fibres	08270/04	Up to 200, down to 10 + few fine fibres of 5-3 or less
Jute fibres	08265/04	~ 80-90 down to 20-5
Carbon fibres	08355/03	~ 7-8
	08356/03	~ 5-6
	08357/03	~ 7-8
	08358/03	~ 7-8
	08359/03	~ 7-8
	08360/03	~ 7-8
Oxidised PAN fibres	08720/04	~ 12-15
Preoxidised fibres	08263/04	~ 10-15
Carbon nanofibres	08269/04	< 3
Nanofibres	08269/04	< 3
Phosphate fibres	08719/04	~ 8 to <3
Silica fibres	08337/03	~ 5-10
Stainless steel fibres / Metal fibres	08542/04	~ 13-15
	08335/03	~ 5-50
	08456/04	< 3
	08457/04	< 3
	22 µm (08397/04), 6.5 µm (08396/04), 12 µm (08394/04), 8 µm (08395/03)	
Polyester / nylon fibres Kanebo bicomponent	08283/04	~ 4-7
	08286/04	~ 5
	08287/04	~ 5-20
	08288/04	~ 5-15
Polyethylene terephtalate (PET) / Polyurethane (PU) Artificial suede	08455/04	~ 3-5
	08454/04	~ 3-4
Novitex - Viscose / polyester fibres	08278/04 to 08277/04	~ 12-15

9.2 FIBRILLATION TESTING RESULTS

The samples were tested for their ability to fibrillate and the results are summarised in Table 8. The degree of fibrillation measured by SEM sizing of the fibres before and after the fibrillation test are given in detail in Appendix 2. A total of 12 samples were measured before and after fibrillation testing, some samples fibrillated so much that accurate sizing of fibres was not possible after the fibrillation test. Two of the materials found to contain a small number of respirable fibres actually increased their length-weighted diameters after the test. This was due to the fibres being flattened by the grinding into oval shaped fibres, which had a larger diameter across the major chord. As described earlier fibres can fibrillate in two ways. Some fibres produced many swarf like fibres. The best analogy are the strips or slivers produced when a knife to peel back thin strips of bark from a branch (see figure 21). Fibres made up from smaller fibrils usually show splayed ends or broke down into finer fibres. The Kevlar pulp was particularly a challenge and the fibrillation was so extensive it could not be accurately sized.

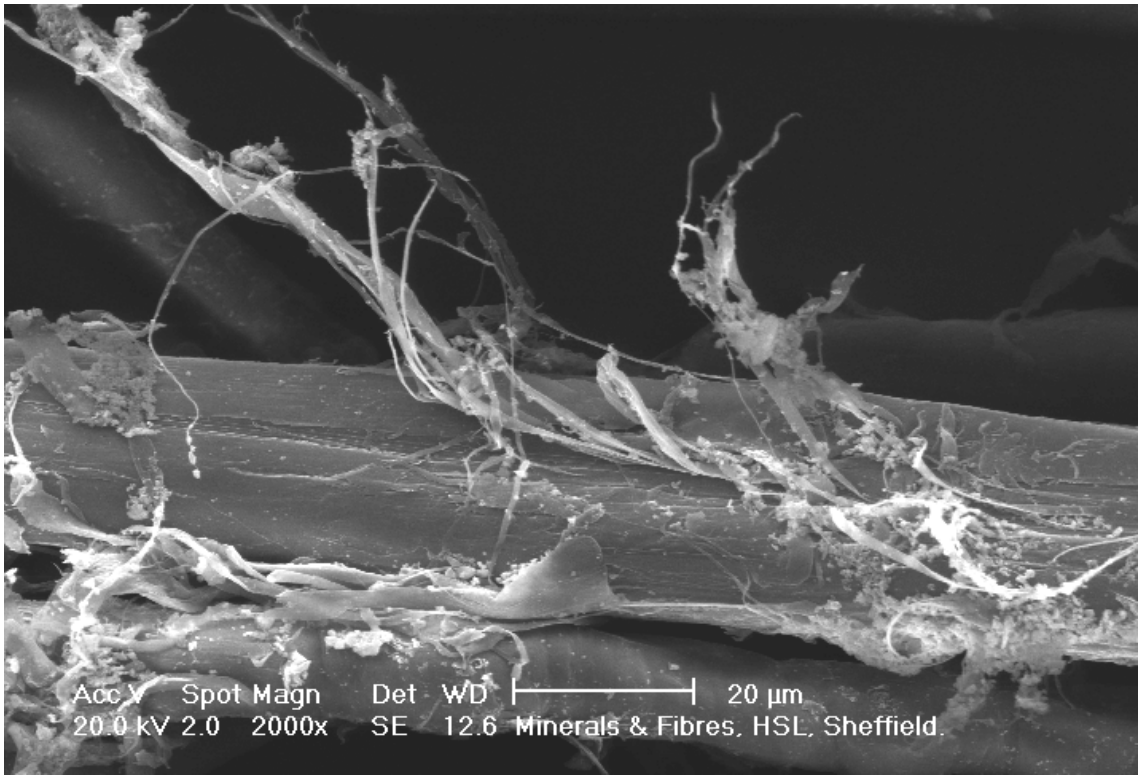


Figure 21: Para-aramid after fibrillation treatment (08334/03)

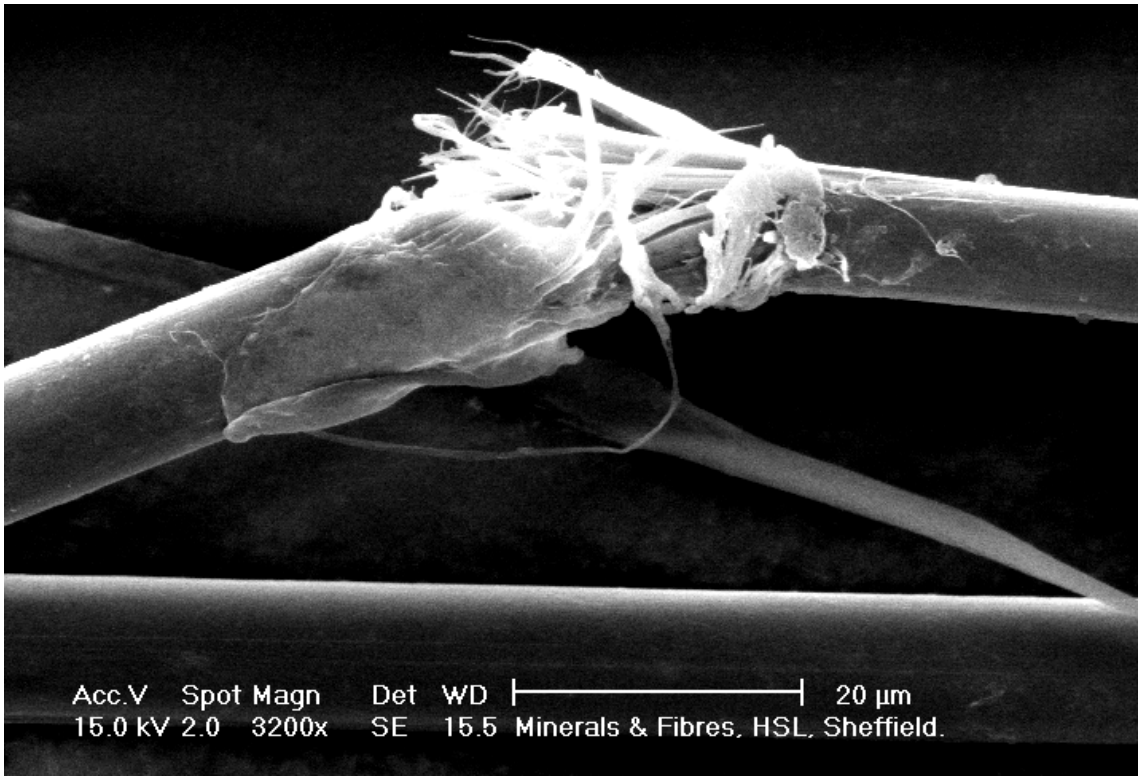


Figure 22 PIPD M5 (08275/04) fibres breaking to reveal the fibrilliar nature of the fibre.

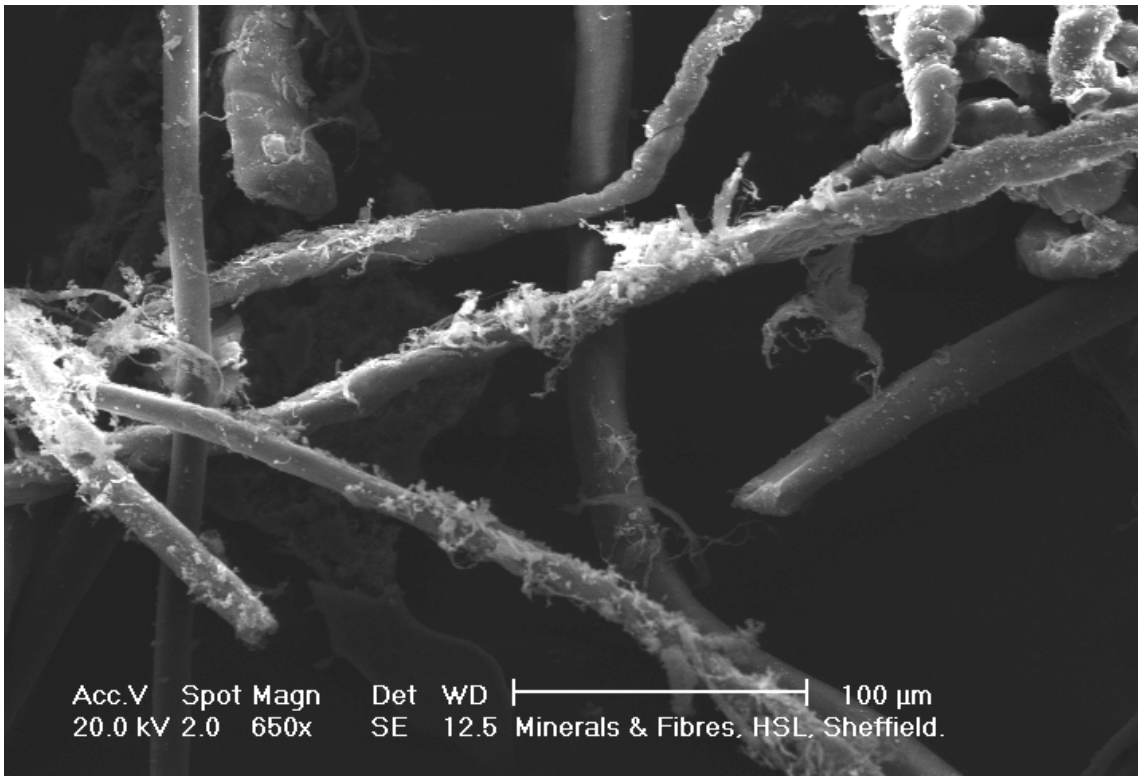


Figure 23: Large polypropylene fibres showing fibrils formed on the fibre surface after testing

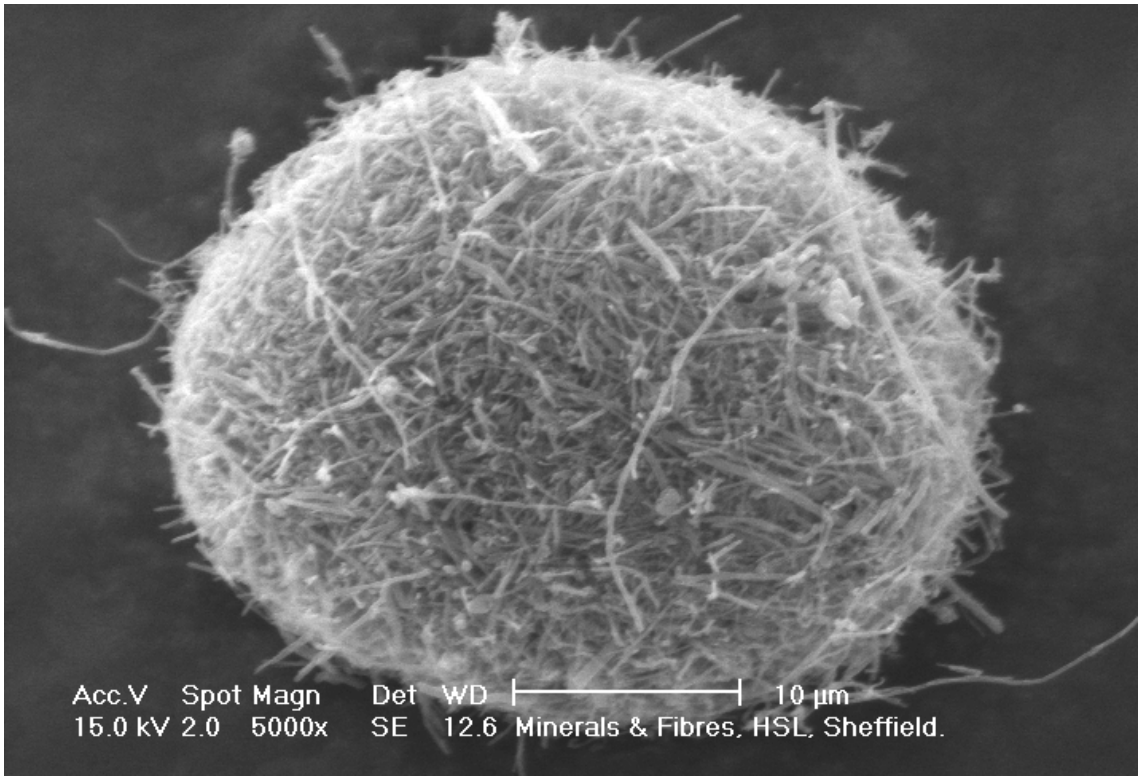


Figure 24: Vapour grown Carbon nanofibres, showing their typical tendency to form agglomerates.

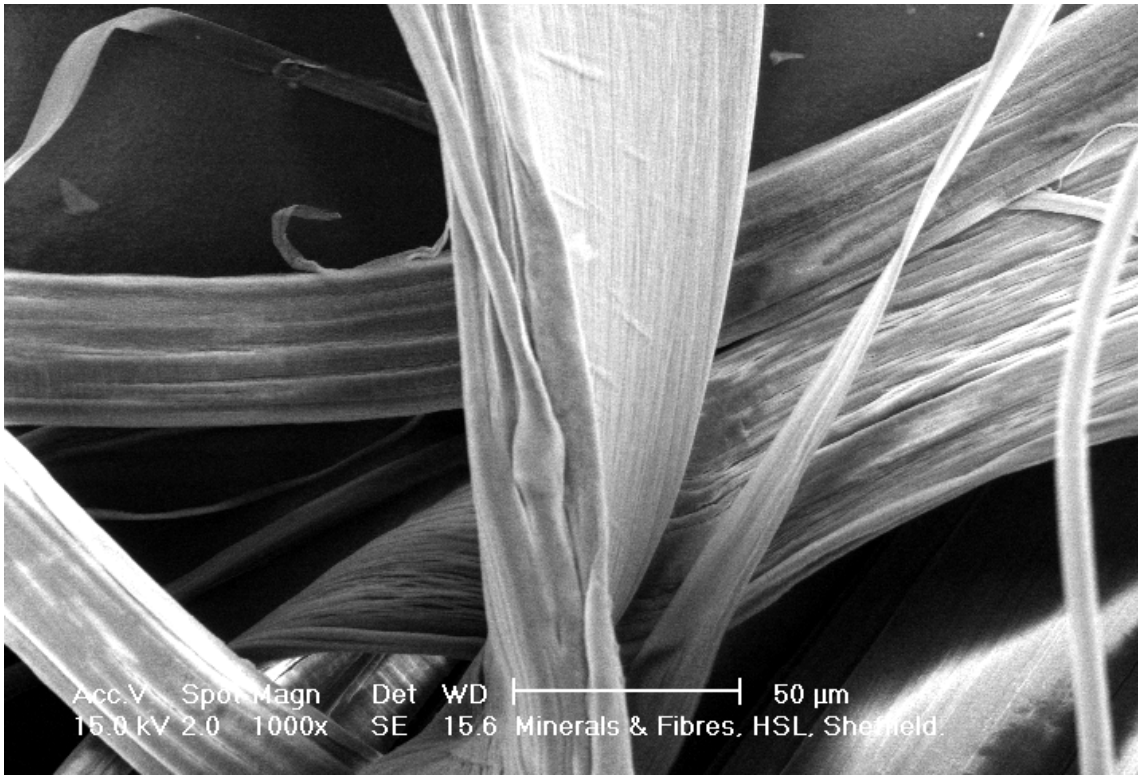


Figure 25: PTFE fibres sample 08332/04 showing some tendency to split longitudinally

Table 8: Summary of results of the fibrillation test and other tests carried out on samples.							
Fibre category	**Company / Sample origin**	**Samples**	**Sample number**	**Grinding test / PLM observation**	**SEM (length weight to geometric mean)**	**Solubity test**	**Dustiness test**
Acrylic / PAN fibres	Acordis	Acrylic fibres - Courtelle acrylic fibres (CFP, Duracol black, LC, TX neochrome, Std ecru)	08353/03 08350/03	Some fibrillation	Yes	Yes	Yes
	Wrigley fibres, Williton, Somerset, UK	Polyacrylonitrile fibres - White polyacrylonitrile fibre flock, PAN 6000	08262/04	Fibrillation	Impossible to count - General photos taken from grinded fibres	Yes	Yes
Para-aramid fibres	Sample origin unknown – From University contact	Para-aramid fibres	08334/03	Fibrillation	Grinded and non-grinded fibres measured	Yes	Yes
	Dupont	Kevlar 10,000 denier	08293/04	Fibrillation	Yes	No	No
	Ex BBA Group CIRCA 1989 – found in the laboratory	Kevlar pulp (aramid fibres)	08340/03	N/A	No	Yes	Yes
Aramid fibres	Cranenonwovens, Pittsfield, USA	Aramid blend coating base – Cranemat CX21.0	08440/04		No	No	No
Meta-aramid fibres	Dupont	Nomex 45,000 denier	08296/04	No fibrillation	No	No	No
	Cranenonwovens, Pittsfield, USA	Nylon 6.6 fibres – Cranemat NY 13.5	08439/04	No fibrillation – Some fibres flattened	No	No	No

Polyamide fibres	Origin unknown – From contact	Filament nylon 6, tricot bright	08348/03	No fibrillation – Surface and end of fibres can be damaged / flattened	No	No	No
	Origin unknown – From contact	Nylon 66 (tricot)	08349/04		No	No	No
	Wrigley fibres, Williton, Somerset, UK	Blend of polyamide fibres with carbon black / resorcinol-formaldehyde treatment - flock, N5000 RFL/CB	08260/04	No fibrillation - Surface and end of fibres can be damaged / flattened	No	Yes	Yes
Metal coated nylon fibres	R. STAT France	Copper coated nylon fibres – R. STAT/N 3.3 dtex	08540/04	No obvious fibrillation - Surface and end of fibres can be damaged / flattened	No	No	No
Cured phenol-aldehyde fibres	American Kynol Inc., Pleasantville, USA	Kynol Novoloid fibres for textile applications and fire protection (18 microns) x 51 mm – KF-0351-HC	08274/04	No fibrillation	No	No	No
Polyurethane fibres	Dupont De Nemours-Found in the laboratory	Elastane fibres - Lycra (elastane fibres) type 259B	08342/03	No real fibrillation – Fibres may split down to individual fibres of about 40 µm diameter	No	No	No
Liquid crystal polymer fibres	Cranenonwovens, Pittsfield, USA	100% liquid crystal polymer saturating base for aggressive environments – Cranemat HB 70	08441/04	Some fibrillation	Yes	No	No

	Celanese acetate / Vectran	Liquid crystal polyester fibres 1500 1300HT	08345/03	Fibrillation	Yes	Yes	Yes
	Celanese acetate / Vectran	Vectran mono-filament	08402/04	No real fibrillation	No	No	No
Melamine fibres	BASF, Germany	Basofil fibres	08449/04	No fibrillation	No	No	No
PIPD fibres	Magellan Systems international	M5 fibres for ballistic protection	08275/04	Fibrillation	Yes	No – Not enough sample	No – not enough sample
Polybenzobisoxazole (PBO) fibres	Toyobo	PBO chopped fibres (HM 6mm) – Zylon fibres	08266/04	Fibrillation	Yes	Yes	Yes
PTFE fibres	Sample origin unknown – from contact at University	PTFE fibres	08332/03	No real fibrillation - Fibres flattened / distorted – Fibres < 3 µm diameter present in original sample	Yes	No	No
Polyester fibres	Consolidated textiles, Charlotte, USA	Polyester fibres (0.9 denier)	08401/04	No fibrillation	No	No	No
	Cranenonwovens, Pittsfield, USA	Polyester fibres – Cranemat SR Laminate base, cover stock SR4.5; SR9.0; SR 13.5; SR18.0; SR 27.0 and SR36.0	08424/04 (SR4.5)		No	No	No
	Dupont	Dacron 3140 denier; 7500 denier; 18,000 denier; 30,000 denier	3140 (08291/04); 7500 (08292/04); 18,000 (08294/04); 30,000 (08295/04)	No fibrillation (08291/04 and 08294/04)	No	No	No
Metal coated polyester fibres	R. STAT France	Copper coated high tenacity polyester –	08541/04	No obvious fibrillation – End	No	No	No

		R.STAT/P 5 dtex		of fibres can be damaged / flattened			
Polyetheretherketone (PEEK) fibres	Zyex	PEEK staple fibres (3.3 dtex)	08268/04	No fibrillation	No	No	No
Polylactic acid fibres	Cargill Dow	PLA fibres	08347/03	No fibrillation – fibres flattened and damaged	No	No	No
Polyphenylene sulphide (PPS) fibres	Cranenonwovens, Pittsfield, USA	PPS fibres – Cranemat PPS CC60.0 and CC21.0	08429/04 (CC60.0); 08428/04 (CC21.0)	No fibrillation	No	No	No
Polyethylene fibres	Sample origin unknown – from contact at University	Polyethylene fibres	08336/03	No fibrillation – Fibres flattened	No	No	No
	Dupont	Very fine high density polyethylene fibres	08453/04	No obvious fibrillation – Tyvek made of very fine fibres	Measurements on non-grinded fibres	No	No
Polypropylene fibres	Cranenonwovens, Pittsfield, USA	100% polypropylene laminate base, cover stock – Cranemat KM 4.5; KM 9.0; KM 18.0; KM 27.0 and KM36.0	08433/04 (KM 4.5)	No fibrillation – Fibres flattened	No	No	No
	Plasticisers Ltd. Drighlington, Bradford, UK – at laboratory	15 Denier polypropylene fibres	08344/03		No	No	No
	Wrigley fibres, Williton, Somerset, UK	Polypropylene fibre flock, PP1	08259/04	No fibrillation – very few finer fibres (20 to 3 µm diameter) detaching from original fibres	No	No	No

	Wrigley fibres, Williton, Somerset, UK	Polypropylene fibre high F - flock, PPHF1	08258/04	No fibrillation – Fibres flattened	No	No	No
	Drake Extrusion Ltd	Polypropylene fibres	08343/03	No fibrillation	No	No	No
Polyvinylalcohol fibres	China textile machinery and technology import and export corporation	Polyvinylalcohol (PVA) fibres	08399/04	No real fibrillation. Fluffy particles generated.	No – General photos taken from grinded fibres	No	No
Polyvinyl chloride fibres	Cranenonwovens, Pittsfield, USA	100% polyvinyl chloride media support, flow channel – Cranemate VS 9.0	08442/04	No fibrillation	No	No	No
Polyvinylidenechloride fibres (PVDC)	Asahi Kasei Live and Living Corporation, Japan	Saran staple fibres SS-4641, 51mm, 15D	08448/04	No fibrillation	No	No	No
Calcium alginate fibres	Sample origin unknown	Calcium alginate fibres	08331/03	Fibres dissolved in water	No	No	No
Solubilized cellulose derivative fibres	Lenzing Lyocell, Austria	Lyocell fibres	08460/04	Fibrillation	Yes	Yes	Yes
Cellulose fibres	Found the the laboratory (1992)	Cellulose CF11 (RL/80894/92)	08452/04	No fibrillation	No	No	No
Viscose fibres	John L. Brieerly Ltd. Turnbridge Mills, Huddersfield, UK - Found in the laboratory	Matt spun viscose fibres and bright spun viscose fibres	08339/03 (matt); 08338/03 (bright)	No fibrillation (08338/03)	No	No	No
	Wrigley fibres, Williton, Somerset, UK	Viscose fibre flock, V1	08257/04	No fibrillation – fibres break down in smaller particles	No	No	No
Soybean fibres	China textile machinery and technology import and export	Soybean yarn	08400/04	No real fibrillation	No	No	No

	corporation						
Cotton fibres	Wrigley fibres, Williton, Somerset, UK	Blend of coloured cotton fibres & flock, MCD 1000/12	08261/04	Fibrillation	Yes	No	No
Flax fibres	Saneco, Nieppe, France – Pointe-Claire (Quebec)	Flax fibres DI 15 cut at 8mm	08272/04	Fibrillation	Impossible to count - General photos taken from grinded fibres	No	No
		Flax fibres EOT3 cut at 60 mm	08271/04	Fibrillation	No	No	No
Hemp fibres	Saneco, Nieppe, France – Pointe-Claire (Quebec)	Hemp fibres DI290/2	08270/04	Fibrillation	Impossible to count - General photos taken from grinded fibres	No	No
Jute fibres	Wrigley fibres, Williton, Somerset, UK	Brown milled jute fibre flock, JW 12000	08265/04	Fibrillation	Impossible to count - General photos taken from grinded fibres	No	No
	From contact at Sheffield University	Tenax HTA 5I31 (Toray)	08355/03	No fibrillation (fibres break / become shorter in length)	No	No	No
		M55JB (Toray)	08356/03	No fibrillation (fibres break / become shorter in length)	No	No	No
		Besfight G30-500 (Toho carbon fibres)	08357/03	No fibrillation (fibres break / become shorter in length)	No	No	No

Carbon fibres		Tenax HTA500 (Toho)	08358/03	No fibrillation (fibres break / become shorter in length)	No	No	No
		T800 HB (Toray)	08359/03	No fibrillation (fibres break / become shorter in length)	No	No	No
		234-57	08360/03	No fibrillation (fibres break / become shorter in length)	No	No	No
Preoxidised / Oxidised PAN fibres	Chapman, Salt Lake City	Carbon X fibres – Blend of O-pan fibres and strengthening fibres	08720/04	Fibrillation and fibres break / become shorter in length	Yes	No	Yes
	Sample origin unknown – from contact at Leeds University	Pre-oxidised acrylic fibres	08333/03	No fibrillation (fibres break / become shorter in length)	No	No	No
Preoxidised fibres	Taiwan KK Corp.	Kanox fire resistant fabric CCBE46B2 – Kanox HM02RP	08263/04	Fibrillation	Yes	No	No
Carbon nanofibres	Pyrograf Products, Inc.	Pyrograph III Carbon fibre, HT grade. 150nm	08269/04	N/A	N/A – General photos taken	No	No
Nanofibres	Donalson	Ultraweb nanofibre filtration	08269/04	N/A	N/A – General photos taken	No	No
Phosphate fibres	Monsanto company	Phosphate fibres – calcium sodium metaphosphate – Found in the laboartory	08719/04	Fibres break / become shorter in length and also split longitudinally	No	No	No
Silica fibres	Sample origin unknown – from contact at Leeds	Silica fibres	08337/03	No fibrillation - Fibres break / become shorter in	No	No	No

	University			length			
Stainless steel fibres / Metal fibres	R. STAT, France	100% stainless steel fibres - R.STAT/S 12/100 – 100% steel 12 μm	08542/04	No fibrillation – Fluffy particles generated	No	No	No
	Sample origin unknown – from contact at Leeds University	Stainless steel fibres	08335/03	No fibrillation	No	No	No
	Bekaert Fibre Technology, Zwevegem, Belgium	Bekinox VK 2 micron 316LV	08456/04	No fibrillation	No	No	No
		Bekinox VK 1.5 micron 316VR	08457/04	No fibrillation	No	Yes	Yes
	China textile machinery and technology import and export corporation	Stainless steel 316L (22 μm, 6.5 μm, 12 μm, 8 μm)	22 μm (08397/04), 6.5 μm (08396/04), 12 μm (08394/04), 8 μm (08395/03)	No fibrillation (08396/03 and 08394/03)	No	No	No
Glass fibres	Cranenonwovens, Pittsfield, USA	CRANEGLAS 230 – continuous chop stand fiberglass (E-glass) – 6.1; 11.0 and 19.4.	08430/04 (6.1)		No	No	No
	Cranenonwovens, Pittsfield, USA	CRANEGLAS 500 manufactered with BelCoTex – reinforced fibre 6 - 75 g/m^2 0.8 mm; 150 g/m^2 1.6 mm and 300 g/m^2 3.2 mm.	08436/04 (75 g/m^2 0.8 mm)		No	No	No
Basalt and glass fibres	EBAS, Georgia	Felt non-woven combined from basalt and glass fibres (FBF G)	Basalt (08289/04) - glass (08290/04)		No	No	No

Polyester / nylon fibres	Kanebo Gohsen Ltd	Savina minimax – 70% polyester / 30% nylon fibres (belima X)	08283/04	No obvious fibrillation – fibres 'flattened' by grinding treatment	General photos taken on non-grinded fibres	No	No
	Kanebo Gohsen Ltd	Savina AS208 – Ultrafine microfibre Belima X (1-5 μm) and conductive Beltron fibres	08286/04	No obvious fibrillation – fibres 'flattened' by grinding treatment	No	No	No
	Kanebo Gohsen Ltd	Savina AS108 – Ultrafine microfibre Belima X (1-5 μm) and conductive Beltron fibres	08287/04	No obvious fibrillation – fibres 'flattened' by grinding treatment	General photos taken on non-grinded fibres	No	No
Flame retardant paper (40% melamine fibres + other fibres)	Engineered fibers technology, Shelton, USA	Flame retardant paper (40% melamine fibres + other pulp? Fibres (acrylic, Vectran?)	08450/04	Fibrillation	Impossible to count – two types of fibres, only one type fibrillate	No	No
Polyethylene terephtalate (PET) / Polyurethane (PU) Artificial suede	Asahi Kasei Fibers Corporation, Japan	Lamous – Artificial suede fabric: - ALS/74E11 (PET 88%, PU 12% - PET fiber: 0.15 d; PET scrim 150d) Upholstery furniture.	08455/04	No fibrillation	General photos taken on non-grinded fibres	No	No
		Lamous – Artificial suede fabric: - RLSB/70B11 (PET 93%, PU 7% - PET fiber: 0.1 d; PET scrim 100d) Fashion garment.	08454/04	No fibrillation	General photos taken on non-grinded fibres	Yes	No
Stainless steel fibres + polyester fibres	R. STAT, France	R.STAT/S 12/50 – 50% PES + 50% steel 12 μm			No	No	No

Viscose / polyester fibres	Novita SA, Zielona Gora, Poland	Novitex E50 TS - Viscose / polyester fibres	08278/04	No fibrillation	No	No	No
	Novita SA, Zielona Gora, Poland	Novitex E50 - Viscose / polyester fibres	08279/04	No fibrillation	No - General photos taken on non-grinded fibres	No	No
	Novita SA, Zielona Gora, Poland	Novitex E100 LM - Viscose / polyester fibres	08276/04	No fibrillation	No	No	No
	Novita SA, Zielona Gora, Poland	Novitex E170 LM - Viscose / polyester fibres	08280/04		No	No	No
	Novita SA, Zielona Gora, Poland	Novitex E80 – Viscose / polyester fibres	08277/04	No fibrillation	No	No	No
Acrylic fibres + melamine fibres?	Newtech, Shanghai new techtextile co ltd	CPF 403 – 33 wt% fibrillated acrylic fibres + 67 wt% melamine fibres	08267/04	No fibrillation	No - General photos taken on non-grinded fibres	No	No
Bi component fibres?	Ibena Germany	Silver polishing cloths	08264/04	Fibrillation	Yes	No	No

9.3 SOLUBILITY TEST RESULTS

Two types of 47 mm diameter filter types were investigated for their weight stability: polycarbonate membrane filters and glass fibre filters. The filters were tested by weighing before and after filtering 200 ml of simulated lung fluid and then 200 ml of pure water through 3 filters of each type. The filters were weighed after 24 hours conditioning/drying. The results showed that the Whatman GFA glass fibre filters were the most weight stable (<0.2% variation before and after filtering) compared with 3.8% for the polycarbonate filters and the former were used for filtering and weighing the fibre samples after each test.

The weight stability (see table 9) of the test fibres was also monitored using ~ 50mg of test sample and an average variation of around 1% was found due to changes in external conditions. The polythene bottles used for the test were also checked for stability over a short term period, the fibres are weighed into the tared bottle and the bottles were seen to increase in weight by up to 1 mg over a few minutes is left on the balance in the weighing room.

Table 9: W eight stability of test fibres in air

		Percentage weight change of a ~50 mg sample after		
Fibre	Fibre ID	1 day	2 days	7 days
Carbon x	08720/04	1.3	0.6	0.4
L.C	08350/03	1.1	0.7	1.0
Para-aramid	08334/03	0.7	0.3	0.4
Lyocell	08460/04	2.2	1.4	1.4
Zylon	08266/04	0.5	0.2	0.7
Nylon flock	08260/04	1.0	0.3	0.1
Metal fibre	08456/04	1.3	1.0	1.0
Pan flock	08262/04	0.7	0.4	-0.1
Vectran	08345/03	0.6	-0.1	-0.7
Kevlar pulp	08340/03	1.6	1.1	0.8
Average		1.1	0.6	0.5

Despite these controls and the use of check weights the samples tested for 7,14, 21 and 28 days all showed an increase in weight compared to the original fibre weight and suggested that there must have been some systematic error in the original weighing procedure. The actual percentage weight changes for the 500 mg samples after being exposed to lung fluid are shown below. It can be seen that the very small changes in weight, usually up to 1% are within the weight change of the original samples in air. This means that the solubility in terms of weight loss were relatively very low and unlikely to be detectable. The pH of the modified Gamble's solution was little changed for all the fibres tested and generally increased from 7.1 at the start of the experiment to 7.4 after 28 days.

Table 10: Weight changes in 500 mg test samples

		Percentage weight change of a ~500 mg sample after			
		7 days	**14 days**	**21 days**	**28 days**
Carbon X	08720/04 2	6.06	5.47	5.09	5.34
L.C.	08350/03 2	1.34	0.72	0.72	0.62
Para aramid	08334/03 2	2.67	1.32	0.70	1.07
Lyocell	08460/04 2	1.86	1.01	-0.10	0.02
Zylon	08266/04 2	1.01	0.24	0.08	1.04
Nylon flock	08260/04 2	0.44	0.16	0.59	-0.54
Metal fibres	08456/04 2	0.09	0.15	0.23	0.31
Pan flock	08262/04 2		0.15	-0.68	-0.09

The low solubility of many of the synthetic fibres has been found to give similar problems to other researchers. Para-aramid and carbon fibres have shown to be insoluble in Gamble's solution by a range of methods: weight (Forster, 1984), atomic absorption spectrometry (Larsen, 1989) and Law et al. 1990 reported polyethylene, polypropylene and polycarbonate found no dissolution and a weight increase after a 180 day test.

It appears that in lung fluid most synthetic fibres have low solubility and would be expected to remain in the pulmonary region of the lung for many years if nor removed by macrophage mediated clearance. However, the importance of enzymes on the clearance of para-aramids (Warheit et al. 2002) and polyester (Mieschental et al., 1987) does mean that the biosolubility inside the lung may be much higher and in-vivo experiments are needed to properly assess the solubility of MMOFs if they show low solubility in in-vitro solubility tests.

9.4 DUSTINESS RESULTS

The samples tested for regulated fibre release in the dustiness tester are listed in table 11

Table 11: Fibres tested for dustiness

Test Sample No	HSL Sample No	Fibre type	Mass (g)
Sample 1	08262/04	Polyacrylonitrile flock	12.0
Sample 2	08260/04	Nylon flock	12.8
Sample 3	08266/04	Polybenzobisoxazole (PBO) fibres	11.8
Sample 4	08340/03	Kevlar Pulp	3.56
Sample 5	08334/03	Para-aramid	12.0
Sample 6	08460/04	Lyocell fibre	12.2
Sample 7	08350/03	Acrylic fibres	12.2
Sample 8	08456/04	Metal fibre	13.2
Sample 9	08345/03	Liquid crystal polyester fibres	12.0
Sample 10	08454/04	Synthetic Leather	11.5

For two of the tests (sample 1 & 8) high fibre releases occurred and gave overloaded samples so the sampling time was reduced to provide a range of filter loadings for analysis. Also on some samples where the first sample had low counts, the sampling time was doubled to see if increased numbers of fibres could be collected on the filter to improve the precision. The results were all normalised based on the stated test conditions 12g of material, a flow rate of 4 L/min and a sampling time of 10 minutes to calculate the f/ml/g of material released.

After each sample had been tested the sample was recovered from the drum and replaced in a sealed bag. This, for most instances, allows a visual comparison of effect of the test process on the sample. A sample mass of ~12g was used except for sample 4 as the amount of material was limited. The effect of the rotating drum on the test samples was noted (see table 12), usually the rotary action resulted in the loose fibres tending to agglomerate and form small balls of fibres, although sample 10 – a fabric sample was unchanged.

The results of the PCM blank and fibre counts for respirable fibres are given in tables13 & 14.

Table 12: Observations of behaviour of test material in the rotating drum		
1	Polyacrylonitrile Flock	Before – Clumps of fluffy fibrous material app 2-3cm After – Broke and balled up into small clumps app 0.5cm
2	Nylon	Before – Short (app 0.5cm) fibre bundles After – Some balling but still mostly individual fibres/bundles
3		Before – Short (app 1cm) metallic looking fibre bundles After – Larger fibres balled together during testing while smaller fibres released
4	Kevlar pulp	Before – Clumps of pulped material app 2cm After – Smaller clumps of pulped material <1cm
5	Para-aramid fibres	Before – Longer (app 5-10cm) fibre bundles After – Became fluffier and many fibres released
6	Lyocell fibre	Before – Clumps of fluffy fibrous material with large long fibres After – Became fluffier but stayed intact with visible long fibres.
7	Liquid crystal fibre	Before – Clumps of fluffy fibrous material After – Pulled apart and became fluffier but stayed together
8	Metal fibres	Before –Metallic fibrous string After – Many small fibres released. Still in long lengths but balled up into lumps
9	Liquid crystal polyester fibres	Before – Fibrous string – cut into app 1-2cm lengths After – Many small fibres released but stayed mostly intact. many fibres visible on filter
10	Synthetic leather	Before – Fabric cut into smaller squares app5cmx5cm After – No visible change in material Note - Refractive index <1.5, etched and mounted in water.

Table 13: Results from PCM MDHS 59 fibre counts of blank samples				
Blank Number	No of graticule areas examined	No of fibres counted	PCM fibres Conc. (f/mm^2)	PCM fibres Conc. (f/ml)
Start Blank	200	7.5	4.87	0.05
Blank 2	200	2.0	1.30	0.01
Blank 3	200	8.0	5.20	0.05
Blank 4	200	7.0	4.55	0.04
Blank 5	200	6.0	3.98	0.04
Blank 6	200	5.5	3.65	0.03
Blank 7	200	2.5	1.66	0.02
Blank 8	200	3.0	1.99	0.02
Blank 9	200	2.5	1.66	0.02
Mean	200	4.8	3.20	0.03

Table 14:Results from PCM fibre counts to MDHS59 rules.							
Sample Number	Volume (L)	No of fields	No of fibres	Mass of sample (g)	Fibre Conc. (f/mm^2)	Normalised PCM Conc. (f/ml)	Normalised PCM Conc. (f/ml /g)
1B	16	47	109.0	12.03	301.28	77.79	6.48
2B	51	200	10.0	12.80	6.50	0.01	0.00

3	58.7	200	9.5	11.80	6.17	0.02	0.00
4	40.6	200	72.5	3.56	47.09	1.37	0.11
5	41.8	200	5.5	12.00	3.65	0.00	0.00
6A	42.6	200	4.5	12.20	2.98	0.00	0.00
6B	81.6	200	11.0	12.20	7.29	0.00	0.00
7A	42.4	212	10.0	12.20	6.25	0.02	0.00
7B	84.2	200	7.5	12.20	4.97	0.00	0.00
8C	4.1	200	19.5	13.20	12.93	10.64	0.89
9	42.5	200	2.0	12.00	1.33	0.00	0.00
10A	42.1	200	5.5	11.50	3.65	0.00	0.00
10B	84.2	200	6.0	11.50	3.98	0.00	0.00

The blank results showed that there was little or no cross contamination between samples and were similar to what would be expected from blank filter counts. Taking a mean of 3.2 f/mm^2 and sampling a volume of air of 40 L gives an equivalent value of 0.03 f/ml. Therefore if the airborne fibre counts exceed 3 times the background (i.e. ~ 0.1 f/ml) using the test it was indicative of potential fibre release from the bulk material. For the purposes of the database values of 0.1 – 1.0 f/ml/g are regarded as low, 1 –10 f/ml/g as medium and 10 – 100 f/ml/g as high release of respirable fibres. During the test the drum rotation speed did slow down but would have had no significant effect on the relative level of release. The dustiness test itself will give fibre concentrations much higher than would be found during normal handling and use because there is little dilution (1 air change) taking place inside the drum and there is a high level of disturbance.

The medium value for respirable fibre release during dustiness testing for the polyacrylonitrile flock was a surprise and many of the fibres looked like slithers shaved off the fibre. It is unlikely this could be due to tumbling in the drum and must have been present in the flock. The Kevlar pulp and metal fibres also gave some low fibre release, which could be of concern.

10 DATABASE

The information from the literature search and the information from the testing was organised into a database for future reference by HSE personnel.

10.1 DATABASE CONSTRUCTION

The database was created in Microsoft Access so it was fully adaptable and searchable in a package common to HSE.

A table was first created, followed by a query and a form called FrmFibres (under Forms), where the data are imputed. Finally, these data on fibres were transferred into a report through the creation of a file called Database fibres report, accessible under Reports.

Each fibre record was created and identified through the key field ‘main chemical name’. Each record was divided in six main sections: Fibre, Properties, Manufacturing process, Toxicity, Epidemiology. The data were introduced through the fibre form FrmForm and the each section had the following fields:

Fibre:
- Category
- Acronym
- Formula

Manufacturing process:
- Trade names
- Supply form
- Fibre type
- Manufacturers
- Manufacturing process
- Applications

Properties:
- Quoted dimension
- Temperature performance
- Chemical resistance
- Fracture morphology
- Other properties
- Properties reference
- Fibrillation test
- SEM picture (1)
- SEM picture (2)
- Dimension / Arithmetic mean and length weight to geometric mean
- Dustiness
- Measured solubility

Toxicity:
- Biopersistence / Biodegradability
- In-vitro Instillation and Injection tests
- In-vitro inhalation tests

- Cell cultures
- Evaluation
- Toxicity reference
- Occupational exposure data

Epidemiology:
- Epidemiology studies
- Epidemiology references

Epidemiology:

The report ‘Database fibres report’ collected all the information introduced in the fields of the form called ‘FrmForm’.

10.2 INTENDED USE OF THE DATABASE

The database is not produced as an annex to this report as this is intended for HSE use only. At this stage we have not attempted to rank all the fibres by their potential hazard or risk but the information in each record is sufficient to see whether respirable fibres and fibrils are present and whether they have low solubility in-vitro. The available information on toxicity testing is summarised for each fibre type.

11 CONCLUSIONS

Overall the worldwide production of fibres is continuing to increase. The production and use of synthetic (oil based) fibres continues to expand rapidly and has overtaken the production of natural animal and plant fibres. Semi-synthetic fibre made from processing natural materials has also expanded but the development of speciality fibres and processes offer new materials and new hazards.

The perception of textiles of consisting of relatively large fibres with little health risk from the fibres themselves is still largely valid for natural fibres and many familiar synthetic fibres. This is due to the fibre sizes that can be handled by conventional textile machinery are typically above 10 µm diameter and cannot readily penetrate into the pulmonary regions of the lung.

One exception appear to be during flock manufacture of synthetic fibres using worn rotary cutters or potentially during the recycling of the fibres, where slivers of the fibres of finer widths are produced and may enter the lung and produce interstitial fibrosis.

In the development for more silk-like, smooth, soft textiles, ever finer fibres are being produced and due to their low density and aerodynamic behaviour are respirable at diameters larger than traditionally considered respirable.

The development of bi-component fibres where a textile sized fibre is produced but consists of many smaller fibrils bonded together, allows finer fibres to be processed in the conventional way to manufacture textiles. The finished article is then chemically or mechanically treated to separate the fibrils from the fibres, which creates a softer smoother surface but means the fibres are now readily respirable, should they be released to the air due to secondary manufacturing processes, recycling or use.

Nonwovens products do not have a size limitation for processing and increasingly use respirable diameter fibres. The production of filter media is one area where direct production of fine fibres by meltblowing and now electrospinning, is likely to be widely used. The fibres are still long which will limit their respirability but any processing or secondary use that will break the fibres will increase the potential for the fibres to become respirable.

Technical textiles, smart fibres, medical fibres represents a group of specialised products which are enhanced by the addition of specialist coatings or cores that contain a wide range of added materials other than the fibre polymer to enhance properties.

The development and production of nanofibres and nanotubes represents a significant increased in the potential of fibres to reach the lung and other organs.

The mechanical grinding test carried out showed that a significant number (15 of the 68) synthetic fibres (and some natural fibres) tested had an ability to fibrillate and break down into fine respirable fibres.

The dustiness test is a more suitable test to estimate the risk of release of fine fibres. The medium value for respirable fibre release during dustiness testing for the polyacrylonitrile flock was a surprise and many of the fibres looked like slithers shaved off the fibre. It is unlikely this could be due to tumbling in the drum and must have been present in the flock. The Kevlar pulp and metal fibres also gave low levels of respirable fibre release.

The solubility test showed that the fibres tested had very limited solubility in modified Gambles solution and had a potential to remain in the lung. However, the biosolubility of these fibres in the lung may be substantially different and the solubility test should be regarded as an initial assessment.

The database collates available information and provides a useful resource to determine the known health hazards associated with a range of existing fibres.

Although the test data is aimed at identifying the dimensions, durability/solubility, dose and dustiness which are useful predictors of lung related health hazards and risks, the carcinogenic behaviour of fibres is still not well-understood and fibre carcinogenicity may also be modified by the surface chemistry, surface structure and chemical composition.

The current advances in technology reviewed in the report show that there is a need to monitor the new fibre technologies as they are introducing fine respirable, non-soluble fibres into many new and traditional products.

There are a number of implications from this research for HSE strategy:

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13 APPENDIX 1: LIST OF CANDIDATE FIBRES OF INTEREST FROM LITERATURE SEARCH (MANY LARGE DIAMETER FIBRES EXCLUDED)

Trade name	Fibre type	Company / Distributor
Metal fibres	Stainless steel, high temperature resistant alloys, Ni and Ni alloys, Ti, Al, Cu Interested in: Bundle drawing, chopped and free flowing short fibres, diameter = 1.5 or 2 m	BFT (Beakert Fibres Technologies), President Kennedypark 18, B-8500 Kortrijk, Germany? Tel: 32 5623 0548
SiC wiskers, Al borate wiskers, potassium titanate wiskers	Diameter = 0.3 to 1.5 m	Heibei advanced materials inc. (China), 14 floor, 3 North Zongha Street, Shijiazhuang, China 050000
Nicalon	SiC – fibres or wiskers?	Nippon Carbon (Japan)
SCS2	SiC – fibres or wiskers?	AVCO
Tyranno	SiC with organic precursor – fibres or wiskers?	Ube Nitto Kasei (Japan)
TISMO (still manufactured?)	Potassium titanate wiskers	Otsuka Chemicals Co Ltd Tel: 0886 651689 ex 3410 E-mail: sales@otsukany.com
Boron fibres	Boron fibres	Ultrafine (USA)
Textron Boron	BO – fibres or wiskers?	Textron
Sigrafil C type – Interested in C25M250UNS	Carbon fibres C25M250UNS: diameter = 7 m, >95% C	SGL Technick GmbH (UK)
T300, T800, T1000, M55J (improvement in carbon fibres strength for T800 and T1000)	PAN fibres	Toray
IM7	PAN fibres	Hercules
Magnamite IM4	Carbon fibre, PAN based fibre - Filament? Diameter = 6.6 m	Hexcel Fibres 6400 West 5400 South, Salt Lake City, Utah 84118, Tel: 800 987 0658
KCF200	GP-Pitch (general purpose)	Kureha
Thornel P25, Thornel P75, Thornel P120	HP-Pitch (high performance)	BP Amoco
	Vapour grown carbon fibres	
Pyrograph® III and Pyrograph® I	Diameter of 0.07 to 0.2 m Carbon nanofibres	Pyrograph products incorporated (USA)
	Carbon nanotubes	
Lyocell	Solubilized cellulose derivative – Staple fibres available?	Lencing Lyocell GmbH and Co KG
Acetate tow		Celanese acetate Lanaken, Industrieweg 80

		B3620, Lanaken, Belgium Tel: +32 89 710 111
BioSteel® performance fibres	Man-made spider dragline silk	Nexia
Panox® - Interested in SMM400EE4	50% of oxidised PAN fibres SMM400EE4: staple and milled fibres, diameter = 15 m	SGL Technick GmbH (UK)
Nanofibres: - organic (nylon, polyaramid, acrylic, etc…) - biological polymers (protein, collagen…)	Organic and biological polymers	e-spin Technologies Inc, 100 Cherokee Blvd Suite 325, Chattanooga, TN 37405 Tel: 423-267 (6266) Email: info@espintechnologies.com
Spider-Web® / Endurance®	Nanofibres?	Donaldson Company (USA)
Toray micron	Electret technologies?	Toray Industries Inc (Japan) Tel 81 3 3245 5555
Ecsaine	Man made suede of ultrafine fibres, 0.01 to 0.2 denier	Toray (Japan)
Lofela	Artificial suede	Toyobo
Cordley	Artificial leather – non-woven fabric made of Tetoron staple fibres and polyurethane material	Teijin
Toraysee	Ultrafine microfibre	Toray (Japan)
Glore Valcana	Ultrafine acrylics fibres	Mitsubishi Rayon Co. Ltd (Japan)
Microguard	Ultrafine microfibre fabric	Teijin
Microstar	Ultrafine microfibre fabric	Teijin
Abanzaru	Nylon 6 microfibre – available as staple fibres?	Toray Industries Inc (Japan) Tel 81 3 3245 5555
Dralon microfibre / Meryl micrifibre / Tactel micro / Trevira Finesse / Trevira micro	Microfibres	(Germany)
Nonwovens from PTT (polytrimethylene terephthalate) staple		Coterra Polymers, Shell Chemical Company, PO Box 2463, Houston, Texas (USA) Tel: 77 2522463
Axtar	Polyester superbonded non-wovens	Toray Industries Inc (Japan) Tel 81 3 3245 5555
Polyester non-wovens	Interested in staple type	Toyobo
Fybrel® Y type	Polypropylene pulp	Mitsui Chemicals Inc, Synthetic pulp department, 3-2-5 Kasumigaseki, Chigoda-Ku, Tokyo, Japan - Tel: +81335924430 (Distributor: Minifibres Inc. 2923 Boones Creek Road, Johnson City, TN 37615, USA) – Tel: 423 282 4242
Spectra - Spectra 1000	High-performance polyethylene fibres	Honeywell (formely Allied Sigma or Allied Fibres)

Dyneema - Dyneema SK60	High-performance polyethylene fibres	DSM High Performance Fibres (Netherlands) and Toyobo / DSM (Japan)
Dyneema UD and Spectra shield	High-performance polyethylene fibres - Non-wovens, only produced by licensed companies	
Dyneema Fraglight	High-performance polyethylene fibres - Needle felt non-wovens produced from staple fibres	
Thermotropic liquid crystal polymer (e.g. wholly aromatic polyester)	TLCP fibres supplied in very low denier for non-implant medical applications (e.g. catheters and surgical device control cables).' Insulating papers are produced from short-cut fibre and pulp made from TLCP	Kuraray Saijo (Japan) and Celanese (USA) (speciality products)
Bocell	Spinned from a liquid crystal solution in phosphoric acid	Acordis or Newco
Vectran		Celanese
Zylon	High modulus-high tenacity fibres. PBO (poly(p-phenylene benzobisoxazole)) - Interested in chopped fibres pulp	Toyobo
PIPD or M5	High modulus-high tenacity fibres. PIPD (poly{2,6-diimidazo[4,5-b:4',5'-e]pyridinylene-1,4-(2,5-dihydroxy)phenylene}	Magellan
PIPD or M5 rigid-rod polymer	High modulus-high tenacity fibres. PIPD (poly{2,6-diimidazo[4,5-b:4',5'-e]pyridinylene-1,4-(2,5-dihydroxy)phenylene}	Akzo-Nobel?
P-86	Polyimide fibres?	Toyobo
Twaron	p-aramid (PPTA)	Teijin
Kevlar49 and Kevlar 149	Supermolecular structure of a high modulus polyaromatic material. (PPTA)	
Technora	Aramid copolymer	Teijin
Terlon	Russian aromatic fibres - PPTA copolymer	
SVM	Russian aromatic fibres - para copolyamide PHA (paraheteroarylene) - aromatic heterocyclic polyamide.	
Armos yarns	Russian aromatic fibres (KEP) - Copolyamide - Armos: aromatic heterocyclic copolyamide. The main types are: high modulus reinforcement yarns and roving (Armos HMR); high modulus yarn for technical textile; highly thermally stable yarns for textiles.'	Tverchimvolokno Joint Stock Company in Tver City (near Moscow) – Russian .
Saran	Chemically resistant fibre:	Asahi Kasei

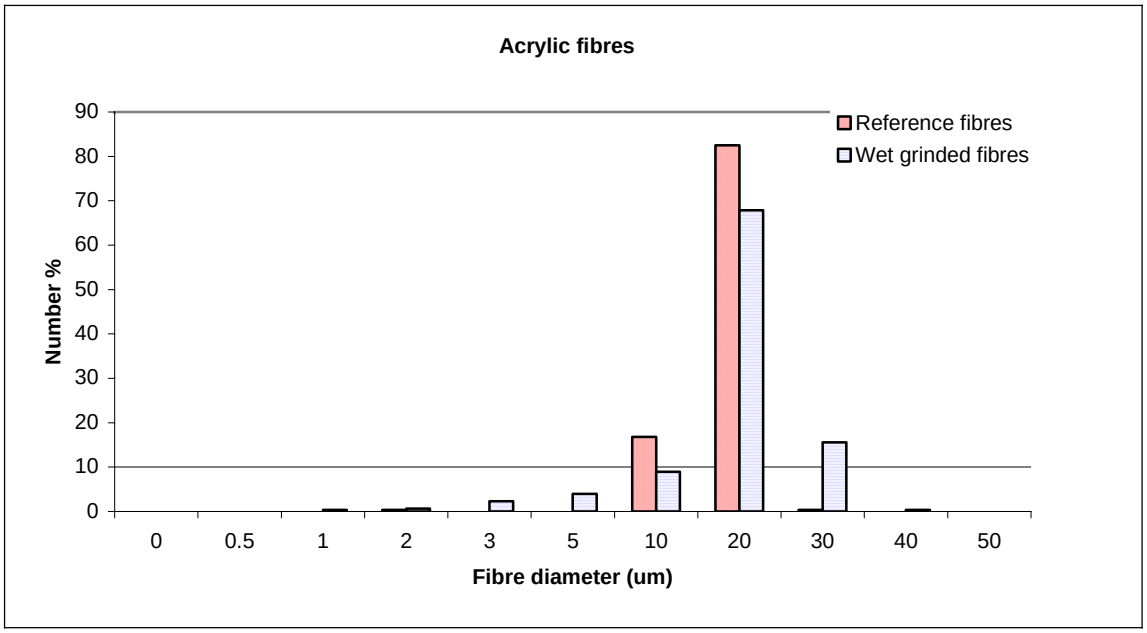
	chlorinated fibres: PVDC (ARH) fibres based on poly (vinylidenechloride).	
Permalon	Chemically resistant fibre: chlorinated fibres: PVDC (ARH) fibres based on poly (vinylidenechloride).	
Verlon	Chemically resistant fibre: chlorinated fibres: PVDC (ARH) fibres based on poly (vinylidenechloride).	
Fugafil	Chemically resistant fibre: chlorinated fibres: PVDC (ARH) fibres based on poly (vinylidenechloride).	Saran GmbH (Germany)
Teflon	Chemically resistant fibre: fluorinated fibres PTFE (poly(tetrafluoroethylene)) Continuous filament, staple and flock forms of Teflon	Dupont
	Chemically resistant fibre: fluorinated fibres PTFE (poly(tetrafluoroethylene)) Continuous filament, staple and flock forms of Teflon (Dupont)	Lenzing Albany WL Gore
	Chemically resistant fibre: fluorinated fibres PVF (poly(vinylfluoride))	
Kynar	Chemically resistant fibre: fluorinated fibres PVDF (poly(vinylidenefluoride)	Albany
Solef	Chemically resistant fibre: fluorinated fibres PVDF (poly(vinylidenefluoride)	Solvay
Trofil	Chemically resistant fibre: fluorinated fibres PVDF (poly(vinylidenefluoride)	Dynamit
Halar-ECTFE and Tefzel ETFE	Chemically resistant fibre: fluorinated fibres FEP (fluorinated ethylene polymers)	Albany
Teflon FEP	Chemically resistant fibre: fluorinated fibres FEP (fluorinated ethylene polymers)	Dupont
	Chemically resistant fibre : PEEK (polyetheretherketone)	Zyex ltd, Teijin, Kosa, Shakespeare, Luxilon and Albany international.
Procon PPS	Chemically resistant fibre: PPS (poly(phenylene sulphide) - Flame retardant fibres	Toyobo

14 APPENDIX 2: SEM LENGTH WEIGHTED SIZE DATA FROM BEFORE AND AFTER FIBRILLATION TEST

14.1.1 PAN / Acrylic fibres

1.a. Acrylic fibres (08350/04)

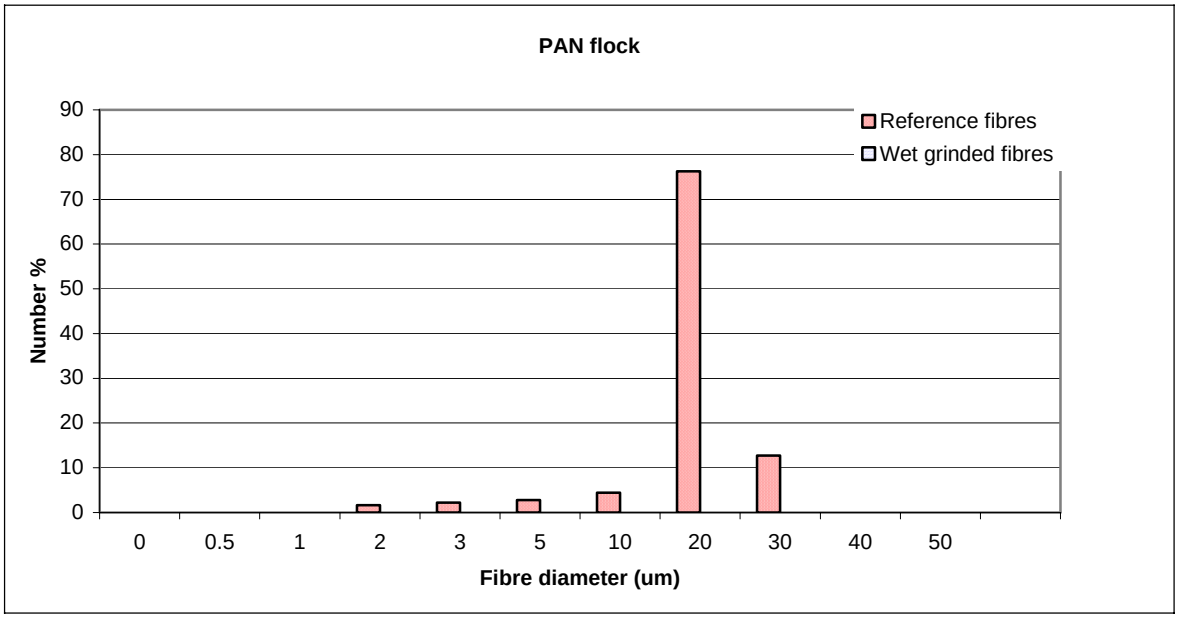
Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	9.5	Arith Mean	15.5
Arith Std Dev	0.08	Arith Std Dev	0.31
Median	9.6	Median	16.6
Geo Mean	11.8	Geo Mean	13.9
Geo Std Dev	1.25	Geo Std Dev	1.73
Geo Mean - 2SE	11.5	Geo Mean - 2SE	13.1



1.b. PAN flock (08262/04)

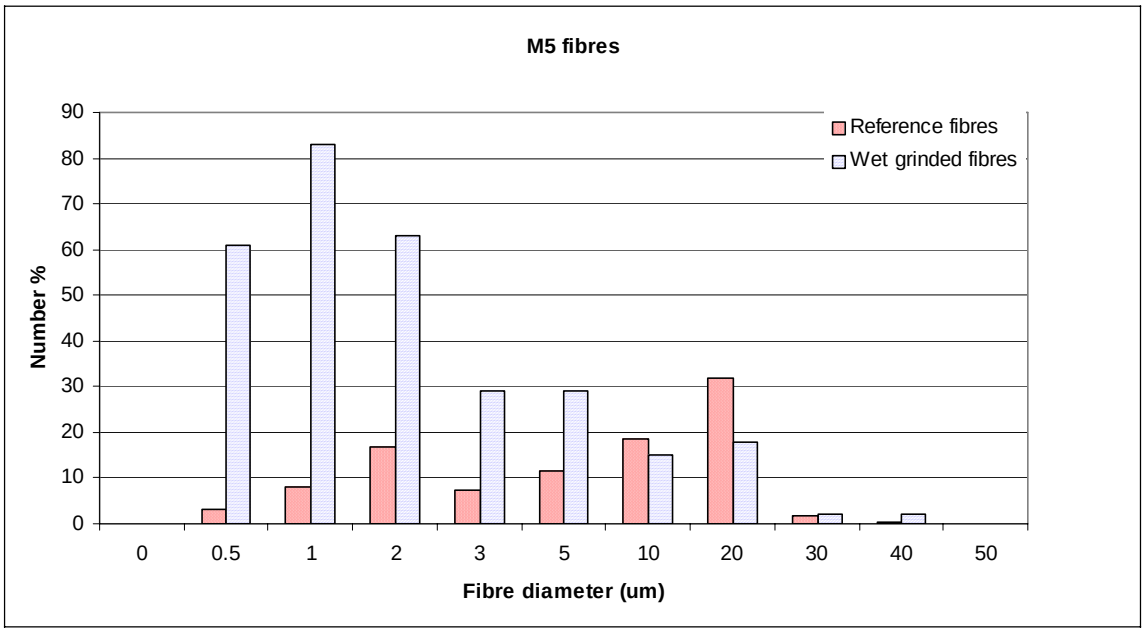
Before fibrillation test Diameter (µm)	
Arith Mean	15.75536
Arith Std Dev	0.359645
Median	16.71361
Geo Mean	14.38607
Geo Std Dev	1.690705
Geo Mean - 2SE	13.30571

The fibres fibrillated under the standard one minute wet grinding test. The measurement was not completed after the fibrillation test because of the difficulties to distinguish individual fibrils.



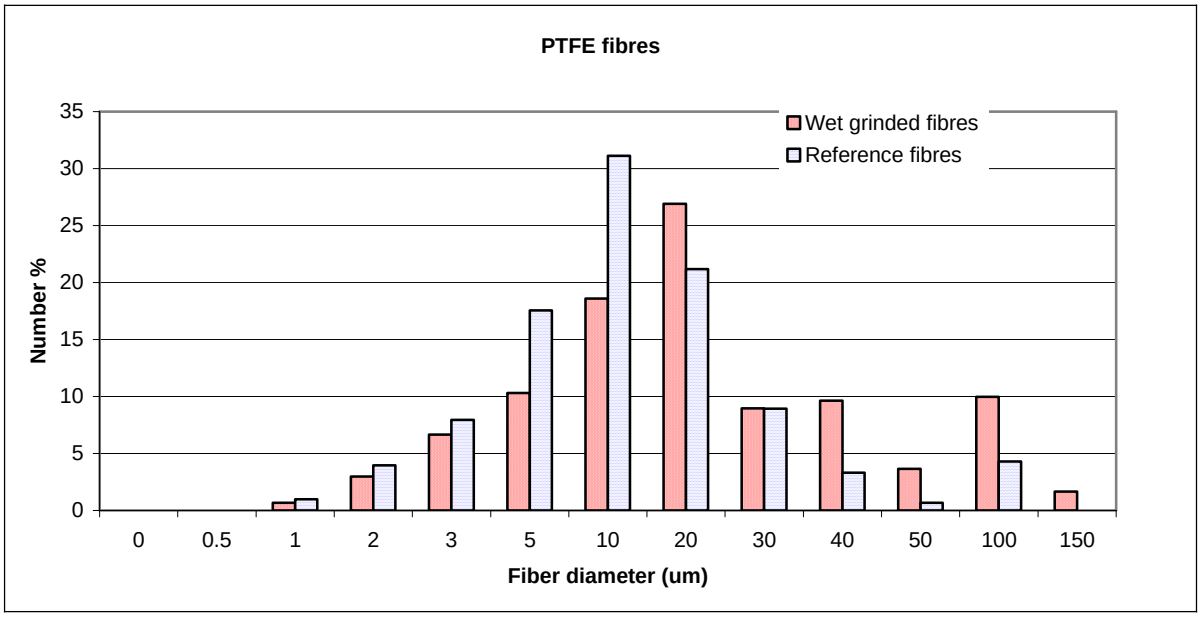
14.1.2 PIPD fibres (M5 fibres 08275/04)

Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	6.9	Arith Mean	2.7
Arith Std Dev	0.36	Arith Std Dev	0.26
Median	5.9	Median	1.1
Geo Mean	4.4	Geo Mean	1.3
Geo Std Dev	2.91	Geo Std Dev	3.09
Geo Mean - 2SE	3.9	Geo Mean - 2SE	1.1



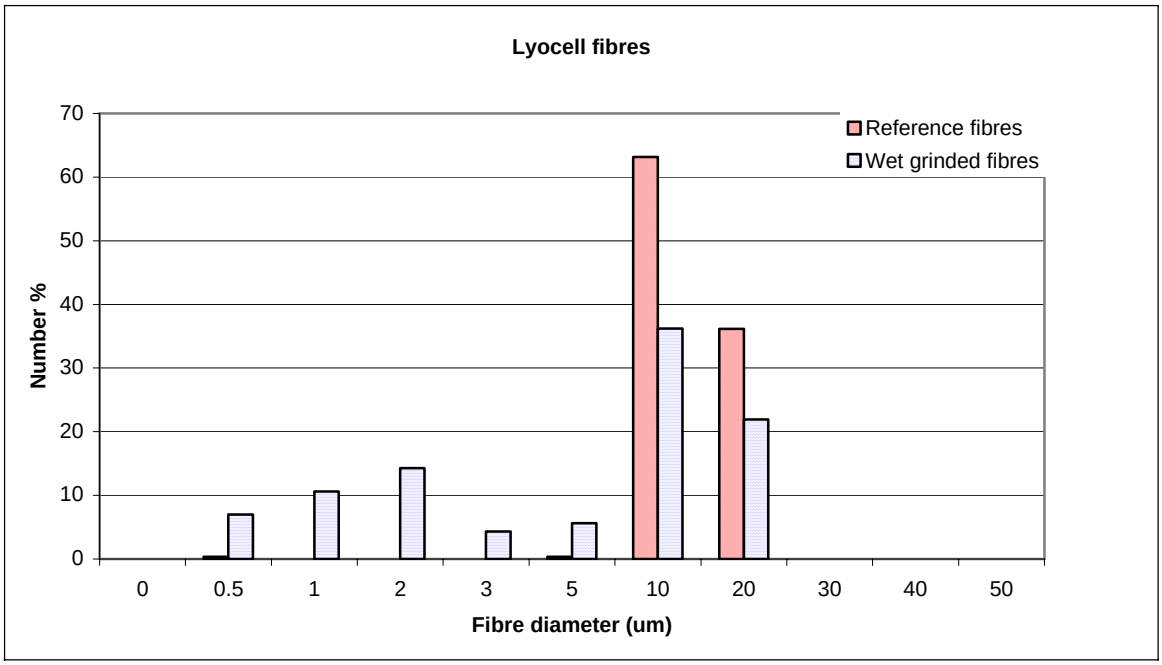
14.1.3 PTFE fibres (08332/03)

Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	12.5	Arith Mean	21.7
Arith Std Dev	0.77	Arith Std Dev	1.3
Median	7.7	Median	13.8
Geo Mean	8.2	Geo Mean	13.1
Geo Std Dev	2.5	Geo Std Dev	2.88
Geo Mean – 2SE	7.4	Geo Mean - 2SE	11.6



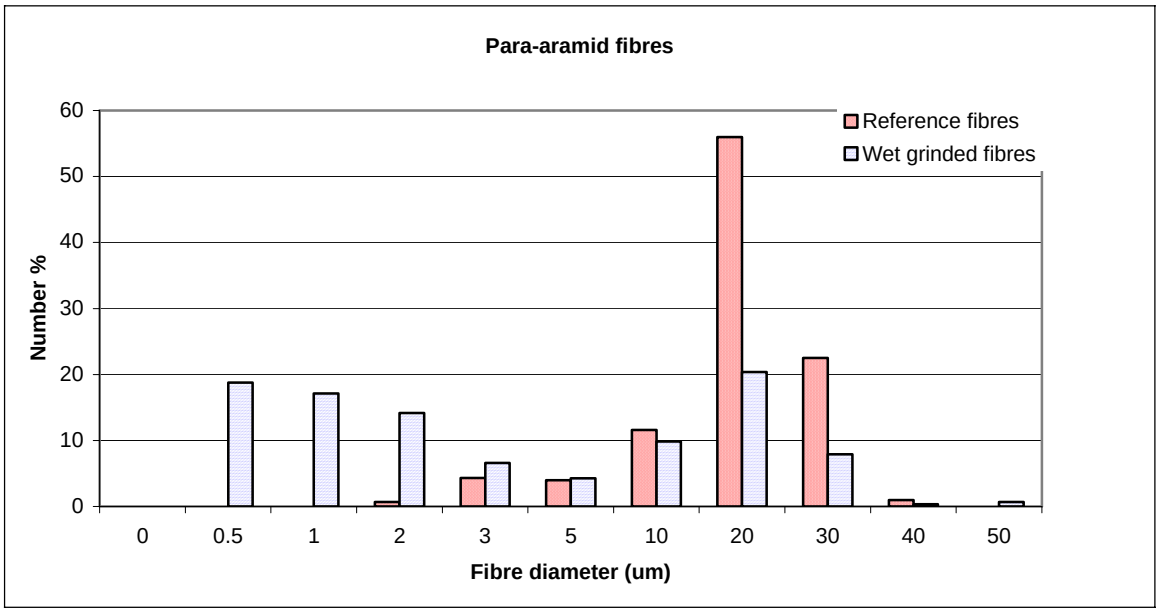
14.1.4 Solubilized cellulose derivative fibres (Lyocell fibres 08460/04)

Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	9.5	Arith Mean	6
Arith Std Dev	0.08	Arith Std Dev	0.24
Median	9.6	Median	7.1
Geo Mean	9.3	Geo Mean	3.9
Geo Std Dev	1.29	Geo Std Dev	3.12
Geo Mean – 2SE	9	Geo Mean - 2SE	3.4



14.1.5 Para-aramid fibres

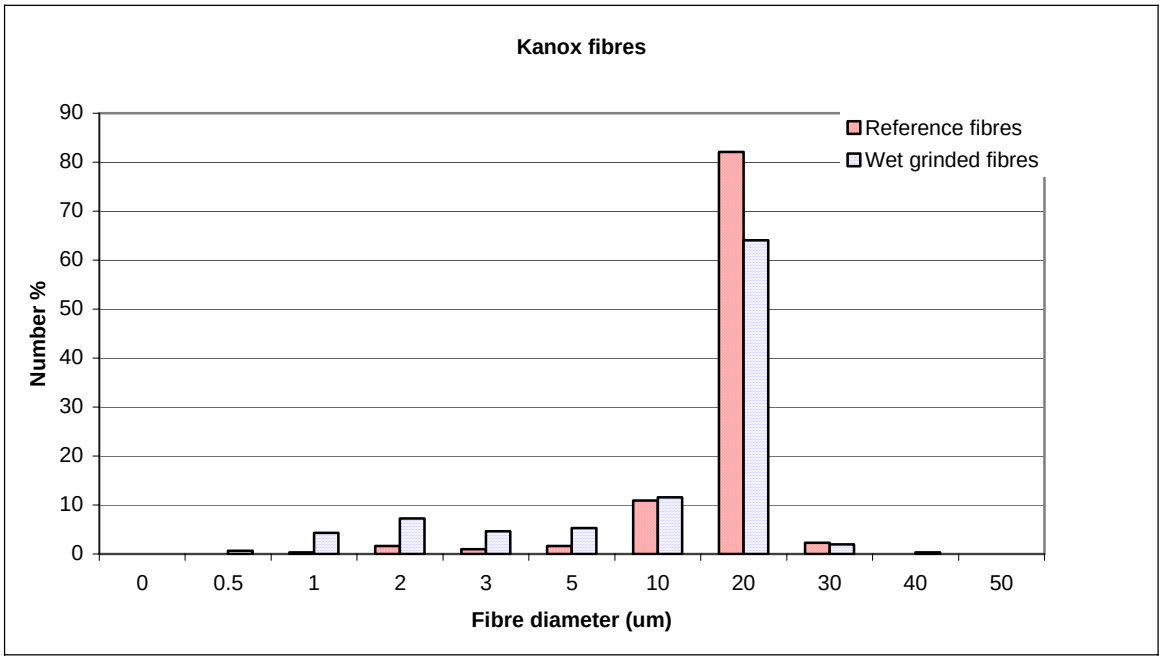
Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	15.3	Arith Mean	7
Arith Std Dev	0.38	Arith Std Dev	0.49
Median	15.4	Median	2
Geo Mean	12.4	Geo Mean	2.5
Geo Std Dev	1.81	Geo Std Dev	4.85
Geo Mean - 2SE	12.4	Geo Mean - 2SE	2.1



14.1.6 Oxidised / Pre-oxidised acrylic fibres

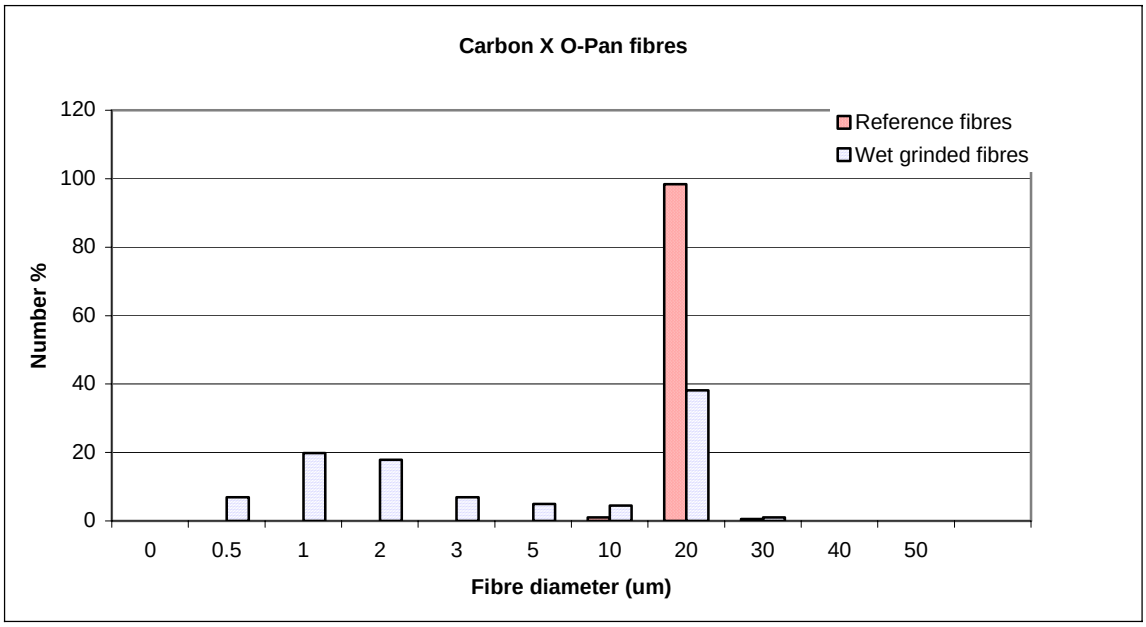
6.a. Kanox fibres (08263/04)

Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	12.9	Arith Mean	10.6
Arith Std Dev	0.22	Arith Std Dev	0.32
Median	13	Median	12.2
Geo Mean	12	Geo Mean	8.1
Geo Std Dev	1.57	Geo Std Dev	2.49
Geo Mean - 2SE	11.4	Geo Mean - 2SE	7.3



6.b. Carbon X O-pan fibres (08720/04)

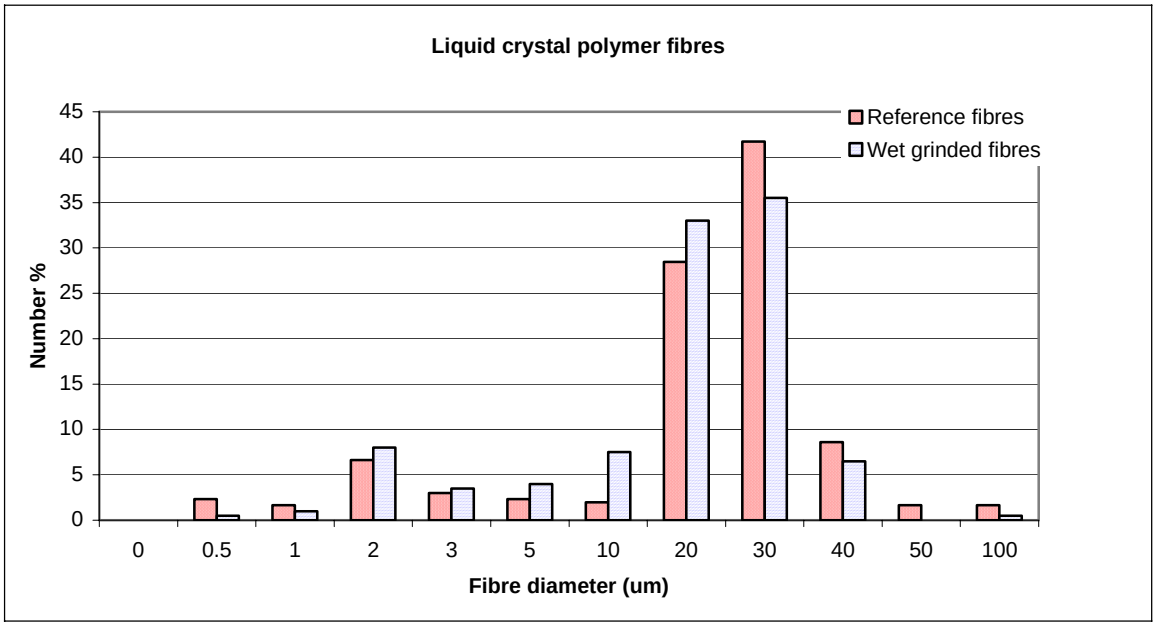
Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	13.8	Arith Mean	6.5
Arith Std Dev	0.1	Arith Std Dev	0.4
Median	13.9	Median	2.6
Geo Mean	13.7	Geo Mean	3.2
Geo Std Dev	1.1	Geo Std Dev	3.7
Geo Mean - 2SE	13.5	Geo Mean - 2SE	2.7



14.1.7 Liquid crystal polymer /polyester fibres

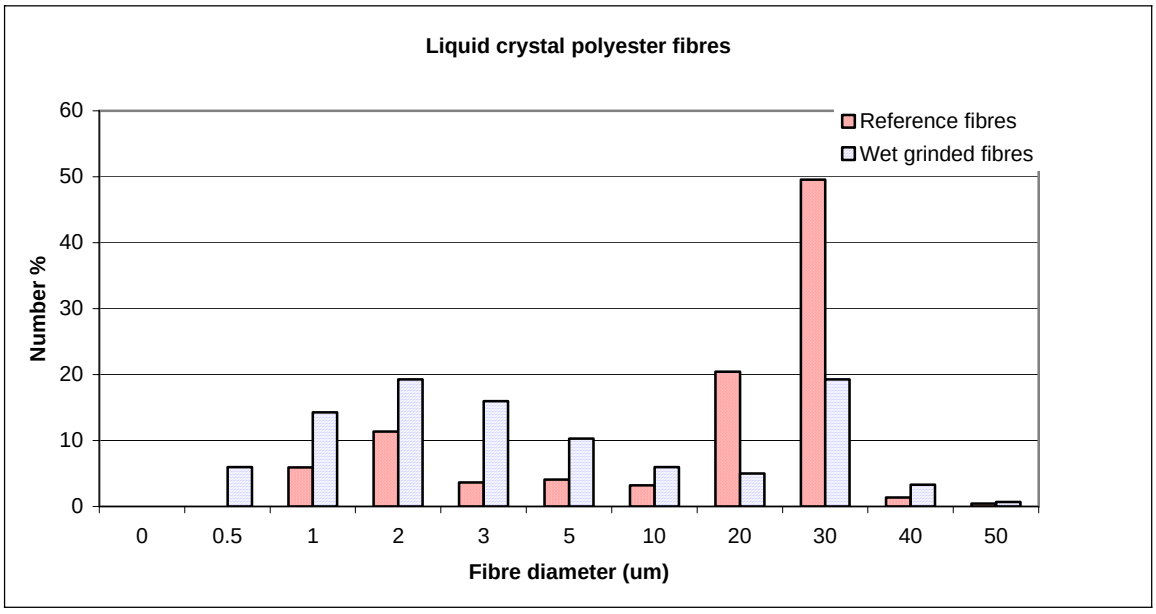
7.a. Liquid crystal polymer fibres (08441/04)

Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	19.9	Arith Mean	17.6
Arith Std Dev	0.67	Arith Std Dev	0.74
Median	20.3	Median	18.3
Geo Mean	14.1	Geo Mean	12.9
Geo Std Dev	3	Geo Std Dev	2.67
Geo Mean - 2SE	12.4	Geo Mean - 2SE	11.2



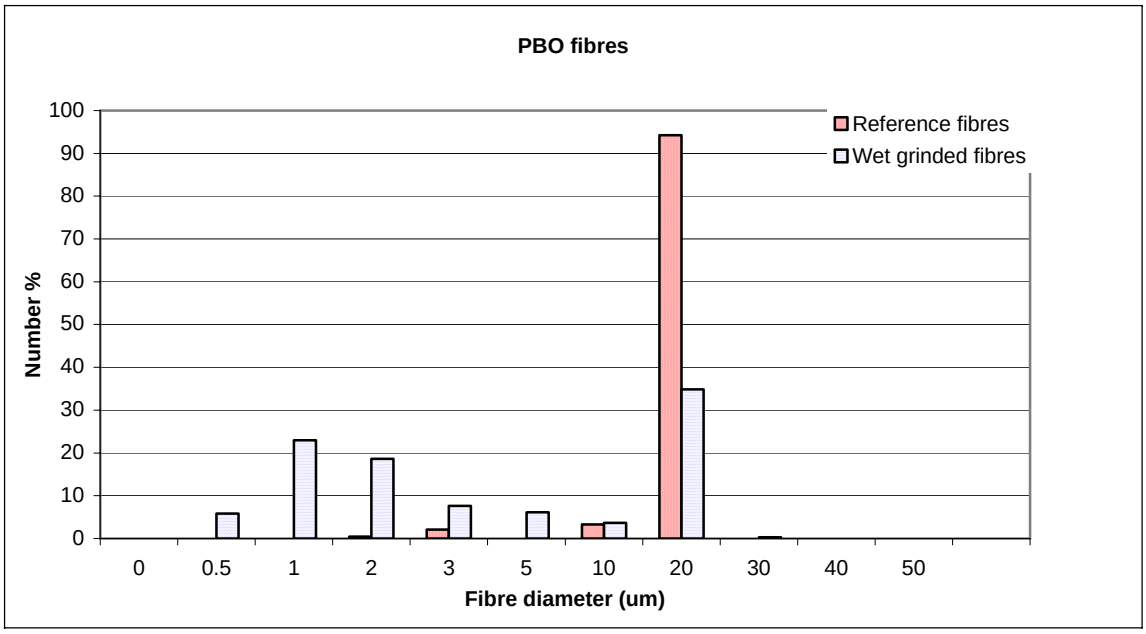
7.b. Liquid crystal polyester fibres (Vectran) (08345/04)

Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	16.1	Arith Mean	8.8
Arith Std Dev	0.64	Arith Std Dev	0.66
Median	20.4	Median	2.4
Geo Mean	10.6	Geo Mean	3.6
Geo Std Dev	3.18	Geo Std Dev	4.03
Geo Mean - 2SE	9.1	Geo Mean - 2SE	3



14.1.8 PBO fibres (08266/04)

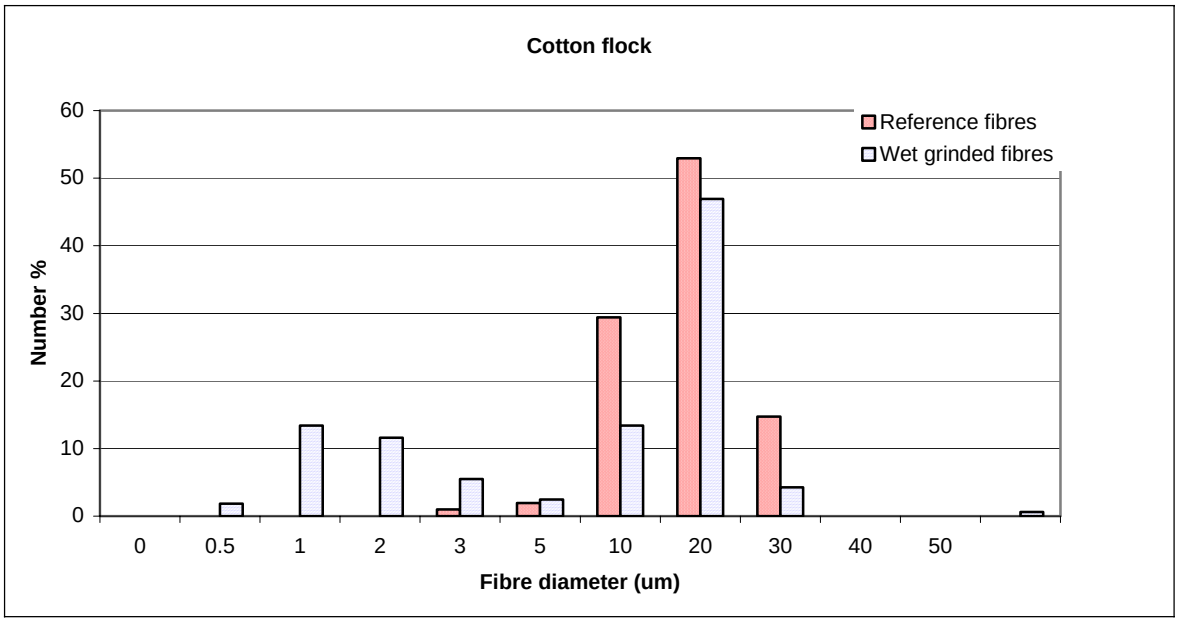
Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	12.2	Arith Mean	5.5
Arith Std Dev	0.13	Arith Std Dev	0.3
Median	12.4	Median	2.3
Geo Mean	11.9	Geo Mean	2.8
Geo Std Dev	1.33	Geo Std Dev	3.51
Geo Mean - 2SE	11.4	Geo Mean - 2SE	2.5



14.1.9 Cotton flock (08261/04)

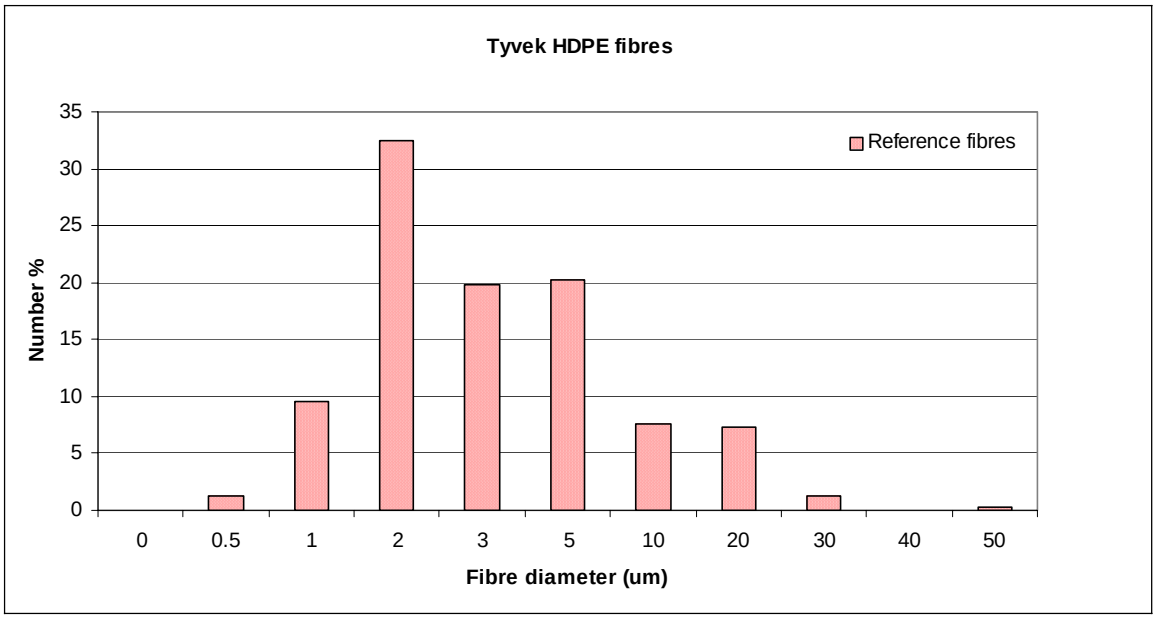
Before fibrillation test Diameter (µm)		After fibrillation test Diameter (µm)	
Arith Mean	13.2	Arith Mean	10.3
Arith Std Dev	0.38	Arith Std Dev	1.24
Median	12.6	Median	10.6
Geo Mean	12	Geo Mean	5.7
Geo Std Dev	1.59	Geo Std Dev	3.41
Geo Mean - 2SE	11.2	Geo Mean - 2SE	4.7

The twisted fibres were counted as one and some fibres were flattened and unrolled resulting in a difference in diameters.



14.1.10 Tyvek HDPE fibres (08453/04)

Before fibrillation test Diameter (µm)	
Arith Mean	3.8
Arith Std Dev	0.27
Median	2.4
Geo Mean	2.5
Geo Std Dev	2.31
Geo Mean - 2SE	2.3



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