

Review the Current Flame Retardant Systems for Polyamide 6, to Develop and Produce a Novel 'Masterbatch' suitable for melt spinning filaments; by means of TGA analysis and vertical flame tests in association with Americhem Europe.

A dissertation submitted to The University of Manchester for the degree of Textile Science and Technology MSc by Research in the Faculty of Engineering and Physical Sciences.

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I hereby confirm that the work submitted is my own and that appropriate credit has been given where references have been made to the work of others. While registered for the Masters award, I have not been a registered candidate for another award at any other University.

**Abstract:**

Polyamide 6 is popular engineering polymer used for many applications including filament production via melt spinning. Currently there is no market leading masterbatch suitable for addition at the melt spinning stage used for imparting flame retardant properties. Flaming drips are a common problem and new tighter regulations are causing new additives to be assessed and greater consideration to be taken when developing such product. Flame retardant additives were assessed for dispersion, thermal gravimetric analysis, melt spinning performance, mechanical properties retention and efficacy under DIN 4102-B2 testing.

A masterbatch was developed in association with Americhem Europe, masterbatch supplier for the thermoplastic industry in Europe. Although further investigation into certain aspects of the development are necessary to optimise the product.

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### **List of Abbreviations**

AI	Americhem Incorporated
AE	Americhem Europe
PA	Polyamide
PA6	Polyamide 6
PA66	Polyamide 6, 6
BCF	Bulk Continuous Filament
LOI	Limited Oxygen Index
FRA	Flame Retardant Additive
APP	Ammonium Polyphosphate
MCA	Melamine Cyanurate
PEO	Polyethylene Oxide
FR	Flame Retardant
MMT	Montmorillonite (Nano-Layered Silicate)
PTFE	Polytetrafluoroethylene
OP	Exolit OP 1230
THF	Triazine HF
CP44	Polybromostyrene
ZB	Zinc Borate
ATO	Antimony Trioxide
TGA	Thermal Gravimetric Analysis
DSC	Differential Scanning Calorimetry

## **Chapter 1: Introduction**

This chapter offers an introduction to the organisation involved in the dissertation and goes on to generate the objectives of the dissertation and the challenges that have been and will be faced to achieve those objectives.

### **1.1 Americhem Incorporated**

Americhem Incorporated (AI) is a privately owned family company founded in 1941, the headquarters of which are located in Cuyahoga Falls, Ohio, USA. The company supply concentrated colour and chemical additive dispersions to the plastics industry worldwide. For the purpose of the dissertation the focus is on the synthetic fibres segment of the business.

AI operates from seven manufacturing sites, spread across North America and one in Manchester with the other being in Suzhou, China. To maintain effective regional service to global customers, the company has sales offices in Luxembourg, Monterrey and Mexico.

To date, the company has continually strived to differentiate itself from competitors by adopting a technology led strategy, resulting in innovative product designs and a desire to solve problems experienced by customers. This approach has given rise to the fact that almost every Americhem product has been developed as a solution to one particular problem for one particular customer. As a result of the technological focus, Americhem has taken advantage of niche market areas where the company's core technologies such as pigment dispersing, mixing, colour science and polymer processing can be used to generate competitive advantage.

The manufacturing sites are managed independently but are grouped by geographical locations. The four manufacturing sites in the USA are grouped under 'NAFTA' whereas Europe and China is grouped under 'International'.

For the purpose of this dissertation the focus of the research is centralised around the European manufacturing site.

### **1.2 Americhem Europe**

Established in Manchester, England in 1995 Americhem Europe (AE) was Americhem Incorporated's first plant outside the USA.

From Manchester AE is charged with supplying EMEA (Europe, Middle East and Asia). One core business area is Single Business Unit (SBU) 90 Fibres. This covers a broad range of applications including carpeting, synthetic turf, non-woven and many more textile applications.

Americhem Europe has ISO 9001 accreditation and has recently passed TS16949 Audit for automotive accreditation.

More information can be found at [www.americhem.com](http://www.americhem.com).

### **1.3 Research Problem**

As of 2006 the population of Earth was approximately 6.3 billion inhabitants, there are approximately 7-8 million fires reported annually resulting in 70-80 thousand deaths and 500-800 thousand injuries [1].

In Europe alone the annual reported fires was 2-2.5 million causing 20-25 thousand deaths and 250-500 thousand injuries [1].

Of worldwide fires 30% occur in dwellings where 80% of fire related deaths are also associated [1].

It is reported that toxic gases account for 50% of fire related deaths whereas, 25% of deaths are caused from burns [2].

The market for flame retardant textiles is increasing and there are many areas where these are applicable such as; home textiles i.e. curtains, upholstery and carpets. Technical and functional textiles like automotive carpet and protective clothing [2].

Common synthetic fibres such as polyamide are difficult to flame retard effectively for many reasons [81].

- Their chemical structures are not substantive to common functional flame retardant.

- During fibre production the fluid polymer has low compatibility with the flame retardant additive.
- Usually high loadings are required, which create spinning issues and greatly alters their physical and textile properties.
- As they are thermoplastics they have a tendency to melt and flow which leads to flaming drips.

Currently no flame retardant additive has been found for PA6 / PA66 textile fibres. Various attempts have been made to incorporate flame retardants during polymerisation and a couple are discussed by Levchick (2009) [37].

Post treatments have been around for many years and are well established, whilst carpets can pass certain flame retardant tests on their own with no flame retardant additive [37].

#### **1.4 Research Objective**

The objective of the dissertation is to develop a masterbatch suitable for processing during Polyamide 6 filament production, which will impart flame retardant properties to the Polyamide 6 yarns, taking into account issues mentioned in 1.3 and reviewing previous work carried out.

Gamino & Costa (1988) [81] stated that flame retardants should be:

- Thermally stable at desired polymers processing temperature
- Compatible with the host polymer to avoid migration which will reduce the flame retardant effect over time.
- Not impair the physical and chemical properties of the fibre.
- Be characterised as low toxicity and should not originate toxic and/ or obscuring smoke upon burning.

The dissertation will focus on yarns suitable for home textiles where there are also environmental issues to understand. The flame retardants must be non-persistent, bio



accumulative, toxic (PBT) and non-CMR (carcinogenic, mutagenic, reprotoxic). They must also be durable (non-leaching) and insoluble and non-hydrolysable [2].

This dissertation will explore these issues and the numerous issues surrounding the subject area throughout Chapter 2 and 3 with a view to developing a suitable masterbatch for imparting flame retardant properties to PA6 fibres in line with regulations, as well as meeting the required processing parameters needed to satisfy yarn producers.

Flame retardance efficacy will be analysed using common test standards carried out at accredited laboratories and simulated tests carried out internally at Americhem Europe.

### **1.5 Chapter 1 Conclusion**

Chapter 1 has briefly introduced to the reader; Americhem Inc. and Americhem Europe and given a brief insight into the nature of the business and the current structure.

From the research problem presented we can conclude that the main objective is to develop a masterbatch that will impart flame retardant properties to PA6 yarns whilst maintaining physical and mechanical properties.

In Chapter 2, the dissertation will review the multiple chemistries available for achieving the goal, the problems associated with the application and conclude which chemistries and materials provide the best option to proceed with development.

## **Chapter 2: Literature Review; Polyamide 6**

This chapter provides a literature review on the key areas identified within the research problems, aims and objectives mentioned in chapter 1.

Using the literature the dissertation will discuss in more detail the problems and challenges faced when developing flame retardant masterbatch for PA6.

### **2.1 Polyamide, Fibre Production and Masterbatch Introduction.**

#### **2.1.1 Brief History**

'Nylon' was the first synthetic fibre to go into full scale production. The first development was from the work of W.H. Carothers for DuPont in USA during the 1930's. Carothers' work focused on the polymerisation of di-amines and di-carboxylic acids. Both monomers contained six carbon atoms and Nylon (PA 6, 6) went into first production in 1938 with the first stocking being sold in 1939 [5-6].

A parallel development was carried out in Germany attempting to circumvent DuPont patents; chemists investigated synthetic fibre forming polymers. This led to the development of 'Perlon' (PA6), some monofilaments were produced in 1939 and continuous filament followed in 1940. Full scale production began in 1941 but due to the war was put on hold until 1950 [5-6].

Throughout the project we will focus on the PA6.

#### **2.1.2 Market Overview**

Since the economic downturn in 2008 polyamide filaments have enjoyed a revival. Between 2009 and 2010 the annual volumes rose 15.6% to 3.8 million tonnes global production [7].

Breaking this down into specific applications, the textile market saw an increased production of 19.4% whilst the industrial filament sector grew 15.4% respectively. These two applications account for approximately 80% of the PA filament production. The remainder being used for carpet applications which saw a less impressive growth of 7.7% between 2009 and 2010, this is believed to be due to the sluggish housing market within the United States [7].

To summarise polyamides are still an important fibre on the market and have many applications. They are a long way from conquering polyesters dominance within the synthetic fibres market but still occupy a healthy 8% [7].

### 2.1.3 Caprolactam Production

Caprolactam is the monomer used for the production of PA6. It is preferred to self-condensation of  $\omega$ -amino-caproic acid because it is easier to make and purify [6].

For reference Figure 2.1 shows the major commercial routes for bulk caprolactam production via cyclohexanone and cyclohexanone oxime [11].

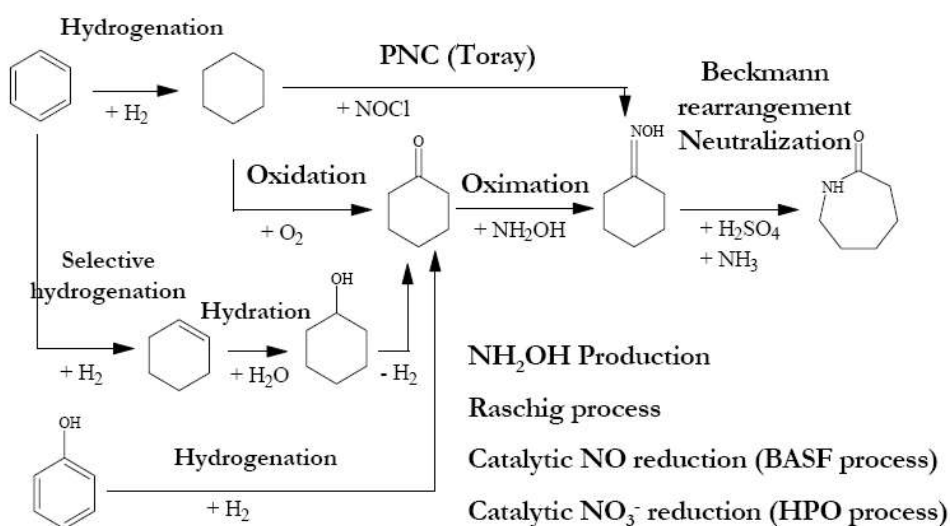


Figure 2.1; Caprolactam production process [11]

Figure 2.2 further explains process one from figure 2.5. Starting with (1) cyclohexane, this is converted to (2) cyclohexanol, then (3) cyclohexanone, followed by the (4) oxime of cyclohexanone. (5) Cyclohexanone oxime undergoes Beckman rearrangement upon treatment with sulphuric acid to produce caprolactam. Caprolactam can then be polymerized to make nylon [9].

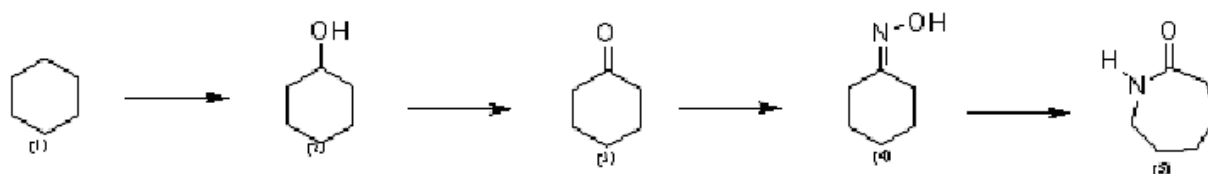


Figure 2.2; Caprolactam production process [9]

The production of caprolactam produces large amounts of by product ammonium sulphate. In 2000 DSM and Shell released that they had developed a new process, The 'Altam' Process uses butadiene ( $C_4H_6$ ), carbon monoxide, ammonia and hydrogen as raw materials which are considered inexpensive and easily available and does not produce the unwanted by products [6, 8, 11].

Novel and commercial routes for the production of caprolactam are discussed further by Mettu 2009 [11].

### 2.1.4 Polyamide 6 Production - Ring Opening Mechanism [9]

The ring opening is initiated by heating caprolactam to  $250^\circ\text{C} - 280^\circ\text{C}$  for 12-24 hours with the addition of water as the initiator. Figure 2.3 shows the initial addition of water to caprolactam ring thus creation of electrophilic carbon which is susceptible to nucleophilic attack from the hydroxide which propagates ring opening.

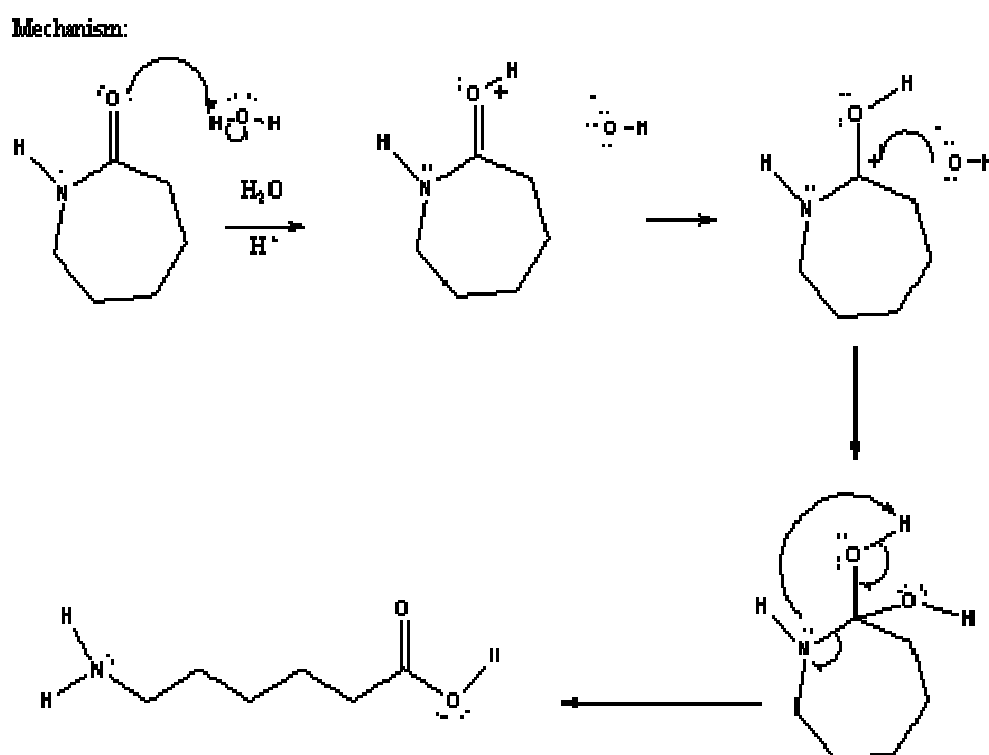
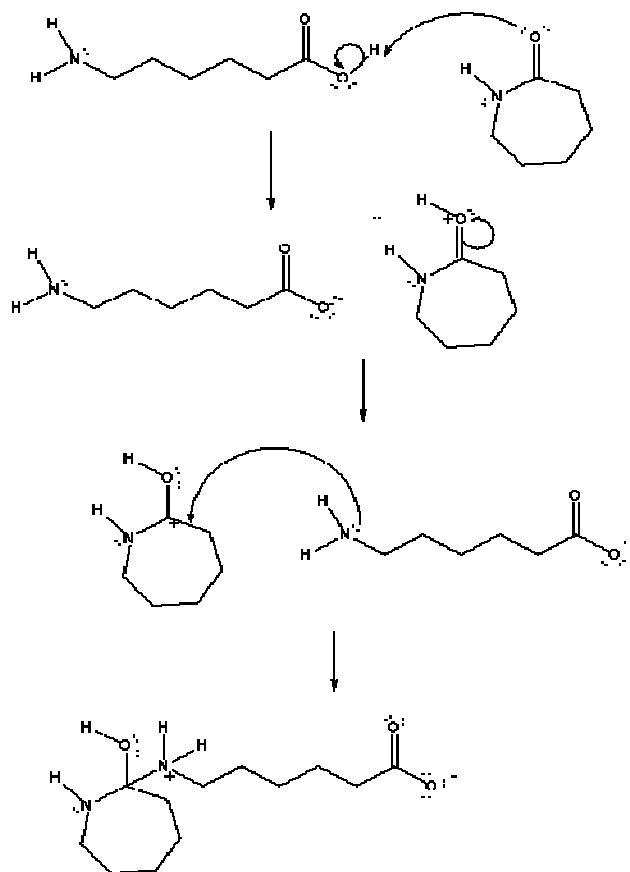


Figure 2.3; Addition of Water to Caprolactam to propagate ring opening [9]

The molecule generated in Figure 2.3 donates a proton to another caprolactam ring creating another electrophilic carbon and causing the fusing of two caprolactam molecules, one in ring form and one in chain form (Figure 2.4) [9, 10].



**Figure 2.4; Fusion of Caprolactam Molecules [9, 10]**

Through further proton transfer and ring opening a caprolactam dimer is formed where both molecules are in chain form (Figure 2.5) [5, 6, 9, and 10].

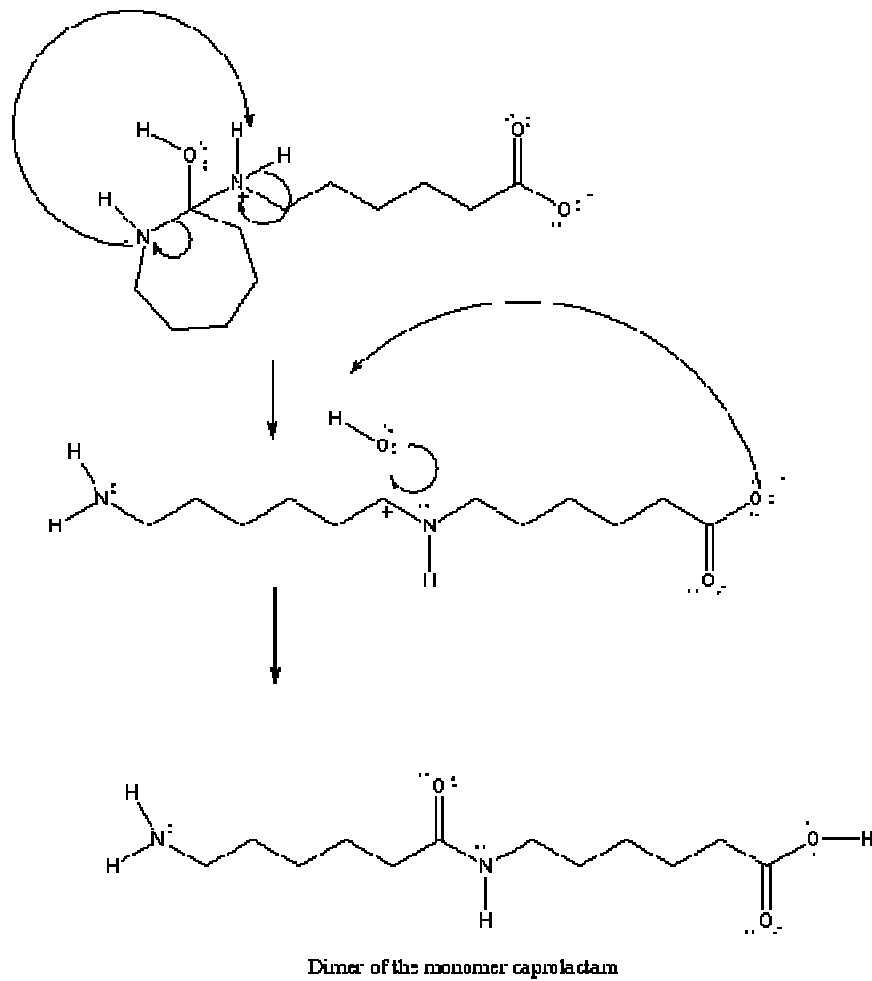


Figure 2.5; Production of Caprolactam Dimer in Chain Form [10]

The dimer reacts with more caprolactam monomer until termination the result being Polyamide 6 (Figure 2.6). [9, 10].

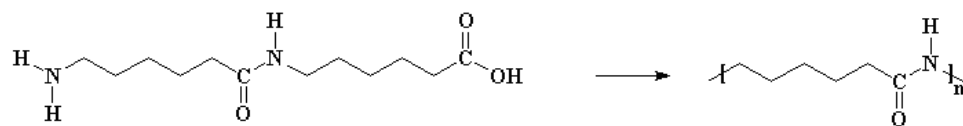


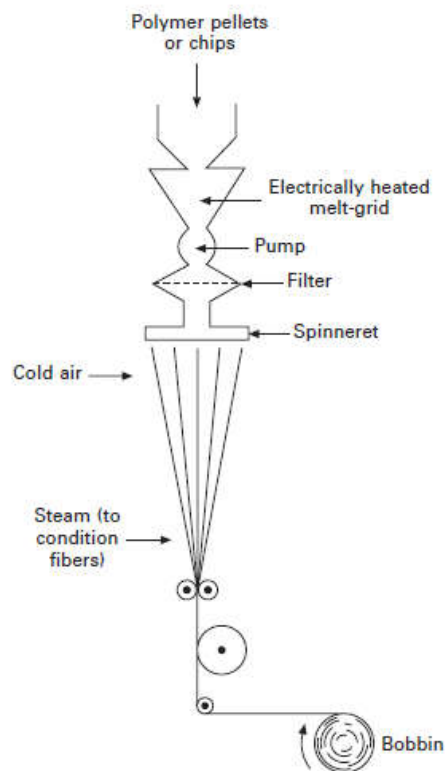
Figure 2.6; Continued Reaction between Caprolactam Dimer and Monomer until Termination – Product Nylon 6 [10]

## 2.2 Melt Spinning – Fibre / Filament Production

### **2.2.1 Introduction**

Melt spinning is one of the most common methods of PA6 filament production. Benefits from melt spinning are the high spinning speeds, low production costs, versatility as can produce continuous filament, staple fibres and monofilaments. They can produce many fibre cross sections for various applications [12].

PA6 granules are melted and transported via an extruder (usually single screw) to a metering pump. The pump is used to control the output of the melt solution. The pump forces the solution through a spinneret at high pressure. This is where the fibre cross section is determined. There are many cross sections available but common ones are trilobal, round and octagonal. The extruded filaments are then cooled via a quench air column, lubricated to reduce static and then drawn and then wound onto a package for continuous filament or chopped into staple fibres [12].



**Figure 2.7; Schematic Melt Spinning Process [12]**

The produced continuous filaments usually get further drawn, texturised and heat set to make the yarn more stable depending on the end application of the yarn. Modern

machinery can perform the spinning and texturing steps in one process. This method of production can be used to produce a broad range of filaments from micro fibres to very coarse yarns. This paper will focus on Bulk Continuous Filament (BCF) production used in carpet yarns [12].

### **2.2.2 Principles**

There are a number of key principles and processing parameters affecting melt spinning process and properties of fibres produced.

Spinneret design is essential for fibre uniformity and production yield. Key parameter within the spinneret is the orifice length/diameter ratio. Usually a length/diameter ratio of  $\geq 3$  is used to eliminate die swell (entrance effect) within the spinneret [14].

Upstream pressure above 600 psi are preferred for uniform polymer melt distribution to the spinneret orifices [14].

Shear rates below  $5000 \text{ sec}^{-1}$  is recommended to avoid melt fracture (entrance effect). Although not associated with polyamides melt fracture can occur at lower spinning temperatures [89].

Other key parameters for fibre uniformity are the polymer material being used and its viscosity, extrusion temperature, jet velocity, spinning path length, take up speed and cooling conditions (quenching rate) and draw ratios [89].

Computer modelling can be used to predict fibre properties however online trials and measurements are still determined to be the best method [14].

A detailed explanation of the complexities to melt spinning were published by Ziabicki (1976) Fundamentals of Fibre Formation [89].

## **2.3 Bulk Continuous Filament Production Processes**

Bulk continuous filaments are used mainly in the textile industry for floor coverings. Here we will discuss their method of production.

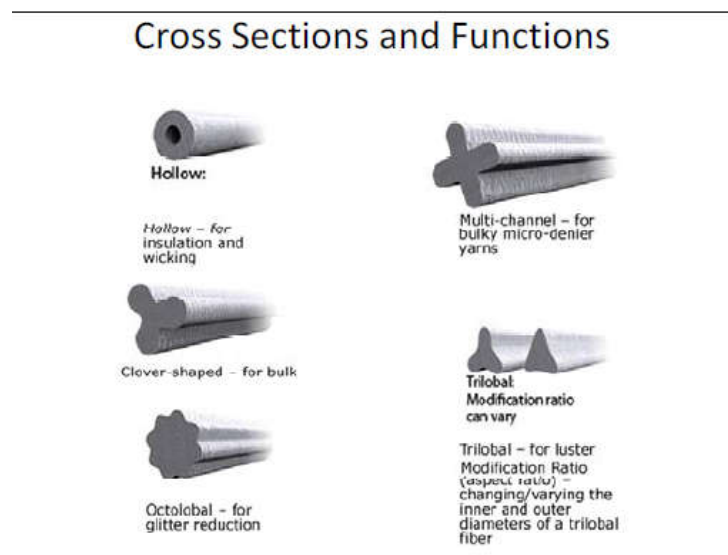
### **2.3.1 Introduction**



As already mentioned briefly BCF yarns are now mostly produced in one continuous sequence initially utilising 'stuffer box' texturing method but now more commonly used is an air jet texturing principle. The polymer granules are melted and transported via an extruder where the melt is then pumped through a spinneret. The number of holes within a spinneret and the shape of those holes determine the number of filaments within the final yarn (or a component of the final yarn) and the cross section of each filament [13].

### 2.3.2 Cross Section

There are various cross sections used for filament production. The cross section is chosen based on the final application of the yarn Figure 2.8 identifies some of the cross sections used and the properties associated with them.



**Figure 2.8; Cross sections available for melt spinning [19]**

Clover and Trilobal are most commonly used for BCF applications for their bulk and lustre properties.

### 2.3.3 Quench and Lubricant Application

The produced filaments are quenched and the 'as spun' filaments have a lubricant applied to them known as spin finish. The spin finish can vary depending on polymer being spun and how the filaments are going to be processed. Spin finish reduces static and aids drawing and texturisation and is applied via a metering pump so the amount applied is known and not in excess. Variants within the application of spin finish are the number of filaments (typically

ranging from 34-140 in BCF production) and the cross section of the filaments. In some cases special air jets are used to apply spin finish for even application [13].

Quenching is an important processing parameter, effecting the molecular orientation of the filaments. The aim is to provide uniform cooling to each filament to ensure they have the same morphology and properties within the yarn bundle. If not done correctly this can affect the yarn in downstream processes such as dyeing and result in streaky colouration as the fibre morphology within the filament bundle is different [14].

Differences in birefringence, filament diameter, tenacity and elongation have been reported from non-uniform quenching. Filaments cooled in lower temperature zones of the quenching area were found to have lower birefringence, lower tenacity and higher elongation compared to filaments in the warmer section of the quench zone [14].

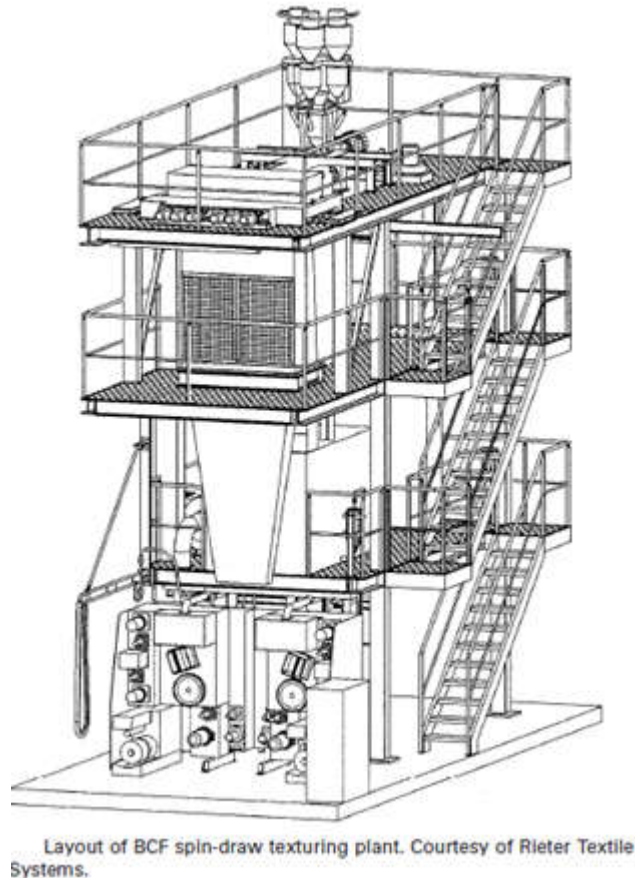
#### **2.3.4 Drawing**

In BCF production drawing is completed before texturising. PA6 can be cold drawn but for bulk texturising hot drawing is used. Godets (driven, heated rolls) are used to draw the filaments. They are usually fitted in pairs 'duo' but can be fitted as singles along with a smaller roll which will not be driven or heated known as a separator. The filaments are wrapped around the godets a number of times so that the heat can penetrate into the filaments. It is important that the wraps do not touch each other [13].

Drawing takes place in two stages. A roll not usually heated (but can be) draws the filaments from the spinneret and through the quench column and finish applicator.

This roll sees the filaments begin to solidify and the pull exerted applies some initial draw to the filaments, meaning that the weight per unit length of the filaments is already lower at this roll than when they left the spinneret. A low level of draw is applied from the draw off roll and the first set of 'duos' to ensure a light but constant input tension [13].

The main drawing takes place between two sets of godets (or duos). The first being heated 50°C-90°C (depending on polymer) the second pair heated to higher temperature. The purpose of the second heat application is to 'set' the yarn and also increase the temperature so that it is closer to that of the texturising unit to facilitate the bulking process [13].



**Figure 2.9 Schematic of Melt Spinning Machine [13]**

A draw ratio is applied between the sets of godets. Draw ratio can vary depending on the polymer being spun. They commonly range between 1.5 and 4.0. Drawing of the filament reduces the denier closer to the final produce denier range. Draw ratio can be calculated following Equation 1.1 [13].

**Eqn 1.1** 
$$\text{Draw Ratio (DR)} = \text{Speed of Final Draw Roll} / \text{Speed of First Draw Roll (m/min)}$$

Drawing the filaments is necessary to develop yarn properties such as tenacity and elongation. These properties are obtained from the orientation of the crystalline and non-crystalline (amorphous) regions of the polymer which drawing imparts [14].

### **2.3.5 Fibre Structure and Crystallinity**

Nylon filaments can take up various crystalline polymorphs. The crystal structure developed during spinning depends on the rate of crystallisation. The two main types are the  $\alpha$  (alpha)

form and  $\gamma$  (gamma) form. From literature it is suggested that the other forms of polymorphs are derivatives of these two main types [15].

Yang summarises that PA6 filaments produced via melt spinning method at moderate spinning speeds contain close to equal amounts of the  $\alpha$  and  $\gamma$  form crystals. On annealing at high temperatures (100°C moist conditions and 150°C in dry) crystal growth will increase but the  $\alpha$  form being favoured conformation [14].

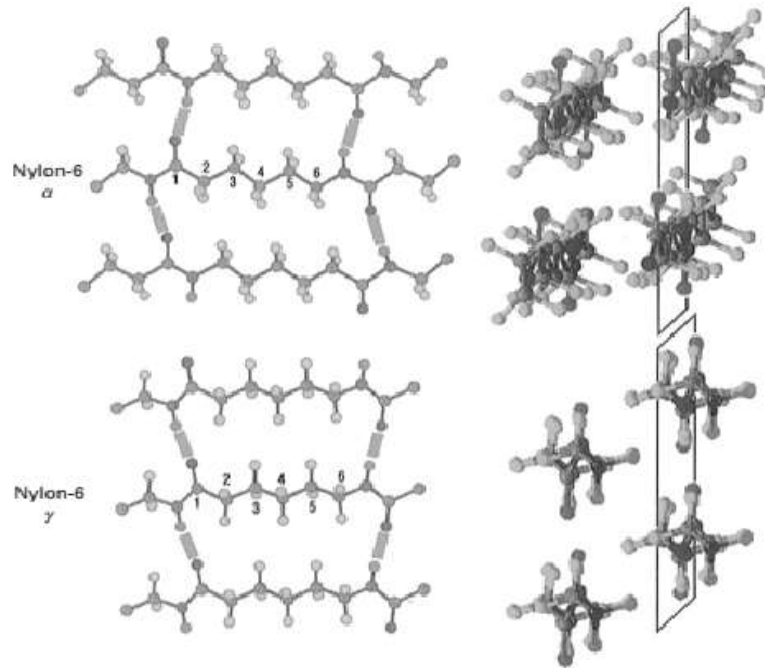
Murthy states the  $\alpha$  form is predominant crystal structure developed during slow crystallisation and  $\gamma$  form is more predominant on rapid crystallisation.  $\gamma$  form is typically present in high speed spinning where the take up speed is greater than 3000 m/min, Yang agrees with this [14, 15].

The chains in  $\alpha$  crystallites are in fully extended conformation whereas the amide (NH) groups in the  $\gamma$  crystal form is rotated 60° from the  $\alpha$  conformation resulting in a shorter chain axis and a more pleated structure (Figure 2.10) [14].

Murthy concludes that the hydrogen bonds are stronger in the  $\gamma$  pleated structure and that the amorphous regions of PA6 can also be orientated and the chains in this region be altered [15].

Experiments carried out by Vasanthan [16] found the density of PA6 to increase with an increasing draw ratio, this attributed to changes in the crystal structure formed, increase in total crystallinity or combination of both.

The study found that crystal to crystal transformation and strain induced crystallisation can both occur at higher draw ratios (>3) At lower draw ratios only strain induced crystallisation takes place. These experiments were carried out under cold drawing conditions [16].



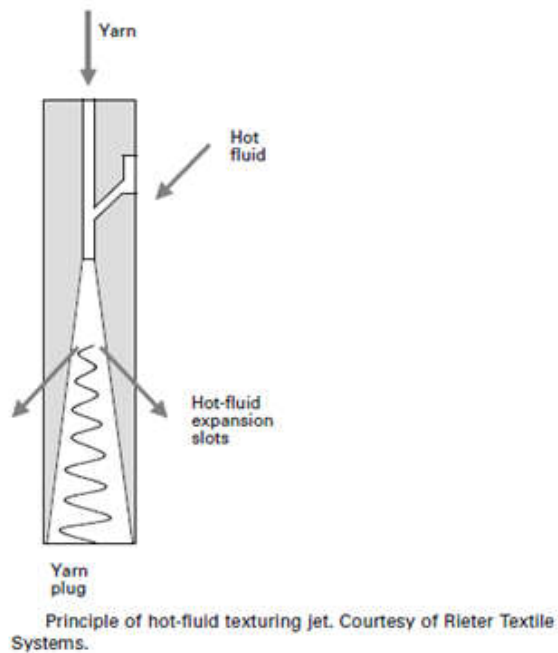
**Figure 2.10; Different Crystal Structure in PA6 filaments [16]**

Gianchandani et al [17] also found that samples with lower orientation contained higher amounts of amorphous region and  $\alpha$  phase with lower amounts of  $\gamma$  form than samples with a higher orientation. The study further leads to how annealing process can the  $\alpha$  form crystal at the expense of amorphous regions thus increasing the density. They also found that the nature of the  $\alpha$  form can change into a more perfect monoclinic conformation [17].

Following the review of literatures 5 and 12-18 the structure and crystallinity of PA6 filaments can vary depending on the method of production and the intended application. Many methods have been developed to examine this phenomena and further exploration is outside the scope of this paper.

### **2.3.6 Texturising and Cooling**

In line texturising takes place immediately after drawing. The yarn is heated in a similar fashion during the drawing stages using heated 'duos'. The filaments are then fed into the jet system.



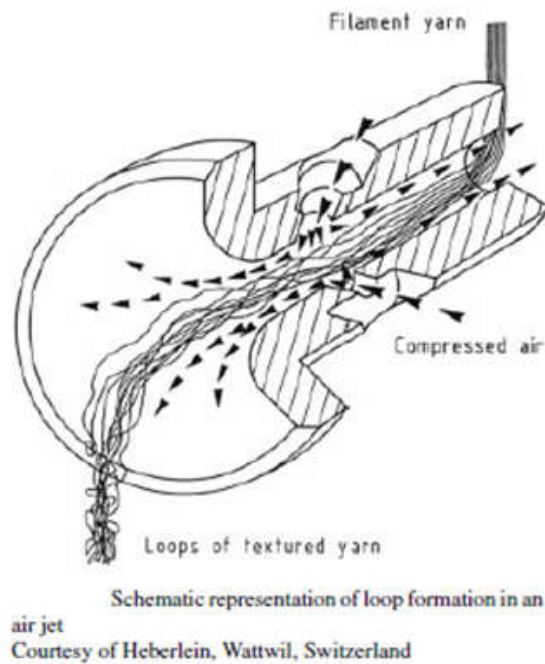
**Figure 2.11; Hot Fluid Texturising jet design. [13]**

Hot air or steam is commonly used as they hot fluid jets, these enter the jet at high velocities which impart a forwarding motion on the filaments and help to transport them through the jet. Turbulence is generated within the jet and this increases the heat transfer from the hot fluid into the filaments [13].

Due to the design of the jet the hot fluid is then allowed to expand and slow down resulting in the yarn creating a plug. (Figure 2.11) The filaments are compressed creating bulk as the filaments shrink, buckle and form loops. It is this compression which restraints the movement of the yarn which creates the bulk. The filaments then leave the jet in a crimped formation and are then cooled and stabilised otherwise the bulk will not be permanent [13, 19, 20].

The crimped yarn then leaves the jet and lands onto a cooling drum. Typically the drum has a mesh surface which draws through air. The ambient air passes through the bulked yarn providing a cooling effect [13].

A similar principle can be observed (figure 2.12) although in air jet texturising, hot compressed air is used in place of hot fluid.



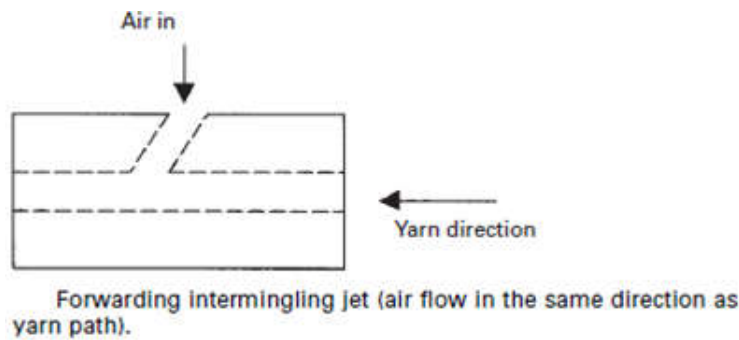
**Figure 2.12; Air Jet Texturing [20]**

The uniformity of the yarn is determined by the flow of fluid within the jet, the regulated temperature, flow and pressure and action of the cooling drum [13].

### **2.3.7 Entanglement**

The cooled yarn is then relaxed via another set of 'duos' and fed for entanglement (intermingling). The purpose of this process is to: [13]

1. Hold yarn bundles together. Especially if multiple yarns (plied yarns) are being used which is common in BCF for processing different colours.
2. When a single ply yarn is being used the intermingling hold the filaments tightly together in a cohesive bundle which will help prevent yarn damage on weaving or tufting.
3. Intermingling yarns lightly can aid unwinding.



**Figure 2.13; Intermingling Schematic [13]**

A visual perception of the intermingling process can be seen in figure 2.13. As the yarn passes through the jet it is met with air flow which creates 'mingle points' or 'knots' in the yarn. These hold the filaments together and help prevent yarn breakages on further processing for example during weaving and the yarn will not be sized [13, 14].

There are many types of jets which have been developed for intermingling which operate at different pressure depending on the denier of the yarn or whether the yarn will be further processed before final fabric production. For a single yarn going for tufting without further twisting, plying or heat setting air entanglement is an important factor as this is the final preparation before final production. Jets can be provided for processing one – four ply yarns. When this occurs for example when three different colours are being plied together for a carpet the guiding arrangement and yarn tension of each yarn is a critical factor as too much tension or a problem with arrangement can cause yarn breaks and issues with the final product appearance [13, 14].

### **2.3.8 Winding**

During winding the nature of the BCF yarns can cause fluctuations in winding tension. The change in tension can have an effect on the finished yarn. If the yarn tension increases then the percentage crimp will reduce while the residual shrinkage will increase and the opposite in the case of a reduction in winding tension. Therefore winding needs to be closely monitored [13, 14].

## **2.4 Introduction to Masterbatch**



Polymer granules containing a high percentage of pigments, additives or fillers are termed a Masterbatch. These granules are mixed with raw polymer before injection moulding, fibre spinning or film production to achieve the desired colour or property modification in the final product [22].

When using additives and pigments they can form agglomerates within a polymer matrix causing problems in the final product. A masterbatch provides these ingredients dispersed and distributed evenly throughout the polymer matrix. This is important for fibre production, if the ingredients are finely dispersed then screen pack life is enhanced and there will be less filament breakages on spinning.

As discussed previously there are generally three types of masterbatch. Colour masterbatch for pigments and dyes. Additive masterbatches can contain UV Stabilisers, Flame Retardant additives plus many more. Filler masterbatches which contain high percentage of fillers. There are often also combination solutions, for example a colour masterbatch can also contain UV and light stabiliser additives providing the user with one masterbatch to provide colour and stabilisation in the final product [22].

The European masterbatch market increased between 2001 and 2006 in terms of tonnes produced across various industries and was predicted to continue growing through to 2010 (Table 2.1) [88].

**Table 2.1; Masterbatch volumes by type – AMI Consulting. [88]**

<b>MASTERBATCH DEMAND IN WESTERN EUROPE BY TYPE 2001-2010</b>				
<i>Units: Tonnes</i>	<b>2001</b>	<b>2005</b>	<b>2006</b>	<b>2010</b>
Black	152,593	170,721	176,174	188,244
White	208,368	230,450	236,959	259,619
Coloured	174,171	191,523	195,978	219,174
Additive	157,305	187,413	195,830	222,895
<b>TOTAL</b>	<b>692,436</b>	<b>780,107</b>	<b>804,941</b>	<b>889,933</b>

The total estimated value of the European masterbatch market as of 2006 was €2.4 billion. The estimated value of the fibres masterbatch market is €205 million [88].

#### **2.4.1 Production of Masterbatch**

Masterbatches are generally produced on an extruder. The three main types are single screw, twin screw and conical screw. Here we will focus on the twin screw production of masterbatches.

As previously mentioned the aim of the extrusion process is to produce highly concentrated granules of finely dispersed ingredients. There are many factors which influence masterbatch production and the dispersion efficacy.

The main factors effecting production and effectiveness are;

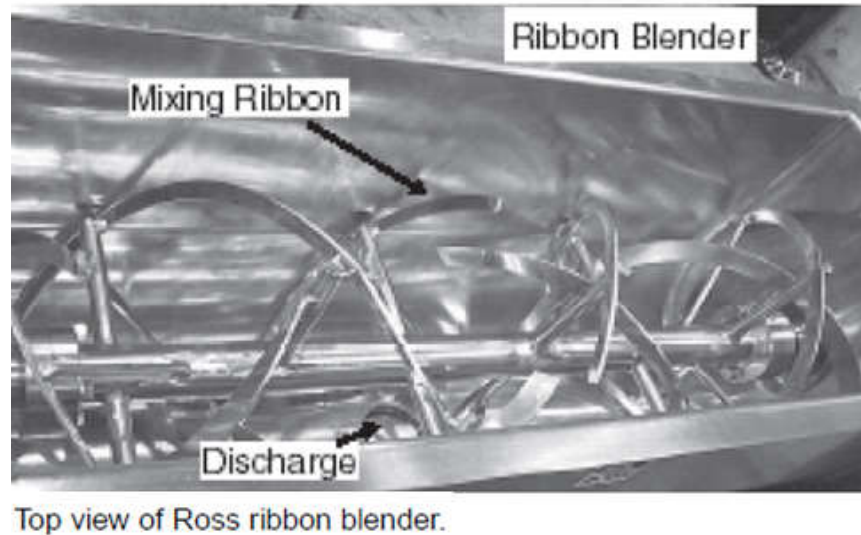
- Raw material mixing / blending
- Raw material feeding
- Temperature profile
- Screw Profile
- Shear Rates

These factors will vary depending on polymer and additives being processed.

#### **2.4.2 Raw Material Mixing / Blending**

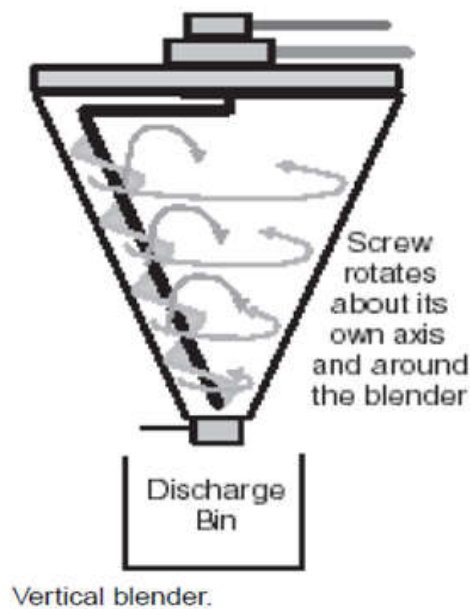
Blending is typically a batch process done prior to extrusion. There are various blending methods around.

Ribbon blenders are semi-circular steel tanks containing double helical rotating blades. (Figure 2.14) The rotating blades cause the material to move back and forth within the blender from the centre outwards and back again. They need at least 40% of the volume to be taken up for effective blending and therefore are used for larger batch sizes. The blending is considered low intensity [24].



**Figure 2.14; Inside Ribbon Blender [24]**

Vertical blenders (Figure 2.15) are cone shaped with a rotating screw within which orbits the blender walls. The screw moves material from the bottom to the top of the cone. These blenders require less floor space but more overhead space than a ribbon blender and can process smaller batches as low as 10% of the volume. Vertical blenders can also be fitted with a heated jacket and run on a vacuum to dry materials during the blending process [24].



**Figure 2.15; Schematic Vertical Blender [24]**

High Intensity Mixers are smaller than both the mentioned methods and are usually on line blending systems. These have blades situated at the bottom of a chamber which rotate at very high speeds. This rotation creates a vortex which then generates shear and heat. They are used for powder/powder blends and the heat generated can cause some of the ingredients to melt and adhere to the carrier resin which leads to improved dispersion on extrusion [24].

It is common for pigments to be blended with wax and polymer in this method. The wax would have a lower melting point and melt through the heat generated, causing the pigment to adhere to the wax and polymer leading to improved dispersion on extrusion.

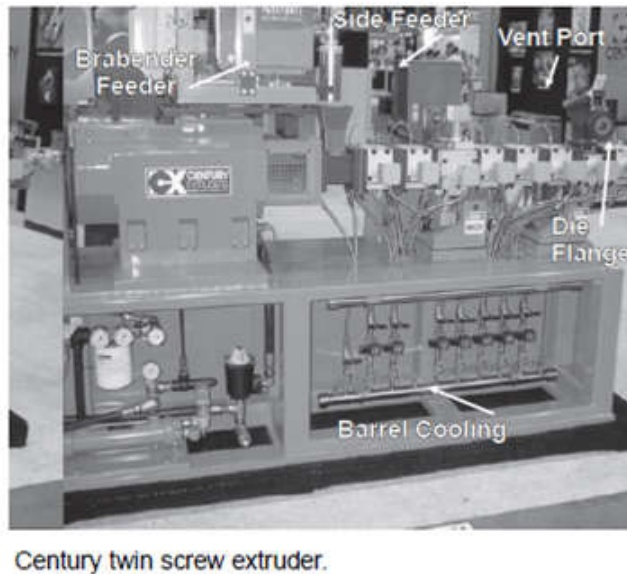
#### **2.4.3 Feeding of Raw Material**

Feeder deposit the formulation directly onto the screws of the extruder, the screw speed will be set at a higher rate than the material is fed as to avoid a build-up of material. This method is known as starve fed. It also limits the possibility of the materials bridging in the extruder throat [24].

The output of the extruder is determined by the feed not the screw speed and measured in Kilograms per hour (Kg/h) or pounds per hour (lbs/h).

Ingredients can also be fed downstream via a side feeder, again these are starve fed and a single or twin screw will convey the additives to the extruder at a controlled rate [24].

Figure 2.16 shows a typical twin screw extruder with a side feeder function.



**Figure 2.16; Twin Screw Extruder – External Layout [24]**

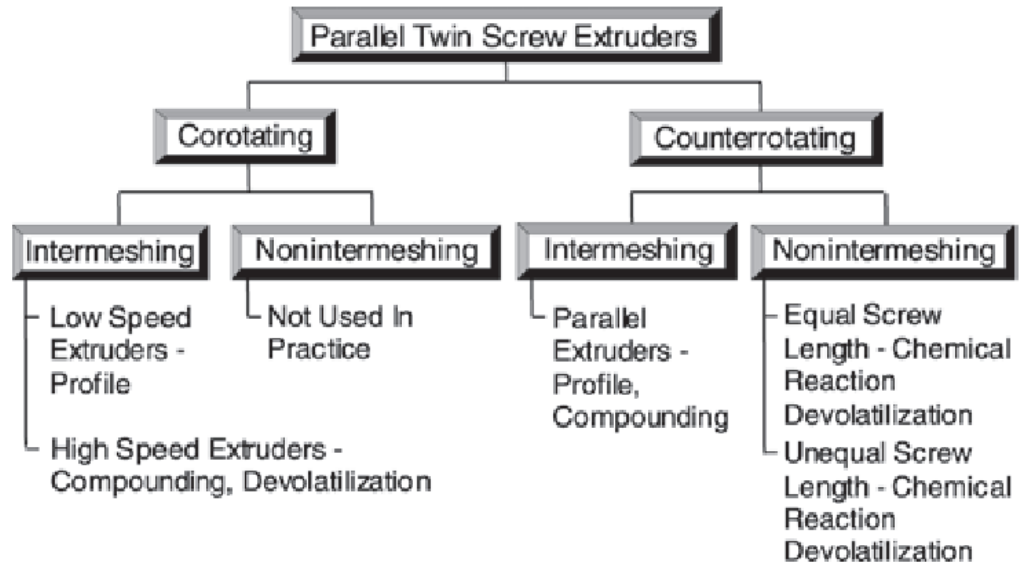
#### **2.4.4 Processing Thermoplastics on a Twin Screw Extruder**

A wide range of thermoplastics can be processed on a twin screw extruder to produce masterbatches. They include but are not limited to Polypropylene, Polyesters and Polyamides.

Twin screw extruders are the preferred choice for the production of masterbatches and compounds as they are able to provide sufficient mixing of ingredients at lower melt temperatures [26].

The screws and barrel of a twin screw are made up of various smaller sections which are, feeding/conveying, mixing and venting. This enables each section to be custom built for the materials being processed providing great flexibility.

There are two type of screw types for twin screw processing. They are 'co' and 'counter' rotating screws. These can also be 'intermeshing' or 'non-intermeshing' Figure 2.17 shows the common screw types.



**Figure 2.17; Screw types available for twin screw extrusion [25]**

The difference between co-rotating and counter rotating twin screw extruders is the screw rotation relative to each other. In co-rotating extruders, both screws rotate in the same direction, while in counter-rotating extruders, one screw rotates clockwise and the other screw rotates counter clockwise. With co-rotating screws, both screws have either right-handed or left-handed thread, depending on the screw rotation (clockwise vs counter clockwise). In counter rotating extruders, one screw has a right-handed thread and the other screw a left-handed thread [25].

Table 2.2 explains the performance variance of differing screw setups.

The screw shafts are fitted with different elements depending on what section they occupy within the extruder.

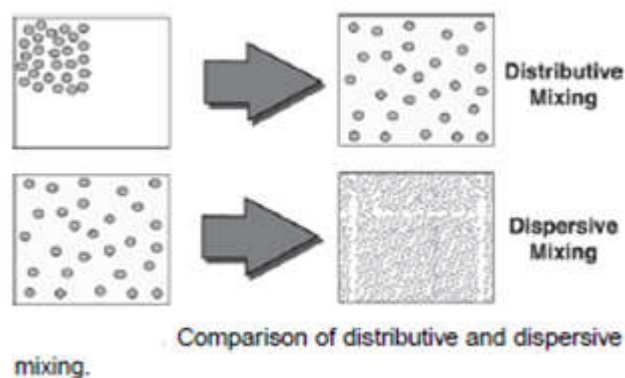
The feeding section is built with open flights to ensure the maximum material intake. This section is followed by conveying and melting section where a large surface area is required to ensure good heat convection and melt the material [25].

**Table 2.2; Performance variance of different screw setups [27]**

	<b>Corotating Intermeshing</b>	<b>Counterrotating Intermeshing</b>	<b>Counterrotating Nonintermeshing</b>
Practical Residence Time, minutes	0.35–6	0.35–6	0.35–6
Residence Time Distribution	Variable	Variable/ Tighter	Variable
Dispersion	High	High	Good
Heat Transfer	Excellent	Excellent	Excellent
Venting	Excellent	Excellent	Excellent
Pumping	Good	Excellent	Fair
Self-Wiping	Excellent	Good	Fair
Zoning	Excellent	Excellent	Good
Output Rate	High	Moderate	High
Distributive Mixing	Good	Good	Excellent

The mixing section consists of kneading and / or mixing elements. There are two main types of mixing, being dispersive mixing and distributive mixing (Figure 2.18).

Dispersive mixing uses kneading block to break up agglomerates. This method breaks up the agglomerates found in pigments using a high shear process and disperses them throughout the melt stream. Distributive mixing is carried out by mixing elements and is suitable for processing fibrous materials, fillers and mixing shear sensitive polymers. It is a low shear process and works by breaking and recombining the melt stream whilst distributing the particles in a uniform manner [27].



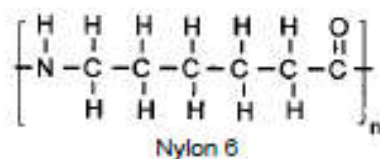
**Figure 2.18; Comparison Distributive and Dispersive Mixing [27]**

Factors affecting mixing are temperature, screw speed, percent fill in the screw channel and screw geometry. There are many types of kneading blocks and mixing elements on the market for use in a twin screw extruder [27].

The degassing section of the screw is to let volatiles and moisture to escape the system, the screw elements in this section are usually open flights to convey material and prevent it passing up into the vent holes [25].

The metering section is used to feed material to the die and increase the pressure by compression. 'Single flighted' forward conveying elements are used to meter the melt to the die [27].

There are many types of polyamides processed on extrusion equipment some are crystalline some are in amorphous form therefore they require quite different processing conditions. Polyamide 6 is a crystalline polyamide [28], Figure 2.19 shows the chemical structure.



**Figure 2.19; Chemical Structure PA6 [28]**

As polyamides are hygroscopic and they absorb relatively high levels of water from the atmosphere the polymer needs to be carefully dried prior to extrusion. If the polymer is 'wet' upon extrusion it is possible that the water molecules can attach the -NH- groups and cause the polymer to degrade reducing the molecular weight and affecting properties [28].

Consequently 'over drying' can also hinder the extrusion process as water acts as a plasticiser within a PA6 extrusion helping the melt flow of the material [28].

Ideally a desiccant dryer system is used to dry the PA6 prior to extrusion. The preferred moisture content is 0.08% (800ppm) and no lower than 0.02% (200ppm), the recommended drying temperature is 82°C, any higher can lead to oxidative thermal degradation of the polymer which can cause dis-colouration [28].



Polyamide 6 viscosity versus shear rate curves provided the conclusion that polyamide is affected by both temperature and shear rate. By increasing the shear rate from 100 to 400  $\text{sec}^{-1}$  can reduce viscosity by approximately 2 times, whilst increasing the temperature profile 20°C from 230°C to 250°C can reduce viscosity between 1.5-2 times [28].

As a brief definition *Shear* is the movement of parallel layers. *Shear rate* is the velocity gradient at which these layers are sliding past each other. It is a measure of deformation of a polymer melt and flow rate of the material and geometry of the extruder influence this. Shear rate is recorded in reciprocal seconds. Measurement are carried out on an oscillating plate rheometer [29] Figure 2.20 shows the shear rates involved for extrusion applications.

The formulation being processed also has to be considered, additives and pigments can affect the melt flow of the system and therefore screw speeds and temperature profile will need to be adjusted and recorded to obtain optimum processing conditions.

To summarise masterbatches are used to supply well dispersed pigments, additives and other materials at high concentrations within a polymer matrix. There are many technical aspects of master batch production to consider from raw material handling, polymer processing, machine make-up and many more. Section 2.5 discusses masterbatch use in fibre / filament production.

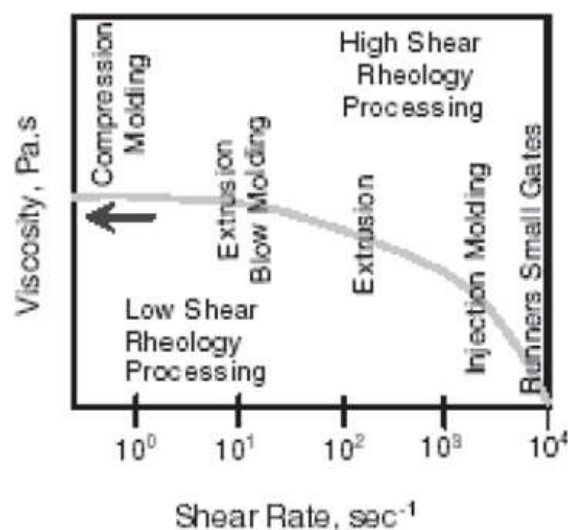


Figure 2.20; Extrusion process shear rates [29]

## **2.5 Solution Dyeing of PA6**

Also known as 'dope-dyed' or 'mass-dyed', solution dyeing is the process where pigments and auxiliaries are incorporated into the PA6 prior to spinning. These materials are usually incorporated into a 'masterbatch' (also known as a concentrate) and added to the polymer chips during spinning. This leads to all the necessary pigments and additives such as UV and Antioxidants being incorporated into the final filament at the melt spinning stage thus the filament coming out of the spinneret will already appeared coloured (Depending on the pigments included) [21, 22].

The aim of the solution dyeing process is to facilitate uniform pigment dispersion within the fibres without any aggregates or agglomerates [50].

The concentrate can typically contain up to 40% pigment in a polymer carrier and can be fed into the melt stream upon fibre production via a side feeder or simply blended with the polymer chips prior to spinning [50].

This method of colouration or incorporating additives into fibres has economic, technological and ecological advantages over the exhaust dyeing method [50]

The advantages with solution dyeing versus post dyeing are;

- One Step Process (removes dyeing process)
- Improved Fastness (Light and Wash)
- Improved Chemical Resistance
- Lower energy and utility consumption
- More Uniform Colour
- Reduction in cost when masterbatch used a low dosing level (3%<)

The disadvantages of solution dyeing are;

- Difficult to achieve bright colours
- Difficult to achieve deep colours

- Less cost effective when high addition levels are necessary

Many yarn producers now use pre-coloured masterbatch for the colouration of their yarns especially carpet yarns. As previously stated masterbatch is not limited to pigments and can also be used for incorporating additives into the synthetic filaments such as Flame Retardants.

## **2.6 Chapter Summary**

Chapter two provided an introduction to polyamides and their use in the textile industry.

Production of polyamide 6 textiles was examined from the polymerisation processes through to melt spinning and bulk continuous filament production.

The extrusion of polyamide 6 was considered and the processes and difficulties were examined.

Finally an introduction to masterbatch was made and also the pros and cons of solution dyeing via masterbatch addition was evaluated.

## Chapter 3 Literature Review; Fire – Retardance Strategy, Materials and Test Methods

### 3.1 Fire Parameters and Triangle

When developing a flame retardant system an understanding of how a fire can develop and its key parameters which govern the fire are required.

The key parameters are [3]:

- Combustibility – Will the material burn
- Ignitability – How will it ignite
- Spread of Flame – How quick the flames will spread
- Heat Release – Rate and amount of heat released.

Tesoro (1978) lists some key definitions in relation to the subject [46];

**Combustion.** Self-catalysed exothermic reaction involving **two** reactants (fuel and oxidiser).

**Fire.** Uncontrolled combustion.

**Flames.** Gas-phase combustion processes with emission of visible light.

**Ignition.** Initiation of combustion.

**To Glow.** To burn without flame, but with visible light.

Using home textiles as an example and incorporating them into the Fire Triangle (Figure 3.1), a fire can be initiated by a cigarette (heat) igniting a piece of combustible upholstered furniture (fuel) which begins to burn. The flame spread to the surroundings (carpets, curtains) which in turn also begin to burn. Once these materials have formed enough flammable gases and there is sufficient heat and oxygen present flashover will occur engulfing the whole room. The fire will begin to decrease once all the fuel or oxygen has been consumed [3].

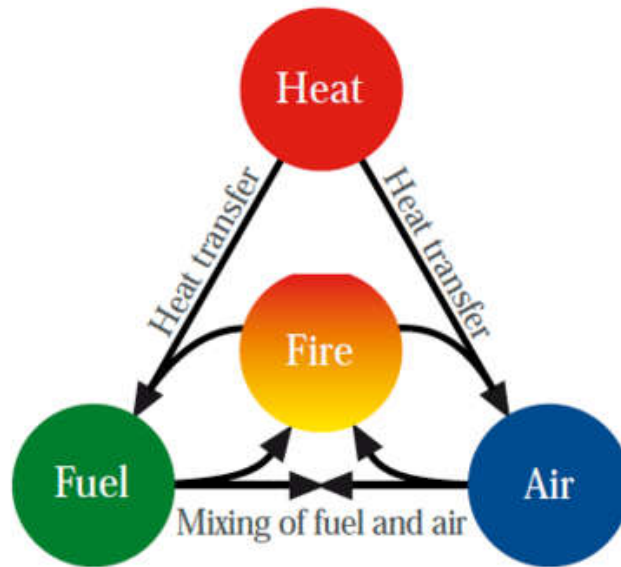
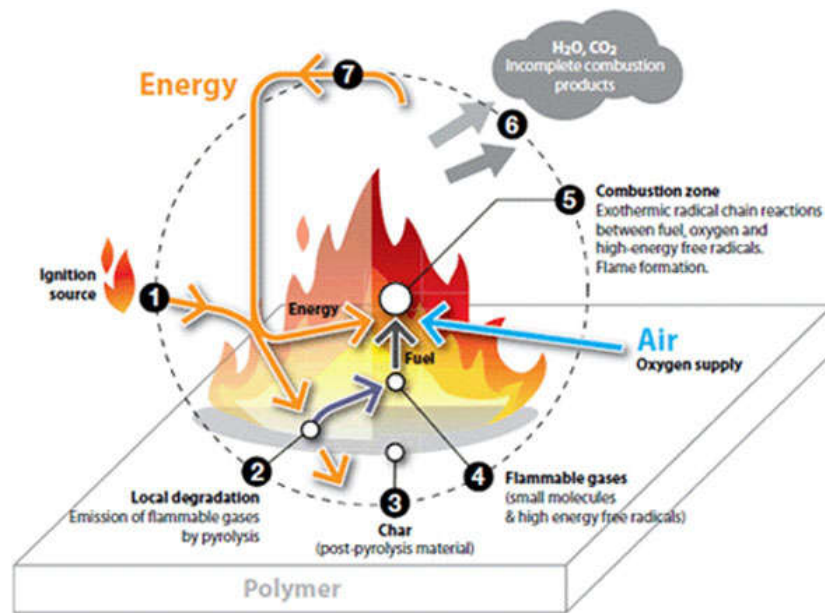


Figure 3.1; the Fire Triangle [3]

### **3.1.2 Fire cycle and how materials burn**

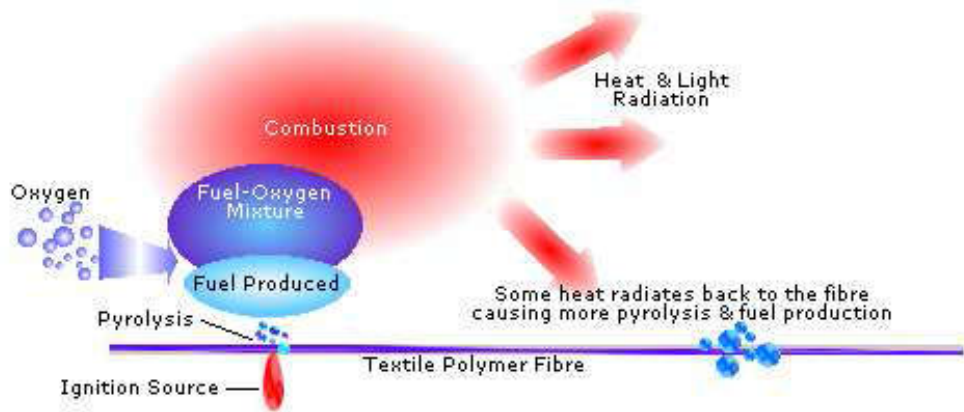
Solid materials do not burn directly. Synthetic textiles such as PA6 textiles need to be decomposed by heat. This process is called pyrolysis and will be discussed in more detail later. The process releases flammable gases which react with oxygen in the air in the presence of heat creating a visible flame [3].

Figure 3.2 explains the fire cycle in seven stages helping us to understand how a material burns and the key processes involved. When developing flame retardant systems we can target which stage we would like the flame retardant to be functional.



**Figure 3.2; Fire Cycle and key stages of fire development [4]**

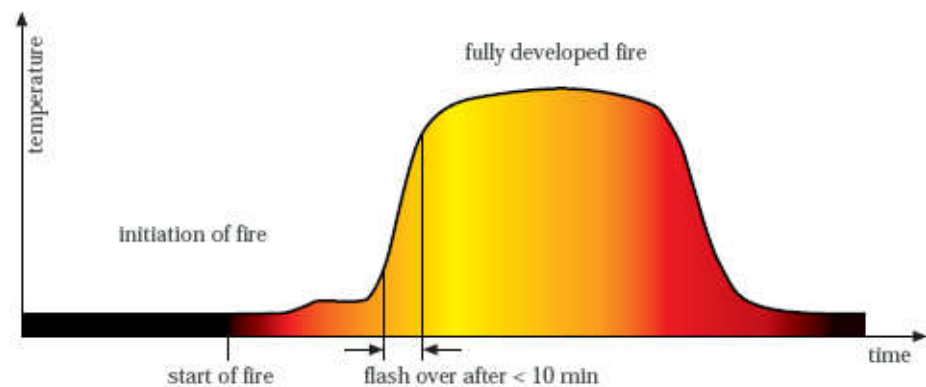
1. Ignition source provide heat to the material.
2. Point in which the heat source first contacts the polymer in our case a textile and initiates pyrolysis of the textile.
3. Polymer long chain molecules break down forming char layer.
4. Polymer long chain molecules break down releasing flammable gases, which are highly energy free radicals.
5. The free radicals, fuel and oxygen react forming visible flames.
6. Side products. Smoke.
7. Energy emitted and re-transmitted to the textile reinforcing pyrolysis enabling the process to continue and sustain itself. [4]



**Figure 3.3; Concept horizontal fire spread on textile material [90]**

Figure 3.3 continues to explain the fuel cycle but gives an easier perception of stage 7 whereby the continued pyrolysis of a textile material can occur. It also aids the understanding of horizontal fire growth.

Using Figure 3.4 we can begin to understand how a fire develops over time. Flame retardants are most effective during the initiation and start of a fire. Once flash over has occurred and a fire is fully developed flame retardants will be ineffective.



**Figure 3.4; Development of fire over time [40]**

In summary a fire needs fuel, oxygen and heat removing one of these parameters will result in fire decrease leading to eventual extinguishment. The textile material is the fuel within the triangle and with continued pyrolysis continues to provide fuel to the system. It is here

where our research can now be to explore methods of retarding the pyrolysis of the textile material to suppress the fuel supply to the fire system.

### **3.2 Pyrolysis**

Eloma et al (1997) [44] summarises combustible gases (fuel) must be produced for ignition of a polymeric material to occur.

Upon heating the polymer will eventually reach temperature in which the weakest bonds rupture. At lower temperatures this process is considered to be degradation and only slight changes in structure and properties will be noticed.

At higher temperatures the chemical structure change of the polymer is more extreme, a significant dissociation of chemical bonds takes place leading to decomposition.

Troitzsch (1983) explains that pyrolysis is the irreversible chemical decomposition of a material due to temperature without oxidation [45].

Pyrolysis plays the main role in the production of combustible gases in the burning of polymers [44].

### **3.3 Burning Mechanism of Fibres**

In 2.5 we have extensively considered the basics of how fires occur and the necessary requirements for continued combustion. To further explore the burning mechanisms of fibres we revert to Broughton and Cerkez (2013) [38].

The first consideration is what is fuel? Different materials provide different amounts of fuel to the fire cycle. Hydrogen although stable in air and oxygen atmospheres is extremely flammable when an ignition source is applied [38].

Organic materials (usually polymeric materials) containing large amount of hydrocarbons can provide a large amount of fuel for oxidation providing they are sufficiently broken down by thermal decomposition to release lower molecular weight volatile fragments. These fragments provide the fuel and can escape into the surrounding atmosphere to be combined with oxygen and burn. The oxidation of these fragments produces enough heat and at a



sufficient rate for additional thermal decomposition to occur producing more fuel and combustion to be sustained until fuel has been used up [38].

**Table 3.1; Energy required to break chemical bonds [38]**

Average energy required to break various chemical bonds (kJ/mol)					
Bond	Bond enthalpy (kJ/mol)	Bond	Bond enthalpy (kJ/mol)	Bond	Bond enthalpy (kJ/mol)
<i>Single bonds</i>					
H-H	436	C-H	414	O-O	142
H-N	393	C-C	347	O-P	502
H-O	460	C-N	276	P-P	197
H-S	368	C-O	351	S-S	268
H-P	326	C-P	264	F-F	151
H-F	568	C-S	255	Cl-Cl	243
H-Cl	431	N-N	393	Br-Br	193
H-Br	366	N-O	176	I-I	151
H-I	298	N-P	209		
<i>Multiple bonds</i>					
C=C	619	N=N	418	O=S	469
C=N	615	P=P	490	C=C	812
C=O	724	S=S	351	C=N	891
C=S	477	O=O	499	N=N	941

Energy is required to begin this decomposition step to break bonds of the polymeric materials to reduce molecular weight and release volatile fragments. Table 3.1 shows energy required to break some common chemical bonds.

Broughton and Cerkez [38] state that two bonds need to be broken to release a volatile fragment from a polymer chain. Factors affecting the release of fragments are the presence of aromatic rings, double bonds and cross linking in the polymer structure.

It is thought that when considering the energy contribution to heat of combustion of individual elements shown in Table 3.2 we can begin to understand the overall fuel values for organic compounds. It can also be used to provide an understanding as to how to reduce the fuel value and therefore flammability of organic solids. It can be seen that elements such as Oxygen, Nitrogen and Chlorine contribute a negative energy and thus are not fuels. Therefore polymers with high oxygen, nitrogen or chlorine contents will provide less fuel to a fire cycle than for example a polyolefin polymer made up of solely carbon and hydrogen [38].

**Table 3.2; Elements and molecules contribution to heat of combustion [38]**

Structural group, small molecule, and polymer contribution to the heat of combustion						
Structural group	Contribution (kJ/mol)	Structural group	Contribution (kJ/g)	Structural group	Contribution (kJ/g)	Oxygen index
H	190	Methanol	22.68	Polyethylene	47.74	17.4
C	431	Ethanol	29.67	Polypropylene	45.8	17.5
O	-132	Isopropanol	33.38	Polyvinylfluoride	21.7	22.6
N	-100	Ethane	51.87	Polyvinylalcohol	23.31	22.5
F	-230	Propane	50.35	Polyacrylonitrile	32.22	18
Cl	-43	Pentane	48.54	Polybutadiene	45.19	18.3
S	311	Hexane	48.31	Polyvinylchloride	17.95	37.1
Si	219	Benzene	41.83	Polyisoprene	44.9	18
OH	-108	Glycerol	17.95	Polystyrene	43.65	18.3
NH	77	Acetone	30.83	PMMA	26.81	17.3
CH	518	Aniline	36.44	Polyoxymethylene	17.39	15
CH <sub>2</sub>	670	Benzoic acid	26.43	Polycarbonate	31.3	25
CH <sub>3</sub>	775	Benzyl alcohol	34.56	Polyvinylbutyral	32.9	
CF <sub>2</sub>	328	Cyclohexane	46.58	Polyimide	26.03	37
CF <sub>3</sub>	213	Dioxane	26.83	Nylon 6	30.9	24
C=N	548	Ethleneglycol	19.17	p-Aramid	26.92	32
C=C	781	Formaldehyde	18.76	m-Aramid	26.45	28.5
C=O	259	Methyl ether	31.7	Cellulose acetate	18.88	18.1

After degradation has occurred and fragments are released they still need to diffuse into the atmosphere. This diffusion can be affected by fabric structure. In a single fibre or light weight fabric like a non-woven web for example with a high surface area these fragments will diffuse rapidly to the atmosphere compared to a tightly woven fabric. These tightly woven materials will melt and coalesce into molten pools and shrink away from the ignition source or drip a flaming molten pool away from the solid fuel. This drip can still be a fire hazard although providing initial protection to the source material [38].

### **3.4 Burning of Polyamide 6**

There have been numerous research projects and studies on the burning of polymers and in particular polyamide 6 and other aliphatic polyamides. We will focus on works by Aminabhavi & Cassidy, Hull & Stec and Levchik et al.

Aminabhavi & Cassidy (1989) [31] reviewed Hilado (1969) and reported the combustion of polymeric materials involves a series of chemical and physical changes.

1. On a micro-scale concerning the behaviour of the polymer
2. On a macro-scale concerning the behaviour of a unit mass of material.
3. On a mass scale concerning the behaviour of the complete system.

It was summarised that on a micro scale hard polymer becomes a viscous liquid after a loss in physical integrity. At high temperature oxidation occurs producing heat and a flame in the gaseous phase.

On a larger scale (macro) Hilado (1969) found polymeric burning occurs in stages. Initial heating leads to decomposition and then ignition (stage 1). Parameters for ignition are:

1. Flash Point of polymeric material (temperature at which flammable gases evolve)
2. Self-Ignition of polymeric material (temperature within the polymer which becomes possible to self-sustain ignition)
3. Oxygen Index (OI) (Minimum level of Oxygen required to sustain ignition and combustion.)

Stage two is combustion in which a unit mass of polymer generates an amount of combustion heat, leading to propagation.

Hilado concluded mass scale burning depends on various aspects being, initial fire, fire build up, flash point, severity of fire, and fire propagation. It was noted combustion can be self-propagating after the removal of an ignition source if sufficient heat is generated and radiated back to the polymer surface to continue the decomposition process. Therefore it was also summarised combustion would be governed by the variables; rate of heat generation, rate of heat transfer to the surface and rate of decomposition.

Hull & Stec (2009) [32] explain the impact of heat on polymeric material causes the breakages of chemical bonds leading to volatile fragments being produced. As they are at elevated temperatures they are buoyant above the surface of the polymer and once they are in sufficient concentration and they are flammable it is possible for a flame to stabilise.

Similarly Aminabhavi & Cassidy suggested that volatile products can be split into three categories;

1. Non-flammable gases
2. Flammable gases

### 3. Carbonaceous Char

Hull & Stec (2009) further evaluate the concept of heat transfer processes, which are critical to the ignition and burning behaviour. Once ignition has occurred a fire usually grows by flame spread [32].

Flame Spread is where surfaces near the initial site of pyrolysis (decomposition) or the flame zone are heated by radiant heat and begin to decompose leading to more flammable products [32].

Horizontal flame spread is slow due to only gas phase conduction, whereas vertical flame spread can be rapid as radiative, convective and conductive heat transfer occurs [32].

Levchik, Weil and Lewin (1999) [33] carried out an extensive review of work previously carried out on the decomposition of aliphatic polyamides.

Levchik, Weil and Lewin reviewed Straus and Wall (1958). They found that heavy volatile products comprised of about 95% of the total volatiles. Straus and Wall suggested that the weakest bonds C-N bonds undergo initial scission and that random breakdown of PA6 occurred along with hydrolytic scission of the peptide bond. C (O)-NH which assumed responsibility for high levels of CO<sub>2</sub> being produced during decomposition [33].

A review of Luderwald et al (1978) revealed that above temperatures of 390°C intensive thermal degradation began. The main products were cyclic oligomers of caprolactam. Similar study by Bletsos et al (1985) observed multiple monomer units as products of decomposition. They explained that this was due to the cleavage of the CH<sub>2</sub>-CH<sub>2</sub>, CH<sub>2</sub>-NH or CH<sub>2</sub>-CO bonds and not cleavage of the peptide bond as mentioned in Straus and Wall [33].

Levchik, Weil and Lewin state PA6 shows three steps of weight loss as shown in TGA analysis in an inert atmosphere. The first step is volatilisation of residual moisture and low molecular weight oligomers. The second step occurs between 280°C and 450°C and is the major decomposition step as most of the material volatilizes. It is assumed that a cross linked structure is formed causing a slowdown in decomposition at 450°C, which on further heating decomposes and yields approximately 5% of stable char [33].

A review on the solid residue products of thermal decomposition of PA6 found that the spectrum of PA6 did not change greatly during the major steps of decomposition. This suggests mostly volatisation of monomer and chain fragments. At a high degree of decomposition nitrile groups (CN triple bond) and C=C double bonds were observed which are attributed to be the cause of the stable layer of char [33].

Levchick, Weil and Lewin conclude that no complete agreement on the mechanism of thermal decomposition of nylons have been found. The three main types of decomposition discussed in the various literatures are hydrolytic scission, homolytic scission and intramolecular hydrogen transfer [33].

There is also disagreement at which the primary bond scission occurs whether that be at the peptide bond or alkyl-amide bond.

It is summarised that PA6 tends to produce monomer and cyclic or linear oligomers upon decomposition. Secondary reactions can lead to the evolution of volatile gases and cross linking which leads to the formation of stable solid char residue consisting of nitrile groups and carbon double bonds.

This topic was also discussed by Price & Horrocks (2013, 'Combustion Processes for Textile Fibres'). Table 3.3 compares various common fibres' thermal properties.

From Table 3.3 we can see PA6 pyrolysis onset is 431°C and ignition is 450°C these are important properties to be aware of when developing a flame retardant product.

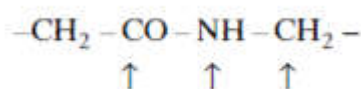
Price and Horrocks (2013) [34] stated that random chain scission occurs during the decomposition of PA6 and resulting products are caprolactam monomer. This summary agrees with more than one study reviewed by Levchik, Weil and Lewin.

**Table 3.3; Thermal Transitions of common Fibres [34]**

Thermal transitions of the more commonly used fibres						
Fibre	T <sub>g</sub> (°C) (softens)	T <sub>m</sub> (°C) (melts)	T <sub>d</sub> (°C) (pyrolysis)	T <sub>c</sub> (°C) (ignition)	LOI (vol%)	ΔH <sub>c</sub> (kJ g <sup>-1</sup> )
Wool			245	600	25	27
Cotton			350	350	18.4	19
Viscose			350	420	18.9	19
Nylon 6	50	215	431	450	20–21.5	39
Nylon 6.6	50	265	403	530	20–21.5	32
Polyester	80–90	255	420–447	480	20–21	24
Acrylic	100	>220	290 (with decomposition)	>250	18.2	32
Polypropylene	–20	165	470	550	18.6	44
Modacrylic	<80	>240	273	690	29–30	—
PVC	<80	>180	>180	450	37–39	21
Oxidised acrylic	—	—	>640	—	—	45
Meta-aramid (e.g., Nomex)	275	375	410	>500	29–30	30
Para-aramid (e.g., Kevlar)	340	560	>590	>550	29	—

Price & Horrocks [34] continue to explain the thermal degradation of aliphatic polyamides are influenced by two major factors.

The first being the strength of the weakest bonds around the amide group (Figure 3.5).



**Figure 3.5; Weakest Bonds in Polyamide Chain [34]**

This agrees with the work carried out by Straus and Wall as reviewed in Levchik, Weil and Lewin. They agreed that these breakages occur randomly and also stated that gas products were NH<sub>3</sub>, CO and CO<sub>2</sub>, other products were low molecular weight fragments and subsequent degradation products. Of the gases evolved only CO is flammable but volatiles from the smaller polymer chain fragments can provide major fuel components.

Reviewing Kohan (1973) Price and Horrocks [34] conclude that decomposition of PA6 can lead to depolymerisation back to monomer caprolactam which leads to the possibility of recycling PA6 from waste like nylon carpets.

The second factor is some aliphatic polyamides can form 3-D structures which lead to gels. This is more common in nylon 6.6.

Price and Horrocks [34] further discuss flammability of simple nylons is determined by their ability to shrink away from the ignition source as well as the volatiles formed. It is also stated that by increasing the Limited Oxygen Index (LOI) to >25 textile materials begin to pass various flame retardant test methods.

It is worth noting that there are many LOI values quoted throughout literature for PA6 ranging from 21-24 which falls into the moderately flammable category.

Another issue associated with the thermal decomposition of polymeric materials is the toxicity of the products from decomposition.

Braun and Levin (1989) reviewed various studies researching the decomposition products of aliphatic nylons. It is generally agreed that the quantity of smoke produced and its toxicity play an important role in determining the possibility of survival during a building fire. Polyamides are common materials within buildings from clothing, home furnishing and possibly moulded parts. Therefore it is important to understand the products from combustion and the toxicity of these products.

Hull and Stec (2009) also comment that most fire deaths are caused by inhalation of toxic gases. The yield of toxic products is affected by the material composition, temperature and oxygen concentration in the atmosphere. It is also mentioned Carbon Monoxide (CO) is the most significant toxic gas.

Braun and Levin (1989) aimed to determine the possible products which aliphatic polyamides would yield under various fire conditions and to evaluate the toxicity of these products [35].

Braun and Levin (1989) concluded that decomposition of nylons began with primary scission of the NH-CH<sub>2</sub> bond then followed by secondary reactions. This results are in some agreement with the conclusions from literatures 30-33.

The studies reviewed analysed the decomposition products from three atmospheres, vacuum, inert and air. For the purpose of this project we will focus on the studies carried out in air which is believed to be more correlative with real life conditions.

Initial studies by Michel et al (1981) and Hartstein and Forshey (1976) focused on the production of hydrocarbons developed from the decomposition of PA6. Both studies had similar results and the main hydrocarbons produced were Butane/ Butene, Pentene-1 and Cyclohexane.

From Braun and Levin (1989) a study carried out but Murata and Takahasni (1974) were able to determine that PA6 began producing Hydrogen Cyanide (HCN) and Ammonia (NH<sub>3</sub>) at approximately 375°C.

Other reviews on pieces by Sugihara (1975), Sumi and Tsuchiya (1976) and Morikawa (1978) used tube furnaces to thermally degrade PA6 between temperature range 400-1000°C. The experiments were carried out in air and nitrogen.

Sugihara (1975) focussed on production of HCN, CO, NH<sub>3</sub> and NO<sub>2</sub>. Sumi and Tsuchiya monitored HCN, CO and CO<sub>2</sub> while Morikawa was concerned with production of NH<sub>3</sub> and HCN.

All three studies found production of HCN increased with an increase in temperature in either air or nitrogen atmosphere.

Sugihara reported CO in air and nitrogen increased with an increase temperature while Sumi stated it was independent from temperature.

From Sugihara's data approximately 270 mg/g of CO was produced in air. Volatiles became present at roughly 400°C. The tests were run to 1000°C. CN- produced was 130 mg/g while NH<sub>3</sub> was considerably lower.

From Morikawa's research approximately 100 mg/g HCN was produced in air over a temperature range 500-1000°C.

Sumi's results can be seen in Table 3.4



Table 3.4; Products from thermal decomposition of PA6 Sumi and Tsuchiya (1976)

<b>Concentrations of selected products from the thermal decomposition of nylon 6 in air</b>			
<b>Temperature (°C)</b>	<b>CO (mg g<sup>-1</sup>)</b>	<b>CO<sub>2</sub> (mg g<sup>-1</sup>)</b>	<b>HCN</b>
<b>500</b>	<b>64</b>	<b>190</b>	<b>52</b>
<b>600</b>	<b>79</b>	<b>232</b>	<b>65</b>
<b>700</b>	<b>71</b>	<b>195</b>	<b>79</b>
<b>800</b>	<b>76</b>	<b>142</b>	<b>95</b>

To summarise Braun and Levin's review it was found that there is a general decrease in quantity of heavier hydrocarbons and an increase in production of CO, CO<sub>2</sub> and HCN as temperature increases or as oxygen concentration within the atmosphere increases.

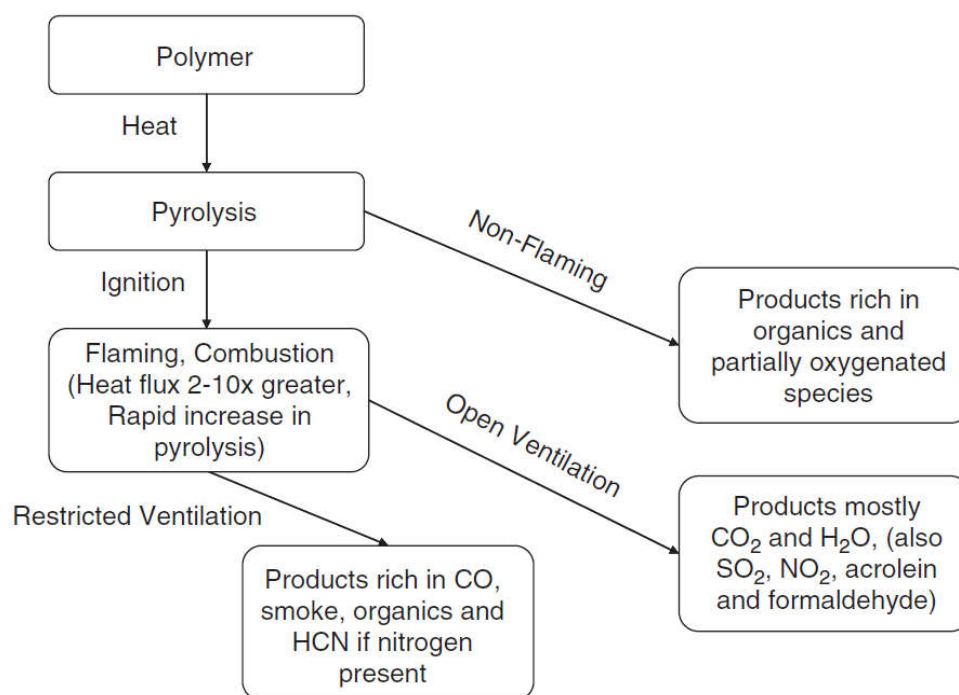
Predominant gases of decomposition of aliphatic nylons are CO, CO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, HCN and NO<sub>x</sub>.

Reverting to Hull and Stec [32] the formation of CO can be favoured by many conditions from smouldering to a fully developing fire.

It is stated that CO arises from incomplete combustion which can be caused by four factors;

1. Insufficient heat in gas phase
2. Quenching of flame reactions
3. Presence of stable molecules such as aromatics which survive longer in the flame zone and give high CO yields in well ventilated conditions and lower yields in under ventilated conditions.
4. Insufficient oxygen where heat flux will cause pyrolysis of the fuel but there is insufficient oxygen to complete the combustion reaction.

Figure 3.6 from Hull and Stec (2009) summarise the yields compared to the fire conditions.



**Figure 3.6; Stage of Toxic Gas Production [32]**

To summarise, the products from decomposition of polymers and specifically PA6, Literature 33-34 conclude there are various products produced some being asphyxiator gases which can inhibit an individual caught in a fire and prevent escape. The literatures whilst not finding a concrete agreement with each other conclude that there are many aspects of the decomposition of PA6 and the various products as a result of this mechanism. When developing a flame retardant system it is important to consider the nature in which the virgin material will burn and then beginning to find a solution to inhibit that. From the literature flame retardant textiles begin to pass flame test standards once they achieve a LOI of greater than 25. This is one aspect to consider, another is to consider what additives we can add to material to alter the burning behaviour. Strategies and current products on the market will now be considered.

### **3.5 Flame Retardant Strategies**

There are two main strategies to achieve flame retardant products. Within these categories there are various mechanisms. We will briefly review each mechanism before exploring in more detail specific materials.

#### **3.5.1 Strategy 1 – Physical Action**

There are three key mechanisms to Physical Action strategy;

- 1) Cooling effect – Endothermic process triggered by additives (commonly fillers) such as aluminium hydroxide. They cool the polymer surface below the temperature required for sustaining combustion. Also known as heat sinks [32, 36].
  - 2) Formation of Protective Layer – Obstructs the flow of heat and oxygen to the polymer therefore obstructing the flow of fuel to the flame [32].
  - 3) Dilution effect – Another heat sink method with the addition of inert fillers which evolve inert gases on decomposition and dilute the fuel in the gaseous phase.
- Common mode of action is the release of water vapour and carbon dioxide.

Aluminium Hydroxide and Magnesium hydroxide are the most common Physical Action flame retardants. They break down endothermically to release water vapour which can dilute free radicals in the gas phase whilst also forming protective layer on the polymer surface [32].

One problem associated with these materials is the high loadings needed for efficacy, leading to large impacts on mechanical properties of polymers. This leads them to be unsuitable for fibre production [32].

### **3.5.2 Strategy 2 - Chemical Action**

Similarly to physical action there are multiple mechanisms associated with the chemical action of flame retardants.

- 1) Gas Phase Reactions – Combustion is a free radical mechanism where oxygen attacks the hydrogen atom in a C-H structure forming OH radical, H atom and C radical. Flame retardants can act in the gas phase to interrupt this process. Halogenated flame retardants decompose at the burning temperature react with the H atoms to form non-combustible vapours such as HCl and HBr. These reduce the concentration of flammable gases below the required level to sustain combustion [32, 36].
- 2) Solid Phase (condensed) Reactions – Flame retardants work by breaking down the polymer so it can melt away from the flame or ignition source. The phenomena can

occasionally be seen with PA6 fabrics without the addition of a flame retardant. Even if this characteristic is exhibited fire safety is usually compromised as flaming drips are usually produced [32].

Char formation is a better mechanism of solid phase flame retardancy. On decomposition the form a carbonaceous layer on the polymer surface which imparts a protective barrier. Formation of char can also coincide with the release of diluting vapours such as water and carbon dioxide depending on the host polymer [32, 36].

Intumescence is the third mechanism of solid phase flame retardant to be mentioned. This is where a layer of material behind the surface layer will swell on the surface providing an insulating protective barrier. Intumescent systems are comprised of a carbon donor, acid donor and spumific compound. On decomposition the system expands and through cross linking reactions forming a protective insulated barrier in a 'foam' like structure [32, 36].

### **3.6 Flame Retardant Additives and the Environment**

Over recent years additive flame retardants have caused concern regarding their effect on the environment. Many are considered 'PBT' (Persistent, Bio accumulate and Toxic) to the environment [83].

New regulations (REACH) have been put in place to limit and prohibit the use of such materials.

Nyholm (2009) [83] reported materials considered CMR (Carcinogenic, Mutagenic and Toxic to Reproduction) are now restricted under REACH as they can potentially increase the risk of cancers.

POPs (Persistent Organic Pollutants) are also restricted under REACH because of their PBT attributes. POPs can accumulate in the ecosystems leading to long term effects on humans and the environment [83].

Nyholm (2009) presented the classification criteria under new regulation. (Figure 3.7)

**Table 3.5: Classification of PBTs under REACH regulations [83]**

	<i>POP classification according to UNEP</i>	<i>PBT classification according to the REACH legislation</i>	<i>vPvB classification according to the REACH legislation</i>
P criteria	>180 days in soil or sediment or >60 days in water	>120 days in soil or sediment or >60 days in marine water or >40 days in fresh water	>180 days in soil or sediment or >60 days in water
B criteria	BCF >5000 or High accumulation in another species or In absence of measured data, Log K <sub>ow</sub> >5	BCF >2000	BCF >5000
T criteria	potential for adverse effects on human health or to the environment	NOEC <0.01 mg/l in an aquatic organism or CMR or evidence for chronic toxicity	Not applicable

Halogen based flame retardants have received the most scrutiny and various popular brominated flame retardants were found in animal and human food chains in the USA [84].

Polybrominated diphenyl ethers (PBDE) and Hexabromocyclododecane (HBCD) were used in many flame retardant systems for use in a variety of industries. These two compounds are not strongly bound within a polymer matrix and can leach out of the plastic material over time becoming environmental pollutants [84].

Nyholm (2009) reported the United Nations Environment Program had identified 12 chlorinated based compounds to be banned globally. Nyholm (2009) attributed the PBDE as a POP as it has a resembling chemical structure to the banned chlorinated POPs [83].

PBDE and HBCD can be released from a material via vapour transfer, dust or leaching out of the materials. All three methods of migration can lead to them becoming indoor air contaminants, atmospheric pollutants, released into the soil and aquatic life and bioaccumulation in people [84].

Waaaijers et al (2013) [82] investigated the PBT characteristics of non-halogenated additive flame retardants. The extensive study is beyond the scope of this paper, but a summary

presented by Waaijers et al (2013) lists the flame non-halogenated flame retardants considered to be most PBT.

**Table 3.6 Summary from Waaijers et al (2013) [82]**

Overview of PBT properties for selected HFFRs						
Compound	Persistence	Bioaccumulation	vPvB?	Toxicity		
				Ecotoxicity	In Vivo toxicity	In vitro toxicity
TPP	Low to high	Low to high	(Yes)	Low to high	Low	Low to high
RDP	Low to high	Low to high	No	Low to high	Low (to moderate)	(Low)
BDP	Low to high	(Low to high)	(No)	Low to high	(Low)	(Low)
ATH	–	(Low)	(no)	Low to high	(Low)	(Low)
ZB	–	n.d.	n.d.	High	Low to high	(Low)
ALPI	Moderate to high	(Low, not specified)	(No)	Low to moderate	Low	Low
PER	Low to high	(Low)	(No)	Low	Low	Low
DOPO	(Low to high)	(Low)	(No)	Low to moderate	n.d.	(Low)
MPP	(High)	(Low)	(No)	Low	Low	n.d.
APP	–	(Low, not specified)	(No)	Low (to moderate)	(Low)	(Low)
ZHS	–	(Low, not specified)	(No)	Low	Low (to moderate)	(Low)
Mg(OH) <sub>2</sub>	–	n.d.	n.d.	n.d.	(Low)	n.d.
ZS	–	(Low, not specified)	(low)	(low)	(Low)	n.d.

The summary presented in Table 3.5 from Waaijers et al (2013) shows that some non-halogenated flame retardants could be considered PBT under certain condition.

Triphenylphosphate (TPP) is a common flame retardant yet has been rated ‘low-high’ for P and B and also possible very persistent and very bio accumulative [82].

Zinc Stannate was summarised as the least risk to the environment. Although Waaijers et al state that at this current time there is not enough data to fully evaluate the risk of these materials including materials such as TPP. There are also many contradictory evaluations for example APP was found to have low PBT properties from literature reviewed, yet there is some data to suggest that it has moderate Eco toxicity [82].

### **3.7 Flame Retardant Mechanisms for Polyamides**

There are numerous research studies available to evaluate which materials impart flame retardant properties to polyamides. Generally the studies are weighted to engineering plastics application and less so towards polyamide textiles. Here we review current flame retardant products, methods and previous research on the subject area.

There are a number of additives that can be considered to impart flame retardant properties to polymers and synthetic fibres. Market research carried out by the Freedonia Group

projected that the ‘Global demand for flame retardants is projected to expand 4.6 percent per year through 2018 to 2.8 million metric tons, valued at \$7.0 billion. Advances will be stimulated by an acceleration in manufacturing output, especially in the US, Japan and Western Europe, as they recover from the recession-impacted 2008-2013 period’ [43].

The most common flame retardant additives are halogen based (more commonly Bromine or Chlorine), Phosphorous based, Metal Hydroxide based and Nitrogen based.

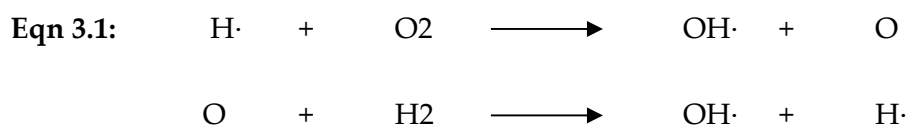
### **3.7.1 Halogen Based Flame Retardant Additives**

Halogens refer to group seven of the periodic table and include Fluorine, Chlorine, Bromine and Iodine. The structure of halogenated flame retardants can vary widely from aliphatic to aromatic structures [47].

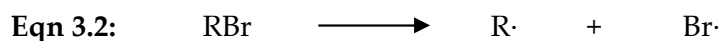
To be effective the halogen containing flame retardant has to release a halogen in the form of a radical or hydrogen halide at below or the same temperature as the polymer decomposition temperature [48].

The organo-halogen compounds have been found to be the most effective as flame retardant additives and as a result organo-chlorine and organo-bromine are most commonly used. [47]. Fluorinated organics are normally more stable than other polymers and as a result do not release the halogen radicals or halides effectively to act as a flame retardant. Iodinated organics have low thermal stability and cannot be processed with other polymers [48]. Organo-bromine is the most commonly used as its properties are considered ‘just right for preventing fires’ as the bond between C-Br is stable enough for the environmental exposure yet can easily release the Br under sufficient thermal stress and fire conditions [47].

Halogen FRA mainly act in the gas phase by means of chemical reaction. The halogen quenches the high energy radical developed during decomposition of the polymer. The series of reactions has been summarised by many and we use Troiszsh (1998) [49] to summarise;



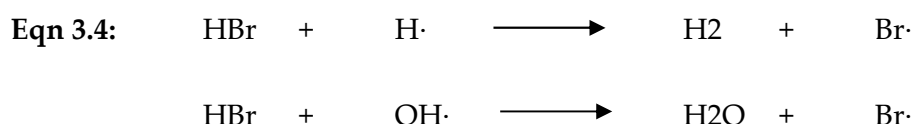
Formations of high energy OH and H radicals



Flame Retardant breaks down to form halogen radical.



Halogen radical reacts to form hydrogen halide.



The halides interfere with the mechanism by reacting with the high energy radicals quenching them and replacing them with the lower energy Br· radicals.



The hydrogen halide consumed is regenerated by the reaction with hydrocarbon.

Disadvantages of HFR's can increase the smoke development from combustion of aliphatic nylons. Bromine additives also cause greater smoke density than chlorinated additives.

Bromine compounds can further affect smoke toxicity as greater concentrations of HCN and CO may be produced [51].

Examples of brominated flame retardants in current practice are summarised extensively by Levchick & Weil (2000) [51] and also Levchick et al (2009) [52].

Polybrominated Diphenyl Oxides have recently come under environmental scrutiny, this includes Albemarle's Saytex 120 which is stable at high processing temperatures, non-blooming and also has good light stability. A typical formulation for unfilled PA66 would be 13% Saytex 120 + 5% ATO [52].

Due to the environmental pressures alternatives were developed. Saytex 8010 (Figure 3.7) and Firemaster 2100 from Chemtura are based on Decabromodiphenylethane. These have similar efficacy to the diphenyl oxides and good thermal stability, however they are more expensive.



Ethane-1,2-bis(pentabromophenyl)

SAYTEX 8010 flame retardant is a non-diphenyl oxide based product containing a high level of aromatic bromine.

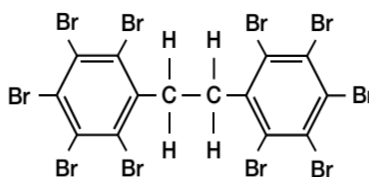


Figure 3.7; Saytex 8010 Chemical structure [54]

Another popular group of brominated flame retardants are Brominated Polystyrenes. There are two methods of production. They were initially manufactured by the post bromination of low molecular weight polystyrenes by ring substitution of H by Br on the benzene ring [51].

Initially this type of BFR had reduced thermal stability due to labile halogen being present after manufacture. Processes were developed to reduce this unstable halogen and improve stabilisation, although some impurities remained which reduced the thermal stability [52].

Two products from this category of post brominated styrene are Pyrocheck 68-PB and FR – 803P (figure 3.8) from Albemarle and ICL-IP respectively.

<b>Chemical name:</b>	Brominated Polystyrene
<b>Formula:</b>	$(C_8H_{8-m}Br_m)_n$
<b>CAS Number:</b>	88497-56-7
<b>Br%:</b>	66 Min.

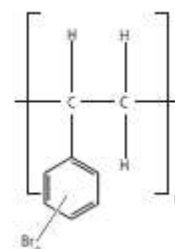


Figure 3.8; FR-803P Chemical Structure [55]

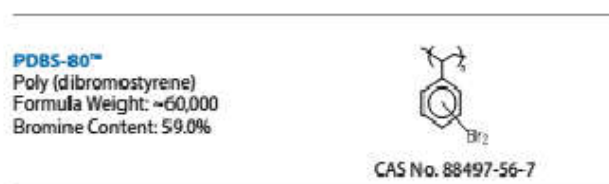
Another method of production is the polymerisation of di-bromostyrene or mixed di / tri-bromostyrene. This method gives the ability to produce products with different bromine contents and various molecular weights [52].

They can also be produced by the addition of co-monomers to aid compatibilisation to specific polymers. A study by Fielding and Elliot (1997) for Great Lakes added Maleic Anhydride and Glycidyl Methacrylate to polydibromostyrene to improve the compatibility with Polyamides [53].

They found that adding these co-monomers enhanced the compatibility to PA and produced a product with enhanced properties with improved flame retardancy and physical properties [53].

Polymerised bromostyrenes are considered more stable than post brominated products. With the added ability to manufacture tailor made molecular weight products properties can be optimised for specific applications [52].

Great Lakes (Chemtura) have many brominated polystyrene products for various applications. PDBS – 80 (figure 3.9) is well established for high temperature polyamides, it can be processed up to 360 °C and aids melt flow. PDBS – 80 has a molecular weight ~60000 and a bromine content of 59% [52, 55].



**Figure 3.9; PDBS-80 Chemical Structure [56]**

PBS-6HW also has molecular weight of 60000 and a slightly higher bromine content at 64%, this product has better tensile and impact properties in polyamide compared to PDBS- 80, but has a lower melt flow [52].

As mentioned earlier typically Brominated polystyrenes are not miscible with polyamide but CP-44B produced with approximately 1% co-polymer glycidyl methacrylate improves this compatibility. These co-polymers can also react with the polyamide end groups. They can provide a drip suppressant effect meaning additives like PTFE may be reduced or removed from the formulation [52].

There are many more brominated flame retardant systems available or somewhat developed. A 25 year summary can be found in Levchick & Weil (2000) [51].

Halogen based flame retardants have been used in conjunction with metal oxides for many years. In particular Antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) [80].

Upon heating halogen and antimony cocktails metal halides are produced in the form of  $\text{SbCl}_3$  or  $\text{SbBr}_3$ . These can transformed in the flame to metal oxides [80].

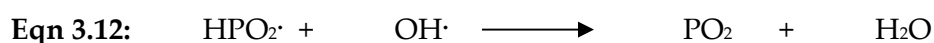
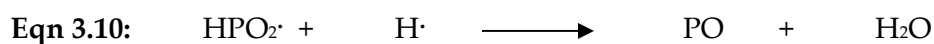


Antimony Trioxide does not show any significant flame retardant properties when used on its own. But it enhances the effect of halogen based flame retardants.  $\text{SbX}_3$  has double function in flame retarding effect. It can inhibit the flame by providing halogen acids (HX) and supplying SbO which catalyses the quenching of reactive radicals in the flame [80].

### 3.7.2 Phosphorus Flame Retardants

Phosphorus containing additives mainly function in the condensed phase [49] although some volatile phosphorus can be oxidised to scavenge radicals in the gas phase [57].

Levchik (2007) [48] explains phosphorus flame retardants can be potent scavengers of H and OH radicals if the conditions are right. It is suggested they can be more effective than both bromine and chlorine at the same molar concentration. Equations 2.6 to 2.10 are some examples of phosphorus scavenging reactions.



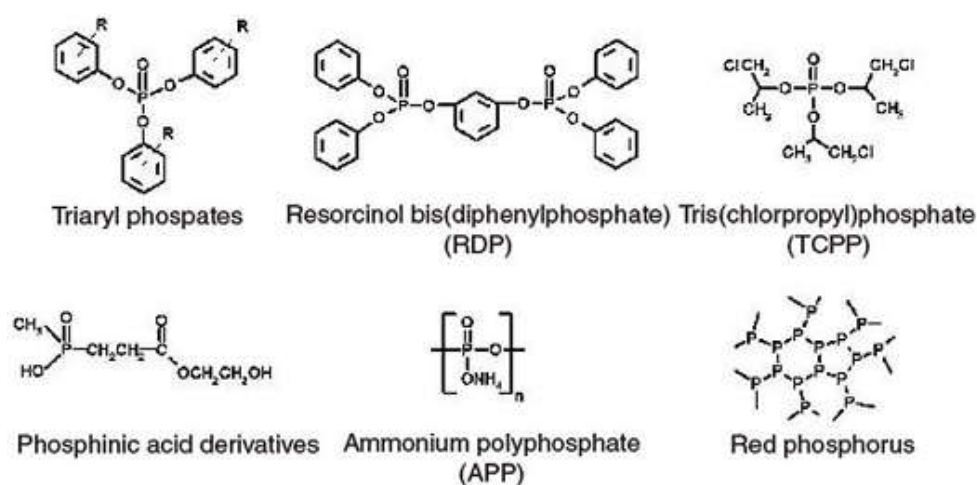
It is however challenging to design a phosphorus based flame retardant which can volatilize at a low enough temperature into the flame which can also survive polymer processing [48].

Phosphorus based flame retardants work well in polymers containing oxygen and nitrogen in the condensed phase [49, 48].

One mode of action is the formation of anhydrides of phosphoric acid or related acids which may act as dehydrating agents and promote char formation [58].

They can also act as heat sinks by retarding oxidation of carbon oxide to carbon dioxide decreasing the heating process [58].

Lastly the acids formed can create a thin glassy or liquid protective coating which lowers oxygen diffusion as well as reducing heat and mass transfer between the condensed and gas phases. This barrier inhibits the oxidation process of carbon to carbon monoxide stage resulting in decreased exothermic of heat combustion [58].



**Figure 3.10; Examples of phosphorus based flame retardants [59]**

There are many phosphorus based flame retardants on the market currently. They can be based on elemental phosphorus (P) for example Red Phosphorus. Alternatively the additive can be supplied as organic or inorganic compounds (Figure 3.10) and come in either solid or liquid form with various physical and chemical properties. The 'P' content can also differ greatly from 100% in Red Phosphorus to less than 10% in some compounds [59].

Red Phosphorus is well established in its use in glass reinforced PA6, 6 following initial concerns over colour, handling/ safety and stability. Stabilised forms of Red Phosphorus are available with improved stability and reduced phosphine gas evolution on processing, there are masterbatch producer's supplying concentrates of Red Phosphorus in various polymers to remove handling concerns [52].

Clariant's Exolit RP Series is a range of stabilised and coated Red Phosphorus [52].

#### **3.7.2.1 Ammonium Polyphosphate**

The mode off flame retardant action for ammonium polyphosphate was studied by Levchik et al (1994) [60]. The experiment compared the combustion behaviour of PA6 with the addition of APP at multiple concentrations using various analytical techniques associated with the flame retardant performances and decomposition properties.

The study found the addition of APP to PA6 promotes formation of intumescent char residue on the surface of burning PA6. Although at levels below 30% APP was observed that the char only formed on the edges and would flow exposing the underlying polymer to the flame. It was also noted that with addition below and up to 30% APP the Oxygen Index was unaffected, but increased significantly at levels of 40% APP and above [60].

PA6 loses 95% of its weight between 330°C and 400 °C, whereas pure APP starts to decompose at 260°C and only loses 18% initially which is attributed to ammonia and water. The remaining polyphosphoric acid undergoes extensive decomposition above 450°C. A stable ash residue of 5% is left at 600°C [60].

From the TGA analysis conducted Levchik et al observed that APP strongly modifies the decomposition behaviour of PA6. The onset temperature was notably the same as pure APP at 20-50% APP concentrations [60].

Mixture of 20% APP and above shown four decomposition steps. It appeared the final amount of stable ash residue was much larger than expected following analysis of PA6 and APP individually, although the amount of ash did not increase with increased loading of APP [60].

Linear pyrolysis experiments at various heat fluxes found that decomposition onset was lower with the addition of APP to PA6. The addition of APP also caused self-ignition to occur faster than pure PA6. A faster initial decomposition was observed for 40% APP mixture, which then slowed down to a much slower rate than pure polymer. At higher heat flux rate of  $50 \text{ kWm}^{-2}$  40% mixture shown a much slower rate of combustion than PA6 [60].

Levchik et al studied the degradation process in detail confirming in PA6/ APP mixtures the first step of degradation caused the formation of alkyl phosphate ester bond, which initiates the depolymerisation of PA6 chain to caprolactam, cyclic oligomer lactams and chain fragments [60].

The first step of degradation would also produce 5-amido-penthyl polyphosphate it is the further degradation of this product which leads to intumescent behaviour. Foaming was observed when 5-amido-penthyl polyphosphate undergoes thermal degradation with the formation of char. Greater effects are witnessed where there is excess of APP and 5-amido-penthyl polyphosphate is mixed with phosphoric-polyphosphoric acid. The blowing action is due to water, ammonia, aliphatic hydrocarbons and nitriles being evolved by the partial fragmentation of the aliphatic amide structure of 5-amido-penthyl polyphosphate [60].

A condensed phase flame retardant mechanism is suggested. Linear pyrolysis experiments suggest that the APP provides a thermal shield to the PA6. The effectiveness is increased as the concentration of APP is increased. Thermal insulation was observed when intumescence occurs, slowing down the rate of thermal decomposition of the material exposed to heat [60].

Intumescent additive formulations are mixtures of a carbonisation agent, carbonisation catalysts (such as phosphoric acids and or boric acid salts which form stable acidic species on heating) and a blowing agent [61].

PA6 mixtures with APP lead to flame retardant properties of interest as the mixtures develop and intumescent shield [60, 61].

However, it is known that the addition of APP to PA6 destabilises the polymer and modifies its degradation behaviour. The intumescent properties induced by APP is the cause of the

flame retardant behaviour when blended with PA, although the PA plays the role of the polymer matrix and carbonizing agent [61].

The compatibility of APP within PA6 is low and upon quenching the APP will migrate out of the polymer matrix. To avoid this migration a compatibiliser must be added [61].

Le Bras et al (1999) [61] suggested possible compatibilisers to be ethylene-vinyl acetate, functional terpolymers of ethylene or siloxane / silane based resins. From Le Bras' investigation ethylene-vinyl acetate was recommended.

The experiment found that when using EVA/PA6 mixture at 6:1 ratio with the addition of 28% APP the oxygen index was increased from 21 (PA6) to 29. A UL-94 V-0 rating was also achieved. This is below the 40% first suggested by Levchik [60, 61].

A previous study by Siat et al (1997) also shown that the mixture of PA6/EVA/APP modified the degradation of PA6 and formed a stable carbonaceous char residue at 400°C -500°C. It was concluded that the addition of APP and EVA initially reduced thermal stability in the first degradation step but forms a more stable residue. It was summarised that the EVA allows a reduction of fuel flow rate feeding the flame [62].

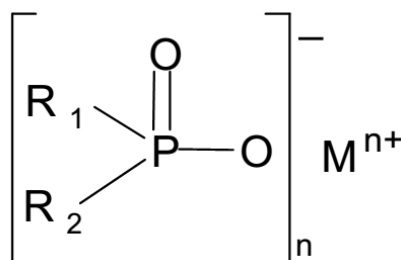
#### **3.7.2.2 Organic Phosphinic Salts**

A relatively new phosphorus based compound has been found to have good flame retardant properties when added to polyamides.

Organic Phosphinic Salts (Exolit OP Range from Clariant) are a broad selection of flame retardant additives for various applications. For polyamides certain grades has shown good colourability, good flow properties, high temperature stability and good mechanical properties [59].

They can be processed on standard polymer processing equipment and suitable for filled and unfilled polymers.

There have been various pieces conducted to investigate the efficacy of these novel Phosphorus based flame retardants particularly in literatures 63-67.



**Figure 3.11; Chemical structure organic Phosphinic salt [59]**

Bourbigot (2008) [65] studied the flame retardant effect of aluminium phosphinate salts in different thermoplastics.

It was possible to achieve a V-0 at 3.2mm specimen thickness by incorporating 23% Exolit OP1311 into PA6. The LOI also increase to 29. 18% additive managed to achieve a V-1 rating. It was also observed that with the addition of 23% Exolit OP1311 in PA6 the peak heat release rate was reduced 60% [65].

A similar study by Quifei (2011) [66] focussed on the differences between Aluminium Hypophosphate and Magnesium Hypophosphate. It was determined that the aluminium hypophosphate had better flame retardant efficacy than the magnesium derivative. 24% addition of Aluminium Hypophosphate achieved a V-0 in 1.6mm specimen [66].

Quifei [66] determined that the phosphine acted as a radical scavenger in the gas phase and appeared to have good charring ability. The additives cause the thermal degradation of PA6 to occur at a lower temperature but slow down the rate of degradation.

Ramani et al (2009) studied the prospect of synergistic flame retardance utilising Nano clay in the form of organo modified montmorillonite. [63, 64].

Again it was concluded that the flame retardant alters the thermal degradation behaviour of PA6 by causing onset decomposition to begin at a lower temperature.

It was also observed that the flame retardant acts in the gas phase as diethyl Phosphinic acid, and the yield of hydrogen cyanide does not increase with the addition of organo phosphorus flame retardants [63, 64].

### **3.7.3 Nitrogen Containing Flame Retardant Additives**



Levchik et al (1997) [68] studied the effects of Nitrogen containing flame retardants in the form of melamine on how it affected the thermal behaviour of polyamide 6.

The study included pure melamine and salt derivatives such as melamine cyanurate, melamine oxalate and a couple of phosphorus containing melamine salts in the form of dimelamine phosphate and melamine pyrophosphate [68].

The flame retardant additives were added to PA6 up to concentrations of 30%. The Limited Oxygen Index, UL-94 and decomposition behaviour were measured and analysed [68].

It was observed melamine and its salts provoke the melt flowing and dripping of PA6 during LOI measurement and UL-94 flame testing. For certain salts as the concentration of the additive increased so did the dripping tendency [68].

However the phosphorus containing salts saw a reduction in dripping as the concentration increased, although they did not offer flame retardant effects until a concentration of 30% was reached [68].

From the LOI measurements the addition of just 10% Melamine o-phthalate caused the LOI to increase to <50 compared to that of 21 for PA6 [68].

The next most significant effect in terms of LOI was caused by melamine cyanurate. 10% addition saw the LOI increase to 35 and greater concentrations saw the LOI approach 40.

From the TGA analysis it was observed that melamine and its salts derivatives alter the thermal behaviour of PA6. They cause decomposition of PA6 to occur earlier, onset temperature is reduced from 350°C to between 250° - 300°C depending on the salt being used [68].

There were three suggestions for the cause of this [68]:

1. Melamine interferes with the hydrogen bonding within polyamide 6 facilitating thermal decomposition.
2. At high temperatures PA6 is at equilibrium with its monomer and the addition of melamine promotes a catalytic effect, or ammonia is evolved which accelerates monomer formation.

3. Aminolysis by the melamine itself or by evolved ammonia contributes to the thermal degradation of PA6.

In summary melamine and its salts can impart flame retardant properties to polyamide 6 and at particularly low concentrations however the phosphorus containing salts are required in concentrations of approximately 30% [68].

It was summarised that melamine cyanurate is more effective in PA66 compare to PA6. The main pyrolysis product of PA66 is cyclopentanone which condenses with the melamine and/or cyanuric acid causing cross linking and the formation of a char residue [52].

The main pyrolysis products of PA6 are caprolactam, alkyl cyanides and ammonia which have very little interaction with the melamine cyanurate pyrolysis products [52].

However melamine cyanurate does reduce the amount of caprolactam produced during the pyrolysis of PA6 and increases the amount of oligomer fragments products which are less flammable but increase the melt flow of the PA6 [52].

Literatures 69-71 present various studies investigating the use of melamine cyanurate as a Flame retardant for Polyamide 6.

Lin et al (2013) [69] added MCA with bicyclic phosphates and PEO to PA6 fibres via melt spinning process in an 8:1:0.4 ratio and at various addition levels.

They found that the addition of FR additive cocktail reduced the burning of PA6 but produced burning drips at addition levels below 8%. According to UL-94 testing a V-0 rating can be achieved at 8% addition [69].

TGA analysis shown that the addition of FR additives caused a two-step degradation process where as PA6 decomposes in a single step. The onset temperature is also reduced with the addition of FR additives [69].

DTG analysis found that the amount of combustible gases produced by PA6 was reduced with when FR additives were added [69].

One disadvantage found when adding FR additives to PA6 was the deterioration of mechanical and physical properties. The tensile strength is severely compromised and spinning draw ratios have to be significantly reduced to produce fibre [69].

Tang et al (2014) [70] analysed how morphology of melamine cyanurate can affect flame retardant performance in PA6. The three morphologies prepared via subtle changes in the production process were irregular sphere, rod like and flakes on a Nano scale particle size. Then 8% MCA was added to the PA6 to form a composite.

It was found that all the Nano particle MCA were evenly dispersed with the PA6 matrix regardless of the morphology.

The flame retardant effect however was different depending on the morphology of the MCA. From UL-94 and LOI testing the sphere shaped particles could only achieve a V-2 and the LOI was increased to 27.4, whereas the rod configuration particle raised the LOI to 28.9 and achieved a V-0. The flake morphology MCA improved the flame retardant properties the most with an LOI of 29.5 and V-0 being achieved. It was observed that the various morphologies performed similarly during cone calorimeter testing [70].

It was concluded that the best results achieved by the flake structured MCA were the result of increased hydrogen bonding between the MCA and PA6. This in turn delayed the decomposition of the MCA resulting in better flame retardant performance effect [70].

Chen et al (2006) [71] attempted to produce MCA via an 'in-situ' process, in which MCA is synthesised in the presence of PA6 via a 'reactive extrusion'. This method is used to produce Nano-sized MCA particles finely dispersed within the polymer leading to the production of MCA containing polyamide in a one step process, the flame retardant performance was analysed.

It was concluded that the MCA Nano particles can be dispersed in PA6 via an 'in-situ' process. The Nano particles improve the flame retardant performance and with the addition of dioctyl phthalate plasticiser mechanical properties maintain comparable to pure PA6. V-0 UL-94 can be achieved for specimens 3.2mm and 1.6mm thickness [71].

Similarly to previous studies reviewed decomposition still occurs in two steps where as pure PA6 decomposes in one step. Onset also occurs at a lower temperature for the flame retarded PA6 although the decomposition rate is slower. This indicates that the MCA particles incorporated in PA6 decreases the release of combustible gases generated on decomposition of PA6 [71].

It was suggested that upon decomposition of the MCA, inert gases are released. These gases dilute oxygen in air playing a role in flame retarding [71].

MCA Technologies presented a novel nitrogen based flame retardant additive at the Fire Resistance in Plastics Conference 2012. Very little research has been published based on this new additive although there have been some positive results for polypropylene when used in conjunction with ammonium polyphosphate [72].

MCA presented that a V-0 can be achieved in glass filled PA6 when used at 3:1 ratio, metal phosphinate in the form of Exolit OP1230 previously discussed at 20% loading and 25% glass fibres [72].

### **3.7.4 Other Flame Retardant Additives**

#### **3.7.4.1 Nano Layered Silicates**

Over recent years Nano-clays have received a large amount of attention in terms of their flame retarding capabilities and how they can improve physical properties of polymers [73].

Layered silicates commonly used such as montmorillonite are from the smectite family. Their crystal structure consists of two tetrahedrons fused to an edge shared octahedral sheet of alumina. They are naturally hydrophilic and therefore immiscible in most polymers. To improve the compatibility the silicate surface is modified usually with organic surfactants [74].

There are two types of nanocomposite that can be formed. Intercalated or exfoliated; Intercalated has a well ordered layered structure whereas exfoliated has the clay layers broken and particles individually dispersed. Exfoliated structure leads to greater improvement in mechanical properties [74].

Polymer Layered Silicate Nanocomposites do not improve flame retardancy of polymers on their own as they reduce the polymers ability to flow and drip away from the flame thus holding the polymer in place fuelling the flame [74].

Bourbigot, Devaux & Flambard (2001) [75] produced PA6/Organo Modified Clay nanocomposite textiles via melt spinning process, produced knitted fabrics for various flame retardant tests.

Incorporating the clay into the PA6 saw the peak heat release reduced 40% and also reduced smoke evolution, particularly a reduction in CO and CO<sub>2</sub> evolution was measured [75].

Although TGA analysis shows the clay begins to decompose at 200°C, although PA6 processing temperatures are higher than this there was no evidence to suggest the clay had a destabilising effect on the PA6. However as the time to ignition was shorter than that of pure PA6, it is believed that some degradation does occur of the organic modifier which creates fibrils on the yarn surface which in turn act as 'little matches' leading to shorter ignition times [75].

Song et al (2004) [73] summarised earlier pieces and suggested that layered silicates need to be used with more conventional flame retardants to achieve flame retardant performance.

Samples were produced comparing pure PA6 and with the addition of 2% organo modified montmorillonite (OMT), PA6 + 8% magnesium hydroxide (MH) + 5% Red Phosphorus (RP) and finally adding 2% OMT to the flame retardant cocktail [73].

When adding the clay to the pure PA6 mechanical properties were improved, the Peak Heat Release Rate (PHRR) was reduced and an increase in char formation was observed. However there were no improvements in flame retardant properties which were evidenced by burning samples on UL-94 and only a 0.5 increase on LOI to 21.5 [73].

A V-0 was achievable when incorporating MH and RP to the PA6 yet the tensile strength was reduced. By adding 2% clay to this mixture the tensile strength was reinstated, a further reduction in PHRR was witnessed a greater char formation [73].

Kilaris et al (2008) [74] investigated synergy of layered silicates and melamine cyanurate, using an organo-modified montmorillonite clay.

Adding clay to PA6 caused a significant reduction in molecular weight, three possible processes of chain scission were suggested [74].

Incorporating MCA saw an increase in molecular weight offsetting the reduction caused by the clay. This was suggested to be caused as MCA encourages scission of the alkyl-amide bonds which provokes formation of carbodiimides that lead to branched or cross linked structures [74].

As discussed earlier (2.2.1.5) PA6 can form different crystal structures depending on cooling rate and other variables. The addition of clay promoted the formation of  $\gamma$ -crystallite causing a reduction in melting temperature and overall crystallinity, adding MCA acted as a nucleator favouring the  $\alpha$ -crystal morphology [74].

Flammability tests shown that adding layered silicates to the PA6 incorporated with MCA provided an antagonistic effect. MCA can achieve a V-0 on its own adding clay caused a non-classification result. The addition of clay prevented the melt dripping of the PA6/MCA blend holding the material in place to fuel the flame [74].

#### **3.7.4.2 Zinc containing additives**

Shen, Kochesfahani & Jouffret (2008) [76] evaluated the use of Zinc Borate in various polymers based on Borax Firebrake range.

Zinc borates are synergists in halogen based formulations, and also display synergism with antimony trioxide. They also act as smoke suppressants and afterglow suppressants. They can promote and stabilise char formation and reduce burning drips [76].

In halogen free systems zinc borates when used in conjunction with metal hydroxides can promote strong char/ceramic residue providing insulating layer to underlying polymer [76].

Zinc borates have been seen to reduce the peak heat release rate, smoke evolution, carbon monoxide evolution and afterglow [76].

Horrocks, Smart, Kandola & Price (2012) [77] investigated the synergy of zinc stannate when used in non-halogenated flame retardant PA6 systems.

They compared the performance of many standard flame retardants additives previously discussed in the form of metal phosphinate, aryl phosphate, cyclic phosphonate, and melamine polyphosphate and melamine cyanurate with and without the addition of zinc species [77].

In summary the addition of zinc species did not appear to positively affect the flame retardance of the all the formulations but did help maintain the mechanical properties closer to that of pure PA6 [77].

The best UL-94 result achieved was a V-2 when used with cyclic phosphonate, melamine polyphosphate and melamine cyanurate. This improved the results for the phosphorus containing additives however it reduced the flame retardant effect of melamine cyanurate [77].

It was observed that the addition of zinc species can reduce the peak heat release rate and the total heat release whilst also reducing smoke evolution [77].

#### **3.7.4.3 Ammonium Sulfamate**

Coquelle et al (2014) [78] considered ammonium sulfamate as a flame retardant additive for PA6 fibres.

Adding the ammonium sulfamate at levels above 7% were not possible to spin. The fibres produced containing 7% additive were very brittle and not capable of elongation [78].

However fibres containing 5% ammonium sulfamate provided mechanical properties very similar to pure PA6. It was found that the addition of ammonium sulfamate caused a reduced peak heat release and total heat release. 5% ammonium sulfamate reduced the PHRR by 20% having some flame retardant characteristics [78].

Ammonium sulfamate was suggested to act in the gas and condensed phases promoting char formation. The additive does de-stabilise the PA6 somewhat changing the decomposition pathway into a three step process and causing onset to occur at a relatively low temperature between 170°C and 270 ° C where ammonia is released [78].

#### **3.7.4.4 Polytetrafluoroethylene (PTFE)**

Polytetrafluoroethylene is known to be useful as a drip suppressant because it tends fibrillate and elongate during processing. Fibrils shrink upon exposure to heat from a flame and hence retard dripping of the matrix in which the fibrils reside [79].

PTFE is used in many flame retardant formulations some of which can be found within literature 37.

### **3.8 Review of Test Standards**

Flammability testing could be considered one of the most important testing procedures within the textile industry. Test methodology is designed to quantify specific burning parameters. Unfortunately there is no governing test norm and there is no one test which can measure all the properties associated with the burning of a textile material [39].

Various countries have their own test standards, some of which have greater acceptance across various industries. There are particular industries for example the automotive and construction industries which have recognised standards. Therefore a review is needed of the more common and accepted test norms to gather a greater understanding.

#### **3.8.1 UL 94**

Possibly the most common and widely accepted test method for plastic materials is the Underwriters Laboratory 94 test.

UL – 94 is designed for assessing the flammability of plastic materials. It is a vertical flame test for plastic specimens (bar) at specified dimensions. The test measures how much a 'bar' of polymer burns when a small Bunsen burner flame (20mm) is applied for 10 seconds on two separate occasions.

Five specimens are tested and are 125mm in length and 12mm in width. Thickness can vary between 3.2mm, 1.6mm and 0.8mm. Occasionally 0.4mm test specimens are tested. A wad of cotton is placed below the test specimen to detect flaming drips. The results classification can be found in table 3.6. Although not specifically for textile materials UL-94 can be used to carry out flame tests on textile specimens.



**Table 3.7; UL-94 Classification [40]**

Criteria	UL-94 V-0	UL-94 V-1	UL-94 V-2
Afterflame time ( $t_1$ or $t_2$ )	< 10 s	< 30 s	< 30 s
Total afterflame time ( $t_1 + t_2$ for 5 specimens)	< 50 s	< 250 s	< 250 s
Afterflame up to the holding clamp	No	No	No
Cotton ignited by flaming drops	No	No	Yes

### **3.8.2 Limited Oxygen Index**

Limited Oxygen Index (LOI) is another well-known test in regards to flame retardance. It is also including in some international standards for example BS ISO 4589-2. Oxygen Index technique offers a method to determine an absolute values which can describe the tendency of any textile fabric to sustain combustion [39].

A high LOI value indicated a material has low flammability, where as a low LOI value can indicate a material will burn easily.

The dimensions of the test specimen are not specified therefore any specimen could be tested, although for rigid plastic materials 100x65x3 dimensions are preferred. The specimen is positioned vertically and clamped at the bottom (Fig 3.12). The chimney is supplied with a controlled mixture of Nitrogen and Oxygen and the specimen has a pilot flame applied until the entire top surface of the specimen is ignited.

If the specimen does not ignite or extinguishes within 30 seconds the concentration of oxygen is increased and the test repeated. This procedure is followed until the specimen demonstrates stable combustion in a 'candle' fashion for 3 minutes after the ignition source has been removed.

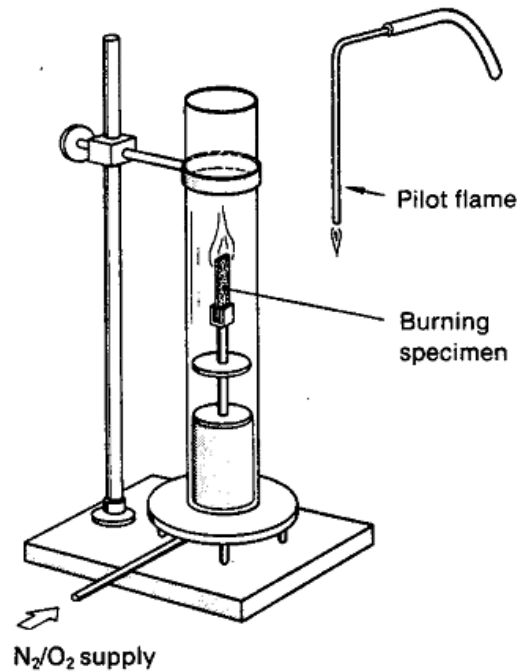


Figure 3.12; LOI test apparatus [40]

If more than 5 mm of the specimen is consumed a fresh specimen is used and the oxygen concentration reduced slightly and the process begins again.

Following this procedure eventually a LOI value is found. This is the highest concentration of oxygen at which the specimen self-extinguishes in less than 3 minutes and less than 5 mm specimen consumption.

LOI Values for Polyamide 6 can range from 21-24 depending on the source literature and the specimen assessed.

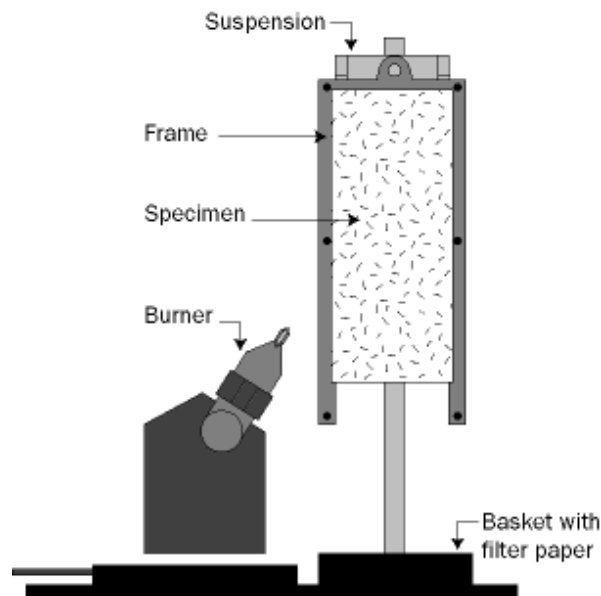
Although LOI does not reflect a real life fire scenario it is a good screening test for flame retardant properties and is reproducible. Film samples and textiles can also be tested.

### **3.8.3 DIN 4102 – B1 and B2 [85]**

In Germany, upholstery fabrics are tested in accordance with DIN 4102 which has been established by the German Institute for Building Technology.

DIN 4102 Part 1 - Kleinbrenner (B2)

All materials used in buildings in Germany need to meet the B2 requirement which is determined using a small flame test.



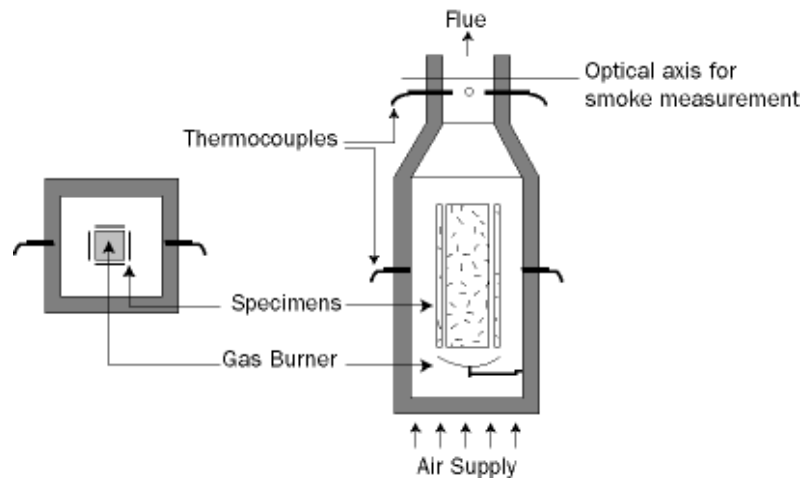
**Figure 3.13; DIN 4102 B2 [85]**

The fabric specimen is suspended vertically and a 20mm high flame is applied for 15 seconds to both the fabric surface and edge. Reference lines are marked on the specimen, which achieves B2 classification if the tip of the flame does not reach the reference marks within 20 seconds on any sample. Five samples are tested with filter paper being placed below each to determine the production of flaming droplets.

#### DIN 4102 Teile 15/16 - Brandschacht (B1)

Referred to as the "Brandschacht test", this is the main test method in Germany which measures reaction to fire and is considered the highest flammability standard in the country for upholstery fabrics.

The term Brandschacht, literally "fire shaft", refers to the testing apparatus itself which consists of a square-shaped vertical housing equipped with a gas burner. Four fabric samples are held vertically in a supporting frame and subjected to flames for 10 minutes. At the same time a constant, uniform flow of air is blown into the Brandschacht from below.



**Figure 3.14; DIN 4102 B1 [85]**

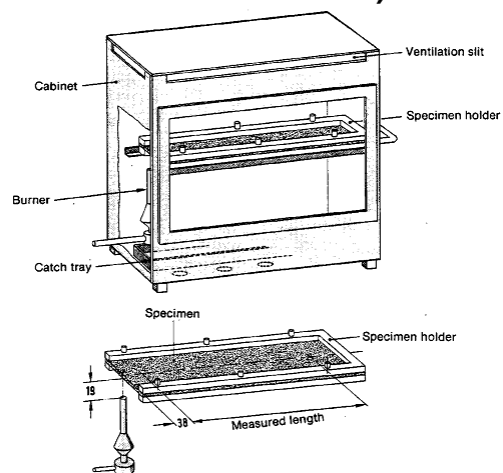
In evaluating the test, smoke gas temperature and the mean residual length of the sample are taken into account (residual length is the part of the specimen which has escaped burning).

In order to be classified as B1, the tested fabric must show:

1. A mean residual burn length of no less than 150mm, with no specimen being burned away completely
2. A mean smoke gas temperature of less than 200°C

### **3.8.4 FMVSS 302 – Transportation**

#### **Global Automotive FR test (FMVSS-302)**



**Figure 3.15; FMVSS-302 Test Chamber [40]**

FMVSS 302 is used to specify the burn resistance of materials used on motor vehicle compartments. Test specimen of 356 mm x 10 mm is used. Maximum thickness of the specimen must be no more than 13mm. A 38 mm flame is applied for 15 seconds and the burn length and time measured. Test chamber can be seen in Figure 3.15.

Testing Classification can be found in table 3.7.

**Table 3.8; Classification of FMVSS 302 [40]**

Classification	
SE	Flame is extinguished before reaching the first mark
SE/ NBR	Flame does not reach the second mark within 60s
SE/ BR	Flame is extinguished before the second mark but burn time > 60s Flame does not reach the third mark
B	Flame over the third mark but burn rate < 101.6 mm/min
Fail	Flame over the third mark but burn rate > 101.06 mm/min

### **3.8.5 Methenamine Pill Test – ASTM D 2859-96**

Standard Test Method for Ignition Characteristics of Finished Textile Floor Covering Materials also known as ‘The Methenamine Pill Test’ is used to determine the flammability of finished textile floor covering materials when exposed to an ignition source under controlled laboratory conditions. It is applicable to all types of textile floor coverings regardless of the method of fabrication or whether they are made from natural or man-made fibres [41].

The test demonstrates that a carpet will self-extinguish when exposed to a small incendiary source of fire, such as a lighted cigarette, match, or a burning ember from a fireplace [42].

The Pill Test relies on the use of a solid white organic compound Hexamine (known also as Hexamethylenetransamine and Methenamine) tablet (i.e., “pill”) approximately the same size as a typical aspirin that is used to replicate the source of a fire the size of a lighted cigarette, a match or a fireplace ember. The carpet test specimen (the sample) is first placed in an oven to remove any moisture that may be present. Next, the sample is cut to a 9” x 9” size, and the

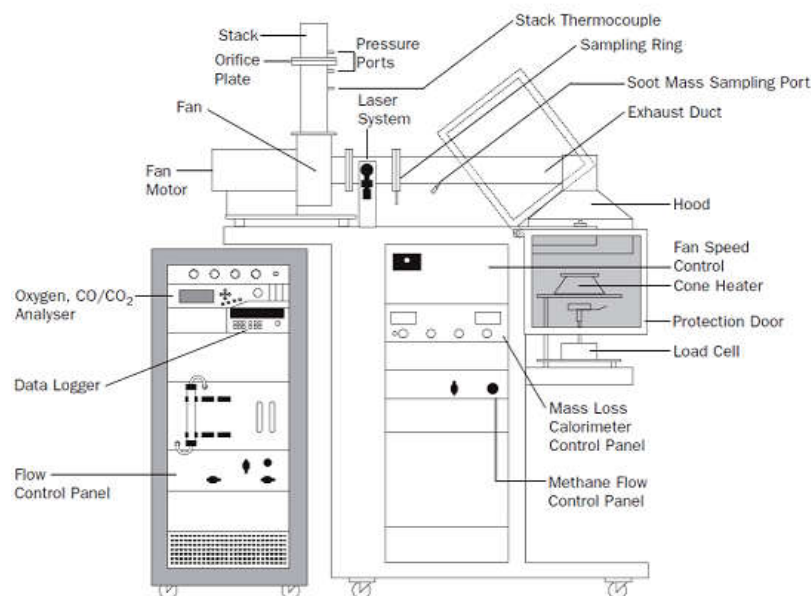
pill is placed in the centre of the sample. The pill is then ignited by a match and allowed to burn for two minutes. If the charred area of the sample extends beyond 3 inches the sample fails [42].

There are many other test methods not to be discussed here. For example French NF P 92 501 and the US NFPA 701. Smoke analysis methods will also not be discussed but many test methods and their application can be found in literature and on the internet.

### **3.8.6 Cone Calorimetry ISO - 5560**

Cone calorimetry has become a well-known test to predict, study and understand burning characteristics and decomposition of materials under a range of conditions. For research purposes probing techniques can be used to extract samples for analysis during various stages of the experiment [86].

ISO 5560 measures the rate of heat release and the heat of combustion from burning materials under controlled radiant heat source. The specimen under test is usually 100mm x 100mm and can be up to 50mm in thickness. The conical electric heater can apply uniform radiance to the specimen ranging from 10kW – 100kW/m<sup>2</sup>.



**Figure 3.16; Cone Calorimeter Schematic [87]**

A spark is applied to ignite the flammable vapours produced, air passes through the apparatus and the test is carried out in well ventilated areas.

Heat release is measured as a function of oxygen consumption calorimetry, other measurements include CO and CO<sub>2</sub> generation along with smoke density. Heat release is an important parameter for predicting fire growth [86, 87].

### **3.9 Literature Review Summary**

Throughout chapter three a variety of areas have been discussed with regards to flame retardance and the materials, processes, regulations and testing procedures involved. The depth of the subject area has to be appreciated and the reader should have a greater understanding of the factors which greatly affect flame retardance, and the considerations to be taken when attempting to produce a flame retardant system.

Chapter three began explaining the basics of fire and the processes involved to initiate, sustain fire and understand why materials burn.

An extensive review was carried out of the burning mechanisms involved and the product produced during combustion of PA6, leading into research surrounding the possible strategies for imparting flame retardance to polyamide fibres, filaments or textiles. The mode of action for materials was considered and reviewed.

Common test methods recognised within a variety of industries have been considered and summarised.

## **Chapter 4: Development of Flame Retardant Masterbatch**

### **4.1 Introduction**

The purpose of the experiment was to develop a masterbatch suitable for imparting flame retardant properties to PA6 filaments via melt spinning of PA6 filaments. The means for development and analysis will be vertical flame tests, TGA analysis and filter pressure performance measurements.

The development will be carried out in three stages. Stage one being the initial selection of additives and a stage gate of their performance.

Stage two will continue to work with these additives trying to improve efficacy and look for synergism, leading onto the final stage (stage three) which will be final masterbatch development.

All results mentioned throughout chapter 4 will be presented in detail in chapter 5.

### **4.2 Materials**

Polyamide 6 was supplied by Radici SPA, PA6 used was Radilon S D4 100.

The four primary flame retardants considered were melamine cyanurate, supplied by Budenheim in the form of Budit 315 (MCA). Metal Phosphinate flame retardant Exolit OP 1230 (OP) was supplied by Clariant. Novel flame retardant Triazine HF (THF) sourced from MCA Technologies GmbH. High flow Polybromostyrene CP-44 HF (CP44) was supplied by Great Lakes Chemtura. Budit 315 contains 48% nitrogen, and has a mean particle size of 2-3  $\mu\text{m}$ . Exolit OP1230 has a particle size of 20 $\mu\text{m}$  and contains 24% phosphorus

CP-44 HF is a co-polymer of di / tri-bromostyrene with glycidyl methacrylate, the methacrylate functionality is attributed to providing greater bonding and compatibility with the host polymer, which should provide better dispersion. Bromine content is 64-65% and molecular weight is approximately 60,000.

Secondary additives were also used for synergistic effects. Nanocor I.30T is a Nano layered silicate suitable for polyamides. Antimony Trioxide suitable for filaments (particle size 1 $\mu\text{m}$ )



was supplied by Chemisphere Ltd. The final additives PTFE (Nanoflon P39B) and Zinc Borate (ZB2335) were supplied by Shamrock Technologies and Wallace FR respectively.

For masterbatch production Montan wax was used as a dispersing aid in the form of Licowax OP supplied by Clariant.

### **4.3 Equipment**

TSA Twin Screw Laboratory Extruder EM-26; 26mm Screw Diameter; 30:1 L/D Ratio; 5kW motor power; 0-500rpm.

Hills Research Melt Spinning Machine; Single thread line 1 inch extruder; 30:1 L/D ratio; Melt pump output 2.92cc/revolution; Maximum operating 45rpm; Quench duct 1.2m x 0.5m; air flow 12m/min – 54m/min; Finish applicator meter 0.292cc Slack and Parr; Draw system, three roll system (two step draw); 0.5m (circumference) x 125mm; Max temperature 180°C; Winding , Leesona 965 precision tension controlled; 0-1200m/min.

Knitted on Lawson Hemphill FAK sampler 88 gauge suitable for 500 - 1500 total denier yarns. The fabrics were weft knitted, technical back structure.

Filter pressure test on Instron 4466 135x1400 twilled Dutch screen (12-14 micron)

TGA analysis Metler Toledo TGA/DSC2

Clariant labs performed DIN 4102-B2

External labs carried out mechanical testing according to ASTM D2256.

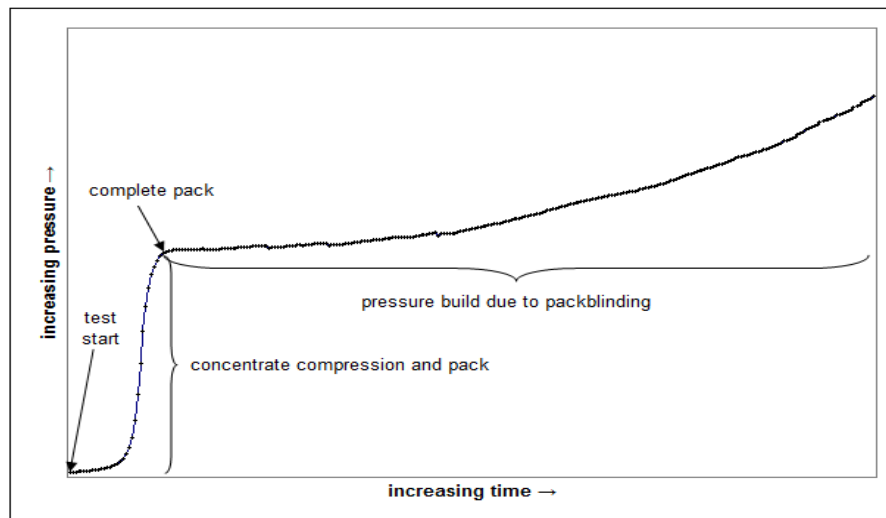
#### **4.3.1 Internal Testing Procedures**

As some of the tests carried out throughout the method are internal tests, here is a brief introduction to each test.

##### **4.3.1.1 Filter Pressure Test**

The filter pressure test is a test that measures a masterbatches characteristics on a fibre spinning filter pack at a specific temperature and screen pack configuration. The test goes

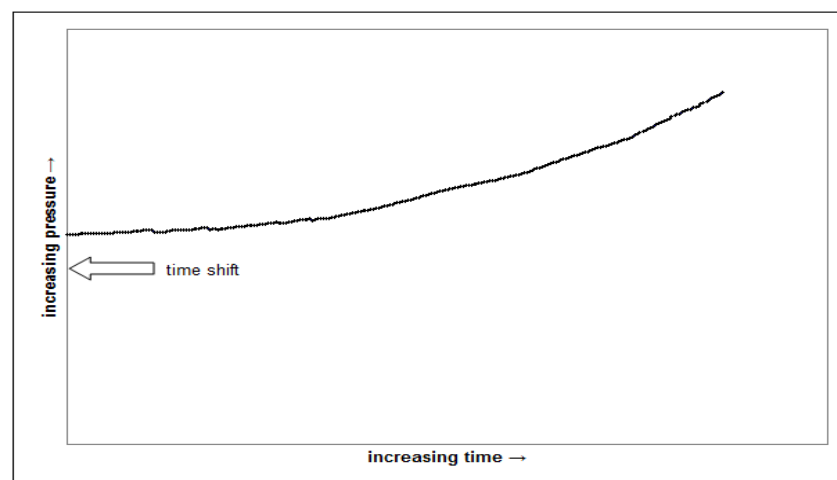
through three phases, compression and pack, complete pack and then pressure build due to pack blinding (figure 4.1).



**Figure 4.1 Internal Filter Pressure Test**

Data analysis is performed on the test results to obtain statistics to be used for further analysis. There are four components to the filter pressure analysis data report. They are initial rise, pack number, normalized pack number and chatter number.

The first step is to remove the concentrate compression and pack data and set the test the first data point to time zero (figure 4.2).



**Figure 4.2 Setting test to zero after removing compression of filter pack**

The second is to fit the data to a 2<sup>nd</sup> order polynomial and generating an equation in the form of  $aX^2 + bX + C$ . Constant C will be the pressure build due to the concentrate viscosity.

Step three is to determine the pack number. The pack number is the slope of the curve fit at the end of test (figure 4.3) To determine the slope take the first derivative of the equation ( $2aX + b$ ) where a and b are the constants of the polynomial fit and X is the standard test time.

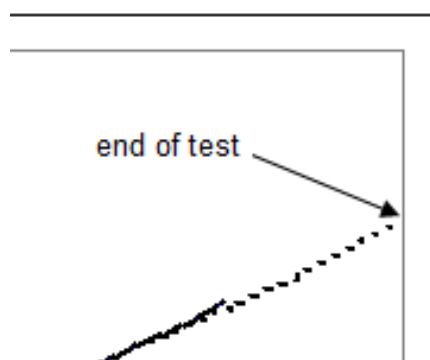


Figure 4.3 Curve fit at end of test

The normalised pack number is obtained from the addition ratio of the masterbatch. The pack number is assumed to be 1% and would be multiplied by 4 for a normalised pack number for a concentrate used at 4%. It is assumed that if you are using 4 times more concentrate then the pack number should be 4 times larger.

#### **4.3.1.2 Flame test procedure**

Internal flame test is similar to the DIN 4102 B2 method discussed in 3.8.3 in terms of setting up the experiment. However there are some minor but critical differences to testing and recording the experiment.

A 150mm specimen is clamped in place vertically, and a 20mm flame is applied directly to the specimen for 10 seconds. If the specimen does not ignite the flame is applied again and so on up to three times. If after three applications the material does not ignite the material is considered to retard combustion.

The burn time is recorded in seconds, whether the material drips and are those drips burning. Some general observations are also made regarding the nature of burning, and how aggressive is the combustion. The tests are also video recorded for reference.

## 4.4 Method & Formulations

### 4.4.1 Phase one

Pre-dispersions of each primary flame retardant were prepared (table 4.1) containing 20% additive in Polyamide 6 host polymer via twin screw extruder. The 20% concentrates were then compounded at 2% and 4% in PA6, these compounds were melt spun at 100% therefore the yarn produced would contain 0.4% and 0.8% active ingredient. The compounds were melt spun via Hills R&D line. (See figure 4.4 for spinning conditions)

The denier of the yarns produced was 13.5 Denier per filament, round cross sections. The spinneret consisted of 38 holes, diameter of the holes was 0.6mm x 2.4mm length.

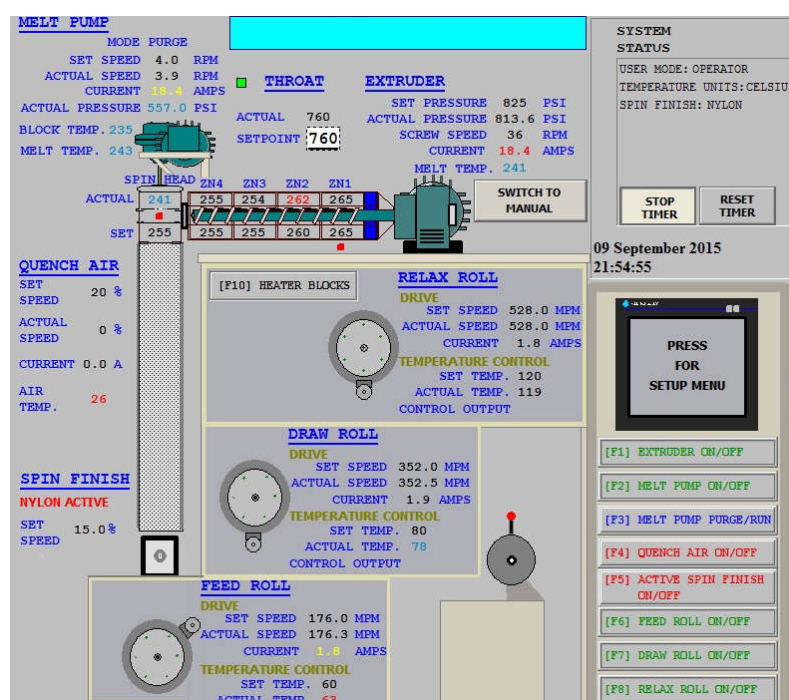


Figure 4.4 Phase one spin setup.

The yarns were then plied, air jet texturised similar to process described in figure 2.12 and wound onto a bobbin. The textured yarn was then knitted via Lawson Hemphill Fak

sampler. 1 metre fabrics were laundered and tested under DIN 4102 – B2 at Clariant laboratory, Gersthofen, Germany.

**Table 4.1 Phase 1 Pre-dispersions formulation**

	PA6	MCA	OP	THF	CP44
A	80	20			
B	80		20		
C	80			20	
D	80				20

TGA / DSC analysis was also carried out on the compounds to assess how the ingredient affected decomposition properties.

Following problems faced when spinning melamine cyanurate additive Budit 315 filter pressure test was carried out to test the dispersion. Spinning temperatures were reduced further and draw ratios were also reduced from 3 to 2.5 in an attempt to spin the yarn. Unfortunately it was not possible to spin the MCA additive at 0.4% and 0.8% concentration in final fibre and therefore MCA was removed from any further consideration.

Problems were also experienced when attempting to spin THF at 0.8% concentration.

#### **4.4.2 Phase two**

**Table 4.2 Phase 2 compound spins – amounts (%) in final fibre**

	PA6	OP	THF	CP44	MMT	ZB	ATO
1	97.450	2.550					
2	96.800	2.300	0.900				
3	97.400	2.300			0.300		
4	97.100	2.300			0.600		
5	97.450	2.300				0.250	
6	97.450	1.275		1.275			

7	96.550	1.275	0.900	1.275		
8	97.150	1.275		1.275	0.300	
9	97.150	1.275		1.275		0.300
10	98.700			1.300		
11	97.450			2.550		
12	98.125			1.575		0.300
13	97.550			2.000		0.450
14	97.525		0.900	1.575		
15	98.125			1.575	0.300	
16	98.125			1.575		0.300

Following phase one two flame retardant additives were considered for further development Exolit OP1230 and Chemtura CP44-HF were the two primary additives still considered. Other secondary additives were selected in and attempt to find synergistic effects.

Multiple formulations found in table 4.2 were melt spun again via spinning conditions set out in figure 4.4. The yarn was air jet texturised and knitted. Fabrics were laundered at 30°C household cycle and again sent to Clariant for DIN 4102 B2 testing.

TGA / DSC was also carried out on the samples.

Phase two flame tests also included a second standard. DSM are in the process of developing a 'spinnable' flame retardant grade of polyamide 6 'NX-140' where the flame retardants are incorporated via in situ polymerisations therefore the additives are incorporated during processes outlines in 2.1..... Unfortunately due to confidentiality no further analysis could be carried out.

#### **4.4.3 Phase three**

Following phases one and two Aluminium Phosphinate (Exolit OP 1230) was chosen for flame retardant masterbatch development. A highly concentrated masterbatch (table 4.3) containing Exolit OP1230, PTFE, anti-oxidant package was extruded via twin screw extruder. The dried masterbatch was tested for filter pressure rise, to gage dispersion quality.

**Table 4.3 Masterbatch formulation**

Ingredient	Amount
PA6	46
ExolitOP1320	40
PTFE	10
B-1171	2
Licowax OP	2

Due to limited success in alternative drip suppressants in phase two, well known drip suppressant additive PTFE was used for phase three.

Although poor filter performance was experienced with the highly concentrated masterbatch an attempt was made to spin the masterbatch at first 7% and secondly 5%.

In an attempt to improve filter performance the highly concentrated masterbatch was 'let down' in a 70 / 30 ratio of MB / PA6. The concentration of the new additives can be found in table 4.4.

**Table 4.4 Formulation of Let-down highly concentrated masterbatch**

Ingredient	Amount
PA6	62.2
Exolit OP1320	28
PTFE	7
B-1171	1.4
Licowax OP	1.4

Again filter pressure tests were carried out on this masterbatch. There was no significant improvement observed by reducing the concentration of the additives. Again attempts were made to spin the masterbatch but were unsuccessful.

Following phase where a 20% concentrate was produced containing Exolit OP1230 which was 'spinnable' throughout phase one and two, it was decided that a new masterbatch was produced with lower concentrations of flame retardant additives (table 4.5).

**Table 4.5 Final masterbatch formulation**

Ingredient	Amount
PA6	73
Exolit OP1320	20
PTFE	5
B-1171	1
Licowax OP	1

The masterbatch produced from formulation in table 4.5 shown a much improved filter pressure test performance.

It was then possible to spin this masterbatch at 10% and 15% addition levels, although the draw ratio and draw temperatures had to be reduced. Final spin setting can be found in figure 4.5.

TGA / DSC analysis was carried out on the masterbatch.



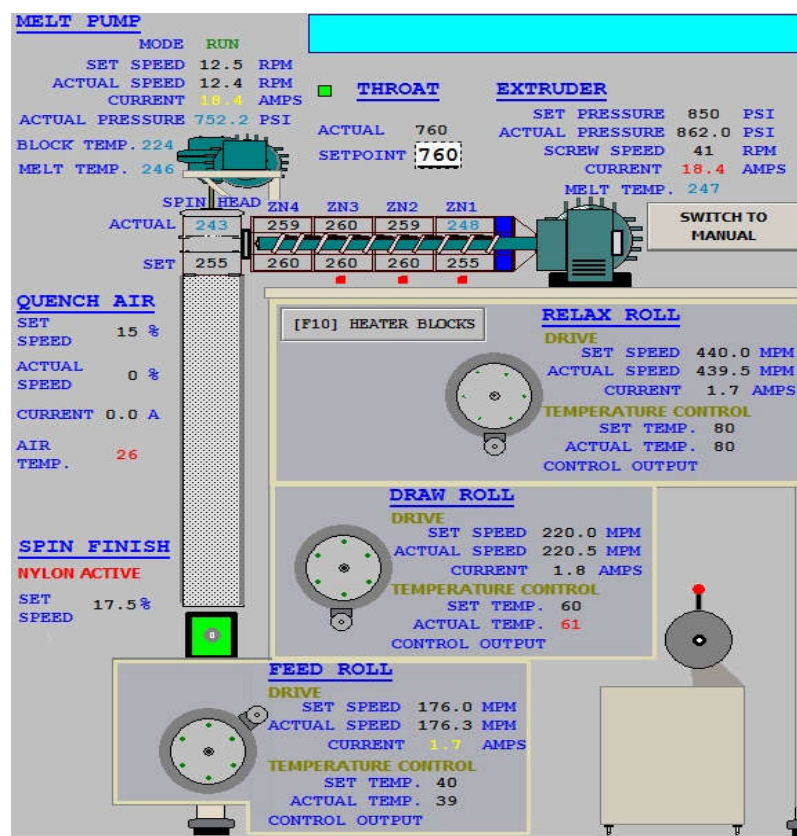


Figure 4.5 Final Spin Setup

Internal flame tests were carried out on the fabrics produced following laundering and conditioning. All results from chapter four will be presented and discussed in chapter five.

## Chapter 5: Results and Discussion

Throughout chapter 5 results taken during the various stages of development will be presented, analysed and discussed.

### 5.1 Phase One

Phase one carried out the initial stage-gating of the selected additive flame retardants. The fabrics were assed under DIN 4102-B2 and yarns were assessed for their mechanical properties. All samples were compared versus virgin PA6 material.

TGA Analysis was carried out on the compounds prior to spinning to investigate how the additive flame retardants affected the decomposition of PA6 (figure 5.1)

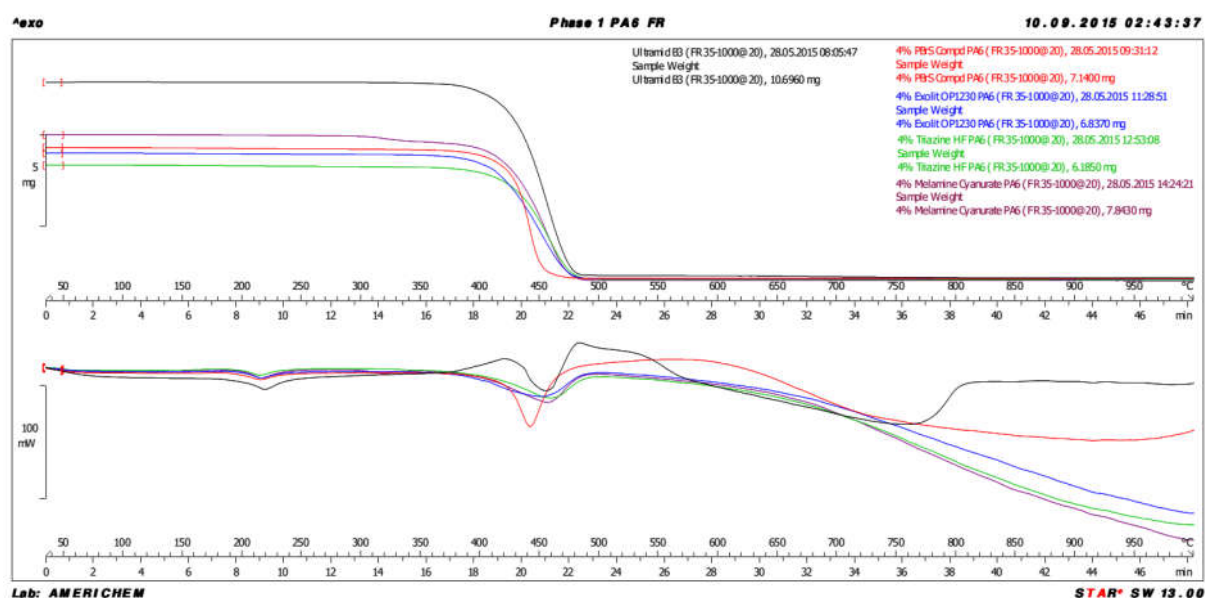


Figure 5.1 TGA Analysis: Primary FRAs vs PA6 in Nitrogen

From the TGA analysis it can be observed that even low levels of melamine cyanurate affects the decomposition of PA6. The decomposition occurred in two steps similarly to findings in chapter three. However at the concentration tested decomposition did not begin to occur until approximately 300°C and therefore considerably above the spinning temperatures used, so it is strange that the compounds containing MCA were unable to be spun, as a result of this an internal filter pressure test was carried out to test dispersion of the concentrate. (Figure 5.2)

It can be seen from the filter pressure analysis that the dispersion of the MCA into a PA6 matrix was poor. The screen was blocked and the maximum load was reached causing the test to end. As a result it was determined that poor dispersion caused the spinning issues of MCA containing compounds.

The other additives perform in a similar fashion; they cause decomposition onset at a lower temperature but reduce the rate of decomposition apart from the CP-44 which appears to decompose faster.

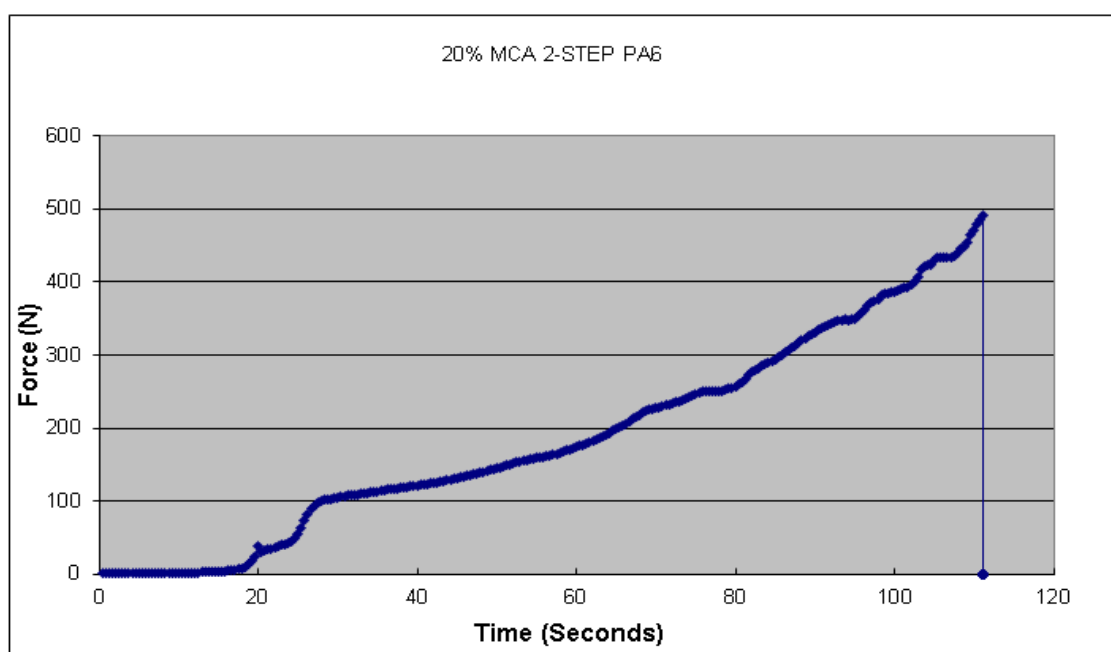


Figure 5.2; Filter pressure analysis 20% MCA in PA6

Results from the mechanical properties assessment can be found in table 5.1.

Table 5.1 Phase One Tensile Assessment ASTM D2256

Tensile			
	Tensile (N)	Elongation at max load (%)	Initial Young's Mod (N/den)
<b>PA6</b>	22.9796	197.683	14.857
<b>OP 0.4%</b>	19.6128	178.983	17.25
<b>OP 0.8%</b>	20.1681	173.517	18.442
<b>CP44 0.4%</b>	22.1538	208.349	16.694
<b>CP44 0.8%</b>	22.3924	209.467	15.81
<b>THF 0.4%</b>	23.7873	167.75	16.722

For the majority it is observed that adding the FRAs to PA6 causes a slight reduction in tensile strength compared to pure PA6. However there was a slight increase when adding THF at 0.4%.

The elongation was reduced approximately 10% when adding the Exolit OP, whereas adding the Polybromostyrene there was a slight increase in elongation. When adding the Triazine the elongation was reduced 15%. This may be one explanation as to why it was not possible to spin the Triazine HF at the higher concentration.



**Figure 5.3; DIN 4102-B2; PA6 Control – burning drips.**

DIN 4102-B2 testing was carried out at Clariant Laboratory, from the assessments we can observe all fabrics passed the DIN4102-B2 testing.

All samples were deemed to burn excessively and all fabrics produced burning drips.

The fabrics containing organic Phosphinic salts appeared to increase the time taken for burning drips occur especially in the 0.8% concentration fabrics.

From figure 5.4 the burning drips are clearly visible all samples performed similarly in terms of burning drips.

All formulations 'self-extinguished', the Pure PA6 material and Exolit OP1230 containing formulations extinguished upon the removal of the heat source for the majority of the

samples tested. The Triazine and Polybromostyrene samples however continued to burn after the heat source had been removed.

It was observed from the flame testing that the pure PA6 extinguished by melting away from the heat source. The Exolit containing formulations appeared to melt away somewhat but there was also char production on the burnt edges.

The Triazine and halogenated formulations shown little melt flow away from the ignition source and once the initial burning drips had been produced continued to burn although very slowly.

## **5.2 Phase two**

Throughout phase two many formulations were tested under DIN 4102 –B2 in an attempt to find synergistic performance between FRAs.

An extra control was also introduced for flame testing; ‘Novamid NX-140’ from DSM a relatively new flame retardant polyamide resin suitable for spinning.

There were 16 formulations compounded (table 4.2) and sent for DIN4102-B2 testing compilation of results can be found in table 5.3.

The control in phase two performed considerably worse than during phase one. On a couple of occasions the maximum burn length was reached causing a test fail. It is worth noting that there is a considerable performance variance between the samples which could be related to the fabrics themselves. One possible cause for the large variance could be if the knit structure was not consistent throughout fabric production, as a more open fabric would ignite and burn more freely than a tightly knitted structure.

**Table 5.2: DIN 4102 – B2 Phase One Compound Spins**

<b>Test-Number:</b>	Control PA6					Exolit 1230 (0.4%ff)					Exolit 1230 (0.8% ff)					Triazine (0.4% ff)				
Sample Number	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Time when reaching the reference mark (s)	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
Total Burn time (inc flame [s])	9	9	14	13	12	12	9	13	15	11	13	12	10	15	17	63	17	27	38	40
Time to drop burning droplets (s)	6	7	7	11	10	11	9	9	9	9	9	11	10	10	11	10	10	8	9	9
Material deemed to be burning excessive (y/n)			Y					Y					Y					Y		
Independent Extinction	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J
Pass B2 (y/n)			Y					Y					Y					Y		

<b>Test Number</b>	CP-44 (0.4% ff)					CP-44 (0.8% ff)				
Sample Number	1	2	3	4	5	1	2	3	4	5
Time when reaching the reference mark (s)	/	/	/	/	/	/	/	/	/	/
Total Burn time (inc flame [s])	14	21	17	19	17	12	19	29	23	39
Time to drop burning droplets (s)	8	10	10	9	11	9	9	9	8	9
Material deemed to be burning excessive (y/n)			Y					Y		
Independent Extinction	J	J	J	J	J	J	J	J	J	J
Pass B2 (y/n)			Y					Y		

**Horizontal Flame Test DIN4102-B2**

**Edge Exposure**

**Flame Time 15s / 150mm measurement mark**



**Figure 5.4; DIN 4102-B2; 0.4% FF Exolit 1230 – flaming drips**

The second control NX-140 from DSM performed well, the material did not burn for more than 20 seconds. However there was still the issue of drips although the drips were not flaming.

When using the Exolit OP1230 on its own there was an improvement in flame retardance properties, almost comparable to the NX-140. However it appeared that as the increase in concentration of Exolit increased the flame retardant performance reduced slightly. The burn times increased with a higher concentration of OP.

The performance of Exolit OP1230 was not improved by the addition of other flame retardant additives. In fact a surprising effect from the addition of Nano-layered silicates was observed. The layered silicates were added as a drip suppressant, yet they actually promoted combustion. There was a considerable increase in total burn time when the MMT was added to Exolit and as the MMT concentration was increased the flame retardant properties were worsened and a test fail was observed. This could be caused as the MMT prevents the melt flow of the PA in turn removing the fabrics ability to flow away from the flame, therefore not removing the fuel. A Similar observation was made when adding the MMT to CP44 as a synergist, although when adding MMT to a blend of OP and CP44 the effect of promoting combustion was less severe.

The addition of Triazine did not really contribute to the flame retardance in any of the systems it was used.

Using Polybromostyrene as flame retardant for PA6 and in synergistic systems provided a variety of results. Spinning performance of the compounds was good even at relatively high concentrations, it was possible to incorporate 16575 parts per million (ppm) bromine into the fibre.

Even at high concentrations it was 'out performed' by the Exolit system containing 6000 ppm Phosphorus although this can be related to the improved efficacy of phosphorus in nitrogen containing polymers.

The CP44 did provide an improvement in flame retardance compared to pure PA6 and some tests performed similarly to the NX-140 although again there was some variance between the tests and no improved performance was observed when the concentration was doubled.

Surprisingly the addition of antimony trioxide did not improve the efficacy of CP44. Two concentrations were assessed and both performed similarly, it could be argued that the higher concentration performed worse.

Although some positive results were obtained when combining the Exolit and CP44 together they did not perform better than when using the additives on their own.

The addition of zinc borate hindered the flame retardancy of the systems it was assessed similarly to the MMT, however no failures were observed.

To summarise the phase two flame tests, the flame retardancy of PA6 can be improved although it appears the materials utilised perform better when used on their own. However all formulations still suffer from drips.

As Exolit OP1230 outperformed the other flame retardant additives used the development continued using this as the primary additive. In phase two MMT and ZB were used as drip suppressants although they exhibited poor performance and had an antagonistic effect.



**Table 5.3; DIN 4102 – B2; Phase Two**

Test Name	OP (2.55% ff)					OP + TRI (2.3 + 0.9% ff)					OP + MMT (2.3 + 0.3% ff)					OP + MMT (2.3 + 0.6% ff)				
Sample Number	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Time when reaching the reference mark ( s )	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	43	58	26	/
Total Burn time (inc flame [s])	20	24	34	19	15	23	15	36	25	24	26	50	45	47	36	16	117	122	94	17
Time to drop burning droplets (s)	14	12	13	13	13	11	13	13	13	13	11	13	13	13	12	13	10	12	10	10
Material deemed to be burning excessive (y/n)	Y					Y					Y					Y				
Independent Extinction	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	N	N	J	J
Pass B2 (y/n)	Y					Y					Y					Y				

Test Name	OP (2% ff)					OP + CP44(1.275 + 1.275%)					OP+ CP44 + TRI (1.275, 1.275, 0.9%)					OP, CP44, MMT (1.275, 1.275, 0.3)				
Sample Number	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Time to reach Reference mark	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
Total Burn time (inc flame [s])	15	23	17	17	26	21	26	36	15	15	37	22	37	45	42	31	37	17	31	19
Time to drop burning droplets (s)	13	13	11	12	11	13	12	13	10	12	13	14	14	13	14	14	12	13	13	13
Material deemed to be burning excessive (y/n)	Y					Y					Y					Y				
Independent Extinction	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J	J
Pass B2 (y/n)	Y					Y					Y					Y				

**Table 5.3 Continued**

Test Name	Control PA6					Novamid NX-140					CP44, ATO (2, 0.45%)					CP44, TRI (1.575, 0.9)				
Sample Number	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Time when reaching the reference mark ( s )	71	77	/	/	/	/	/	/			/	/	/	/	/	/	/	/	/	/
Total Burn time (inc flame [s])	149	89	26	75	30	20	19	18			34	31	19	26	19	40	33	19	18	41
Time to drop burning droplets (s)	11	12	11	11	11	13	12	10			13	10	13	12	11	10	12	10	11	12
Material deemed to be burning excessive (y/n)	Y					Y					Y					Y				
Independent Extinction	N	N	Y	Y	Y	Y	Y	Y			Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Pass B2 (y/n)	Y					Y					Y					Y				
Test Name	OP + ZB (2.3 + 0.3%ff)					CP44 (1.3%)					CP44 (2.55%)					CP44, ATO (1.575, 0.3%)				
Sample Number	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Time when reaching the reference mark ( s )	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
Total Burn time (inc flame [s])	32	51	56	54	52	28	15	40	17	39	33	21	39	44	62	23	35	17	16	29
Time to drop burning droplets (s)	12	12	12	10	11	10	10	11	9	9	10	11	10	10	11	12	11	11	10	12
Material deemed to be burning excessive (y/n)	Y					Y					Y					Y				
Independent Extinction	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Pass B2 (y/n)	Y					Y					Y					Y				

**Table 5.3; continued**

Test Name	OP, CP44, TRI (1.275, 1.275, 0.3)					CP44, MMT (1.575, 0.3%)					CP44, ZB (1.575, 0.3%)				
Sample Number	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Time when reaching the reference mark ( s )	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
Total Burn time (inc flame [s])	22	90	37	20	29	44	100	39	92	28	60	19	28	50	44
Time to drop burning droplets (s)	12	12	13	12	13	10	12	11	12	10	14	10	10	11	10
Material deemed to be burning excessive (y/n)	Y					Y					Y				
Independent Extinction	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Pass B2 (y/n)	Y					Y					Y				

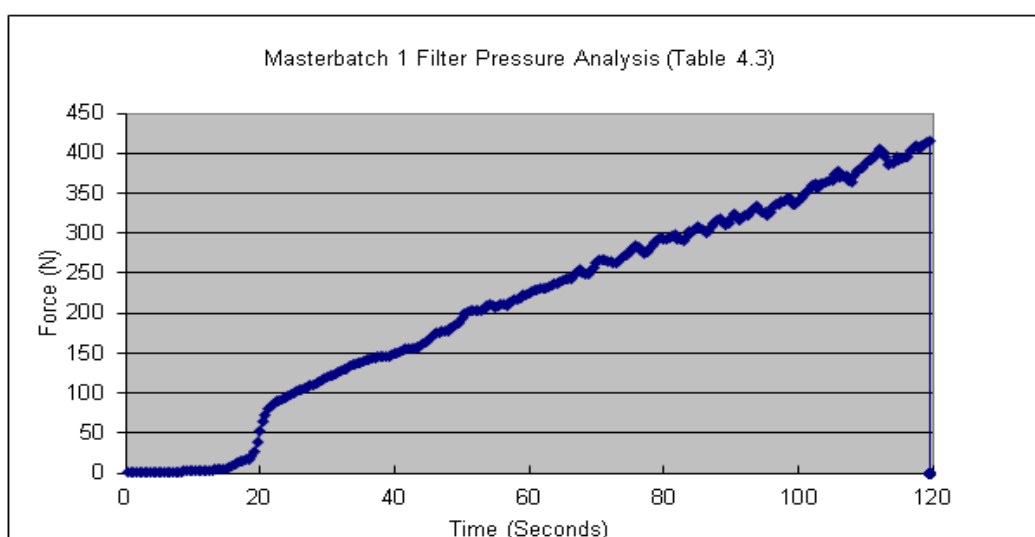
### 5.3 Phase Three

Throughout phase one and two the work has been carried out in compounds. In phase three the focus will be on developing a masterbatch to impart flame retardancy to PA6 fibres.

Flame tests from phases one and two outlined the outstanding issue of dripping during combustion. As no synergistic performance was found well known drip suppressant PTFE was to be utilised in an attempt to solve this problem.

Following flame tests and TGA analysis in phases one and two Exolit OP1230 has been chosen as the primary flame retardant additive.

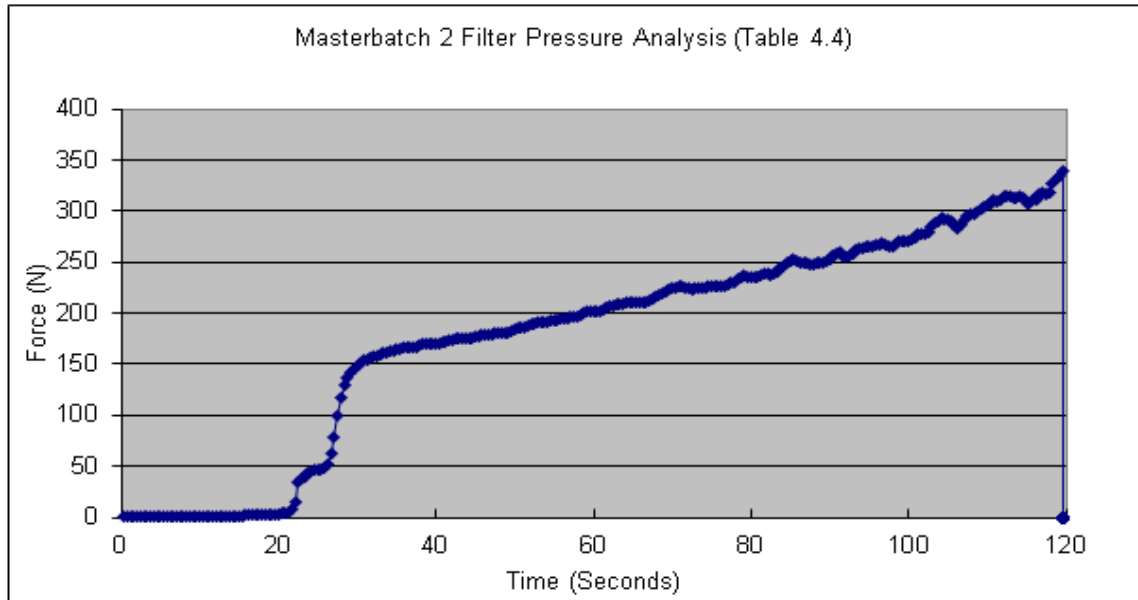
Masterbatch was produced using formulation in table 4.3 and filter pressure performance was assessed figure 5.5.



**Figure 5.5; Filter pressure analysis masterbatch one.**

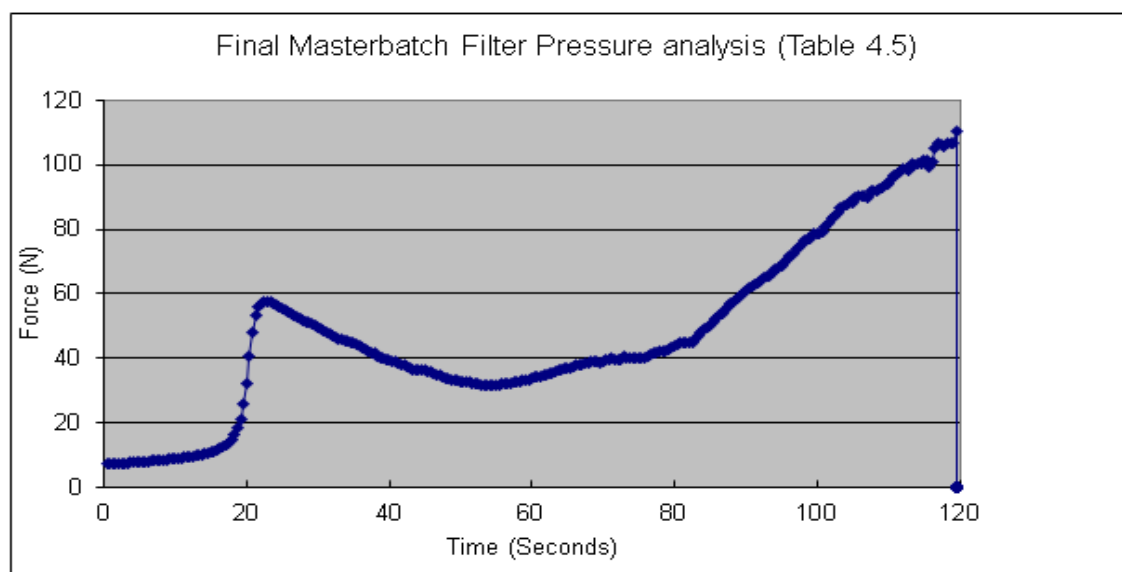
It can be observed from figure 5.5 that the filter pressure performance was poor from masterbatch one. This consistent rise in pressure indicates particulate build up on the screen pack. A pressure filter test like this would relate to poor spinning performance and blockage of spinning filter packs. As a consequence of this performance it was decided to reduce the concentration of the masterbatch in an attempt to improve dispersion and filter performance.

The masterbatch produced was let-down in a 70:30 ratio, MB: PA6 to reduce the concentration of the FRAs. Formulation can be found in table 4.4. Again filter pressure performance was measured figure 5.6.



**Figure 5.6; Filter pressure analysis masterbatch two.**

Observing from figure 5.6 an improvement in filter pressure performance was noticed. Although improved in terms of maximum pressure load reached, the constant rise does not encourage good dispersion and 'spinnability'.



**Figure 5.7; Final masterbatch filter pressure performance**

Therefore it was decided that a new masterbatch be developed reducing the concentration further. (Table 4.5) The filter pressure performance analysis was carried out (figure 5.7).

The new masterbatch shown superior filter pressure performance reaching a relatively low load build-up, and pressure actually reducing after initial compression. It was decided that spinning would commence with this masterbatch. A pack number of 3.17 was achieved which was slightly higher compared to the 28% concentrated masterbatch which was 2.9785. However I attribute this to the increased gradient between 80 and 100 seconds during the filter test.

Initial spin trials using spin setup from figure 4.4 were unsuccessful, the filaments were breaking during draw stage two. As a result the drawing temperatures were reduced and the draw ratio was also reduced (figure 4.5) the final masterbatch was spun at addition levels of 10% and 15%.

It is worth noting that the quenching air was turned off during spinning with the addition of masterbatch as the filament's 'drawability' was significantly reduced when the quenching system was on. It was assumed the additives were reducing the melt viscosity of the filaments and further quenching was causing them to solidify too quickly, leading to filament breakages on the take up roll and preventing further drawing.

Mechanical properties were assessed compared to pure PA6 also produced under the same condition. Results can be found in table 5.4.

**Table 5.4; Final MB at 10% and 15% ASTM D2256**

<b>Tensile</b>			
	<b>Tensile (N)</b>	<b>Elongation at max load (%)</b>	<b>Initial Young's Mod (N/den)</b>
<b>PA6</b>	25.702	254.983	23.781
<b>MB10%</b>	23.517	19.7	27.763
<b>MB15%</b>	26.282	1887.167	23.831

Judging by the results found in table 5.4 it can be stated that the addition of the FR masterbatch does alter the mechanical properties when compared to PA6 although not severely. Adding the masterbatch at 10%, there was a reduction in tensile strength by 5% and

elongation by approximately 20%. The Young's modulus increased more than 15% therefore producing a 'stiffer' yarn.

When adding the masterbatch at 15% then tensile strength increased slightly when compared to PA6, however the elongation reduced further when increasing the concentration. The Young's modulus reduced compared to 10% addition level having modulus properties more comparable to pure PA6. With no severe detrimental effects on mechanical properties it was possible to knit fabrics.



**Figure 5.8; PA6 internal flame testing – melting away from flame**

Pure PA6 supported combustion during the flame tests although when the flame was initially applied there was an attempt to melt flow away from the heat source (figure 5.8). The flame was applied for 10 seconds and within that time the fabric had ignited. Once ignition had occurred PA6 continued to burn producing flaming drips (figure 5.9). Five samples were assessed and recorded in table 5.5.

Again five specimens were assessed for the two fabrics produced using 10% and 15% masterbatch.

For MB10% there were a variety of results attained from the flame tests (table 5.5), ranging from immediate 'flashover' to 'non-ignition'. Once flashover had occurred combustion was supported and flaming drips were produced. From observations combustion was also more 'aggressive' and 'intense' (brighter flame produced).

The time to burning drips was increased and two specimens took more than one flame application to ignite the fabric. From figure 5.10 it is observed the application of the flame and the immediate self-extinction. Therefore some flame retardancy can be observed, however, this was not observed for all five specimens.



**Figure 5.9; PA6 internal flame testing – flaming drips**

To summarise MB10% some flame retardancy can be observed, and more than one specimen did not ignite on first flame application. As the masterbatch was dosed with the PA6 polymer there may have been some separation due to a variance in bulk densities or pellet geometry which could cause under / over feeding at certain points throughout yarn production.

Increasing the addition level of the masterbatch appeared to make the fabrics more difficult to ignite as three of the five specimens tested took three 10 second flame applications; however on two of the three specimens once 'flashover' had occurred the whole specimen was consumed in an aggressive manner.





**Figure 5.10; MB10% internal flame testing – immediate extinction**

Comparing figure 5.9 and 5.11 it is clearly visible how the two specimens burn differently. Pure PA6 has small blue flame on the edge of the fabric once the flaming drip has been removed, comparing to figure 5.11, a bright, intense and larger flame can be observed on the fabric surface, spreading vertically up the fabric in an aggressive manner this was observed for masterbatch containing fabrics.



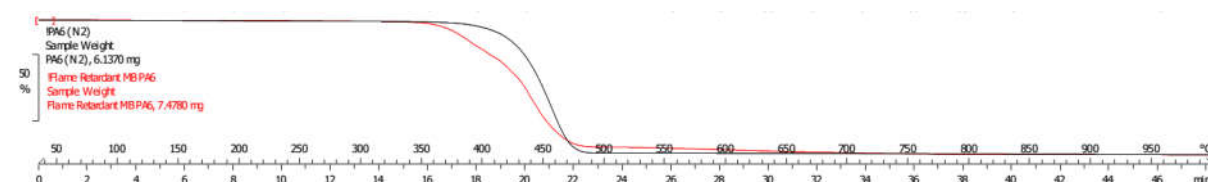
**Figure 5.11; MB10% internal flame testing – aggressive burning**

**Table 5.5; Flame Test Results – Phase three**

Flame Testing Results Table	PA6					MB10%					MB15%				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Burn Time (s) inc flame	116	82	74	92	54	40	121	86	70	101	93	105	82	87	98
Number of applications until combustsion	1	1	1	1	1	1	2	2	2	2	3	2	2	3	3
Flaming Drips	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Comments	All samples attempted to flow away from flame.					4/5 took two flame application for combustion to be supported. Aggressive combustion					Once flash over occurred burned aggressively. 2/5 samples whole fabric was consumed.				

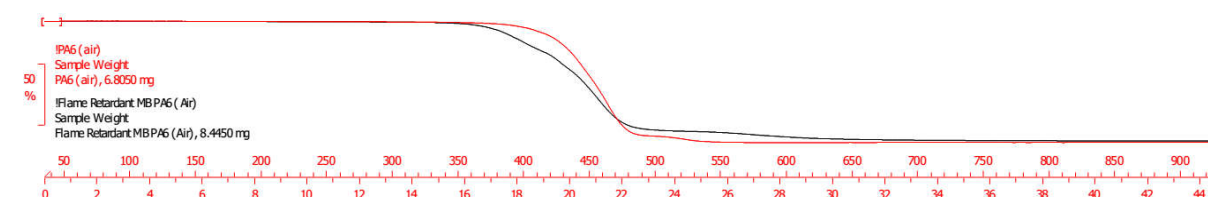
To summarise the flame test results shown in table 5.5 the addition of a flame retardant masterbatch does hinder the ease of ignition, but once ignited the majority of the samples performed similarly to PA6 in terms of burn time and dripping. Yet as mentioned the masterbatch containing fabrics burnt in a more aggressive manner. None of the specimens tested achieved a ‘retard combustion’ rating.

TGA analysis in nitrogen shown that when incorporating additives into the PA6 matrix the thermal decomposition of PA6 occurs at a lower temperature of 350°C compared to 370°C, as observed in figure 5.12.



**Figure 5.12: TGA Analysis N2 – PA6 vs Flame Retardant Masterbatch**

It can also be observed that the decomposition occurs over a longer period of time. The PA6 has completely decomposed by 500°C, whereas the flame retardant masterbatch does not fully decompose until 680°C



**Figure 5.13: TGA Analysis Air, PA6 vs Flame Retardant Masterbatch**

A similar observation can be made from TGA analysis in air. The flame retardant masterbatch onset decomposition occurs at a lower temperature compared to PA6.

However the TGA analysis in air and nitrogen could provide an explanation as to why it took numerous flame applications to ignite the fabrics containing masterbatch.

From table 3.3 it was mentioned the pyrolysis of PA6 begins at 431°C and ignition occurs at 450°C.

At these temperature the rate of decomposition is much slower for the masterbatch compared to the PA6, and as a result inhibiting pyrolysis and thus combustion.

## **Chapter 6: Conclusions and Summary.**

### **6.1 Summary**

Throughout the dissertation a critical review has been carried out on the a variety of subject areas in order to attempt to develop a masterbatch containing flame retardant additives suitable for incorporating flame retardant properties on PA6 filaments via melt spinning.

Polyamide 6 production, melt spinning, flame retardant additives and the environmental issues around such additives have been considered within chapters two and three.

From chapter five we can conclude that the initial ignition of PA6 can be delayed by incorporating additives via masterbatch. In some cases spinning from compound as explained in 5.2 can achieve reduced burn times. However the problem of flaming drips was still observed.

TGA analysis confirms some additives affect the decomposition of PA6 causing a destabilisation effect, in particular melamine cyanurate, as discussed in 3.7.3 and observed in 5.1. Literatures reviewed were able to produce filaments containing melamine cyanurate and some promising results were observed, however in my study it was not possible to produce filaments containing melamine cyanurate.

All the primary flame retardants considered shown this phenomena however it was only the nitrogen containing additives which were not possible to spin.

Polybromosyrene shown some promise in processing and flame retardance in 5.1 and 5.2 however was not selected due to the negative publicity currently surrounding halogenated flame retardants.

A lot of research has been directed at the use of Nanoclays for flame retardance, however in this study they only provide antagonistic effects, similar results were observed for the incorporation of zinc borate.

Novel Polyamide resin NX-140 from DSM was included during phase two and shown promising flame retardance, but due to confidentiality more detail cannot be discussed.

Organophosphorus shown the most suitability for developing flame retardant masterbatch, although the grade selected may have contained a particle size distribution which was too large for filament production. Spinning was more successful via compound and when spinning the additives via masterbatch the spinning parameters had to be changed significantly from standard PA6 spinning conditions.

Research reviewed achieved V-0 on the UL-94 tests in plastic articles down to 1.6mm specimen thickness. The supplier (Clariant) state in their brochures that this additive is suitable for carpets and textiles. From TGA analysis my results are comparable to research reviewed. We both experienced the organo-phosphorus causing thermal degradation to begin at a lower temperature, but slowing down the rate of degradation.

Research summarised that the organophosphorus was a good 'char' former and this could be the cause for the longer burn times when adding masterbatch as the fabrics were attempting to char, whereas the PA6 melt flowed away from the flame.

Achieving dispersion suitable for masterbatches to be used in the dope dyeing process was also difficult using organophosphorus, however the poor dispersion was not investigated thoroughly enough to hold the organophosphorus accountable, but could be linked to particle size.

The addition of PTFE did not stop the flaming drips once combustion has begun during flame tests. It is possible that the grade selected was not the correct grade for the development although it was selected for supply chain issues and on the basis it was known to be suitable for melt spinning.

It is worth noting that blending step usually takes place to aid the wetting of the host polymer and ensure homogenous mixture of the ingredients and no blending was carried out during the development. Dispersion could possibly be improved with adequate blending process.

Summarising the flame tests carried out within the development it can be concluded that vertical flame tests like the internal method and DIN 4102 –B2 are not the most suitable for

comparing flame retardance. In some cases the pure polymer being used as control passed all tests.

Another consideration to take place for the flame testing was the use of knitted fabrics. As discussed in chapter three the fabric structure affects flammability considerably and possibly knitted fabrics were not the best choice, however with no weaving capability available knitted fabrics were the only option. There were also some variances within the knitted fabrics as there was no yarn feeding device on the knitter so fabrics were produced by maintained and standard setting and monitoring changes in knitting tension throughout fabric production.

Ideally more analysis would have been carried out on the filaments and fabrics themselves. For example to detect the distribution of the additives within the filaments via scanning electron microscope (SEM), this would enable determination of how much additives were passing through the spinning filters into the filaments, especially important when the dispersion and particle size of the additive is being questioned.

As the incorporation of the masterbatch caused more aggressive combustion cone calorimetry and smoke analysis would be useful to conclude heat release and toxicity.

In the development other aspects were not considered as the development is not considered optimum. For example how the addition of flame retardant masterbatch affects dyeing and downstream process. Is the masterbatch procurable with hindered amine light stabilisers? As depending on exposure PA6 needs to be UV stabilised.

From the dissertation it can be concluded that the subject area of polyamide fibres and associated flame retardance of filaments and textiles is a vast area of great interest. Many investigations have been carried out previously, some reviewed in chapter 3, and there is yet a single product on the market which meets all the criteria to impart flame retardance on PA6 fibres, filaments and textiles.

After treatments appear to be the most effective in industry yet they affect the handling properties of the fabrics and may not be permanent.

## **6.2 Future Research**

Although the objective of the dissertation was not wholly fulfilled their possibilities to improve or further develop a flame retardant masterbatch.

Further research is necessary and new materials to need to considered and greater screening during additive selection.

Particle size of the additives can play an important factor for masterbatch and filament production. Homogenous dispersion is necessary for melt spinning filaments to obtain optimum performance and properties.

Organophosphorus shown promise as a flame retardant and a suggestion of a new material Exolit OP 945 should be considered due to reduced particle and narrow particle size distribution.

Dispersion techniques should be considered, what affects would pre-blending have on the homogeneity and dispersion? Could high energy dispersion methods using a Banbury mixer for example provide the necessary dispersion and particle stabilisation within the PA matrix?

Future studies should consider analysis of the filaments produced in an attempt to measure how much of the additives make their way in to the final filament and their distribution throughout the filament.

To improve the research carried out here a more controlled method of fabric production should be considered, woven structures may be more suitable for flame tests.

Due to the observed 'more aggressive' combustion cone calorimetry and smoke toxicity should be considered during development.

To fully develop a suitable product for industry a more complete evaluation should be considered, including dyeing performance and how is it affect for raw white yarns going into post dyeing. How is dope dyeing affected with the inclusion of flame retardant masterbatch?

Light Fastness and weathering performance should be analysed to judge if the produced yarn can be used for outdoor applications.

### **6.3 Conclusions**

- Masterbatch incorporating flame retardants additives was developed
- Addition of masterbatch hindered ignition of PA6 knitted fabrics
- Addition of masterbatch caused more aggressive burning
- Addition of masterbatch did not prevent flaming drips on combustion
- Addition of masterbatch lower decomposition onset temperature
- Addition of masterbatch slows down rate of decomposition
- Nanoclays promoted combustion
- Pure PA6 used as control passed flame tests without modification
- More complete analysis needed, cone calorimetry and smoke toxicity to evaluate aggressive burning.
- More investigation needed to improve dispersion of flame retardant additives within PA6 matrix
- More investigation needed to improve development and consider downstream processing e.g. dyeing and UV resistance.
- Further Research and Development necessary



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