

#### Development and characterisation of flame retardant nanoparticulate biobased polymer composites

Hapuarachchi, Tharindu Dhanushka

The copyright of this thesis rests with the author and no quotation from it or information derived from it may be published without the prior written consent of the author

For additional information about this publication click this link. https://qmro.qmul.ac.uk/jspui/handle/123456789/532

Information about this research object was correct at the time of download; we occasionally make corrections to records, please therefore check the published record when citing. For more information contact scholarlycommunications@qmul.ac.uk

# Development and Characterisation of Flame Retardant Nanoparticulate Bio-based Polymer Composites

A THESIS SUBMITTED TO THE UNIVERSITY OF LONDON FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

2010

By

#### Tharindu Dhanushka Hapuarachchi

School of Engineering and Materials Science Queen Mary University of London Mile End Road, London E1 4NS

# **Declaration**

I declare that the work presented in this thesis is performed entirely by myself during the course of my PhD studies at Queen Mary, University of London and has not been submitted for a degree at this or any other university.

Tharindu Dhanushka Hapuarachchi

# Acknowledgements

Completing this thesis has been thoroughly enjoyable and at times gruelling and I could not have completed this work without key people who have played an important part in my studies. Therefore, I would like to acknowledge all those who contributed.

Firstly, I would like to thank Prof. P.J. Hogg and Dr. G. Ren for giving me the opportunity to begin my research. I would then like to give my full appreciation to my supervisor Prof. A.A.J.M. Peijs who encouraged me and supported me through the latter and most significant part of my studies. Thank you for allowing me to continue and finish my research. Thank you also to Prof. M.J. Reece for your guidance, reassurance and support.

In the absence of financial support, this research would have been difficult to undertake. Therefore I would like to give my appreciation to the Engineering and Physical Sciences Research Council (EPSRC) and also to Dr. Mizi Fan of Building Research Establishment (BRE). I must say a thank you to Mr. Steve Crowther and Ms. Ester Wegher of Menzolit Ltd for allowing me to produce the sheet moulding compound and other materials used in Chapters 3 to 5.

All of the fire-testing was carried out at Interscience Communication's laboratory, Watford. So thank you to Mr. Stephen Grayson, Mr. Suresh Kumar and Ms. Carol Franks for allowing me to conduct a large section of my experimental work at the facility. I want to also thank you for inviting me to your conferences, taking part in technical discussions and for allowing me to use your extensive fire science literature resources. I would like to show my gratitude and thanks to Dr. Sean Gregory and Mr. Damon Sibley of Fire Testing Technology Limited for their assistance with the microcalorimeter and specific technical support. The rest of the experiments were carried out at the School of Materials Science and Engineering, Queen Mary University of London. There are many people who made studying here a real delight. I wish to thank Dr. Monisha Phillips for her valuable help during analytical testing, Dr. Zofia Luklinska and Mr. Mick Wills for support on electron microscopy. The Materials department support staff; Mrs. Sandra Wells, Miss. Victoria Wells, Mr. Jonathan Hills, Mr. Bill Godwin, Mr. Colin Langdown and Mr. Chadha. I wish to give a special thank you to my polymer research group members; Emiliano Bilotti, Hua Deng, Rui Zhang, Nattakan Soykeabkaew, Jianmin Zhang, Antonio Scherillo, Raquel Arevalo Peces, Vimalan Balasubramanian, Harish Patel and Doris Wong. I would also like to say thank you to Mohamed Baklar, Botao Xu, and Payam Jamshidi.

I would like to say a big thank you to my work colleagues at Nanoforce Technology Limited; Danniella Samos, Sanam Ghaffari, Isaiah Adekanmbi, Wei Tu, Matthieu Bedard, Fawad Inam, Urszula Stachewicz, Haixue Yan, Fianti Noor. A special thank you to Mr. Brian Matthews for allowing me to use all the facilities during my studies; Chris Reynolds for all the technical discussions, and Anuj Sood for your companionship.

To my circle of inner friends, without you, this journey would have been a struggle. Your companionship and advice, with a complimentary shoulder to lean on, has helped me immensely through the course of my studies. Key to this was Sanah Akram, whose support through my doctorate was warmly felt. To my dear friend's, Victor Raul Teixeira Contreras and Tyrone Dexter Montack, your trust and enthusiasm has helped me a great deal along the way. Sam Bajomo and Ehsan Mahmood look at where we started and look where we are now; your contributions are much appreciated. I cannot forget to say thank you to Iram Ali for all her motivational talks and encouragement to finish. I would not be where I am today without my family. I really appreciate all your sacrifices, as words cannot describe the love and dedication you have shown me throughout my life; thank you Amma and Thatha. Thank you Nangi, you inspire and make me so proud; keep studying hard and reach for the top; and to Uncle Bappi and Kveta Aunty, your influence has had such a positive impact on my life, vielen Dank.

Beste Ton,

Ik wilde graag een kort stukje voor jou schrijven in je moedertaal. Bedankt dat ik mijn studie mocht afronden. Het was een voorrecht om met jou te werken. Aan het begin van mijn promotie was ik het vertrouwen kwijt, maar jij zorgde ervoor dat ik me weer kon focussen en dat ik weer plezier had. Ik ben je erg dankbaar voor jouw loyaliteit en jouw eindeloze bijdrage aan deze belangrijke mijlpaal in mijn leven.

Nogmaals bedankt.

Hartelijke groeten,

Dhanushka

"There is no wealth like knowledge, and no poverty like ignorance."

- Buddha -

## Abstract

Since the discovery of carbon nanotubes (CNTs) and nanoclays, there has been a great deal of research conducted for uses in applications such as: energy storage, molecular electronics, structural composites, biomedical to name but a few. Owing to their unique intrinsic properties and size means that they have an ever growing potential in the consumer and high technology sectors. In recent years the concept of using these as fillers in polymers has shown great potential. One such function is, as flame retardant additives. These possess much better environmental credentials than halogenated based additives as well as only needing to use a small loading content compared to traditional micron sized fillers. The combination of the above make these fillers ideal candidates for polymers and their composites. Especially with regards to natural fibre composites.

Owing to environmental awareness and economical considerations, natural fibre reinforced polymer composites seem to present a viable alternative to synthetic fibre reinforced polymer composites such as glass fibres. However, merely substituting synthetic with natural fibres only solves part of the problem. Therefore selecting a suitable material for the matrix is key. Cellulose is both the most common biopolymer and the most common organic compound on Earth. About 33 % of all plant matter is cellulose; i.e. the cellulose content of cotton is 90 % and that of wood is 50 %. However just like their synthetic counterparts, the poor flame retardancy of bio-derived versions restricts its application and development in important fields such as construction and transportation.

Traditional methods to improve the flame retardancy of polymeric material involve the use of the micron sized inorganic fillers like ammonium polyphosphate (APP) or aluminium trihydroxide (ATH). Imparting flame retardancy with these inorganic fillers is possible but only with relatively high loadings of more than 50 wt. %. This causes detrimental effects to the mechanical properties of the composite and embrittlement. Applying nanofillers can achieve similar if not better flame retarding performances to their micron sized counterparts but at much lower loading levels (<10 wt.%), thus preserving better the characteristics of the unfilled polymer such as good flow, toughness, surface finish and low density. This is the main focus of this study and it will be achieved by using various experimental techniques including the cone calorimeter and the newly developed microcalorimeter.

After a comprehensive literature survey (**Chapter 2**), the experimental part of the thesis starts with a feasibility study of a flame retardant natural reinforced fibre sheet moulding compound (SMC) (**Chapter 3**). This work demonstrated that with a suitable flame retardant the peak heat release rate can be reduced. **Chapter 4** deals with further improving the flame retardancy of the previously used unsaturated polyester resin. The aim is to study any synergistic behaviour by using aluminium trihydroxide in conjunction with ammonium polyphosphate whilst testing in the cone calorimeter. In **Chapter 5**, nanofillers are used to replace traditional micron sized fillers. In unsaturated polyester, multi-walled carbon nanotubes and sepiolite nanoclay are used together to create a ternary polymer nanocomposite. The microcalorimeter was employed for screening of the heat release rate. This work showed that the ternary nanocomposite showed synergistic behaviour with regards to significantly reducing the peak heat release rate.

The same nanofillers were utilised in **Chapters 6 and 7** but this time in combination with a thermoplastic (polypropylene) and bio-derived polymer (polylactic acid), respectively. In both systems an improved flame retardancy behavior was achieved whist meeting the recyclability objective. **Chapter 8** attempts to show how the optimised natural fibre composite would behaviour in a large scale fire test. The ConeTools software package was used to simulate the single burning item test (SBI) and to classify the end product. This is a necessity with regards to commercialising the product for consumer usage. Finally, **Chapter 9** is a summary of the work carried out in this research as well as possible future work that should be conducted.

# **Table of Contents**

Declaration	i
Acknowledgements	ii
Abstract	v
List of Tables	vii
List of Figures	xi
List of Author's Publications	xviii

## Chapter 1.

Introduction	1
1.2 Nano Materials	
1.2.1 Carbon Nanotubes (CNTs)	3
1.2.2 Current Applications	4
1.2.3 Nanoclays	7
1.2.4 Current Applications	10
1.3 Scope of the Thesis	10
1.4 References	11

## Chapter 2.

Literature Review	
2.1 Prologue	14
2.2 Natural Fibre Reinforced Composites (NFCs)	14
2.2.1 Background	14
2.2.2 Manufacturing Processes	
2.2.3 Thermoplastic Manufacturing	17
2.2.4 Thermoset Manufacturing	17
2.2.5 Current Limitations	
2.3 Introduction to Fire	18

2.3.1 The Establishment of Fire Test Methods	20
2.3.2 The Necessity for Heat Release Rate Tests	21
2.3.3 The Vision of the Cone Calorimeter	22
2.4 Flame Retardancy of Natural Fibre Composites by means	
of Conventional Fillers	25
2.5 Nanofillers as Flame Retardant Additives	28
2.6 Pyrolysis Combustion Flow Calorimeter (PCFC)/Microcalorimet	er
2.6 Pyrolysis Combustion Flow Calorimeter (PCFC)/Microcalorimet 2.6.1 Introduction	er 34
<ul> <li>2.6 Pyrolysis Combustion Flow Calorimeter (PCFC)/Microcalorimet</li> <li>2.6.1 Introduction</li> <li>2.6.2 The Experimental Technique</li> </ul>	er 34 35
<ul> <li>2.6 Pyrolysis Combustion Flow Calorimeter (PCFC)/Microcalorimet</li> <li>2.6.1 Introduction</li></ul>	er 34 35 38
<ul> <li>2.6 Pyrolysis Combustion Flow Calorimeter (PCFC)/Microcalorimet</li> <li>2.6.1 Introduction</li> <li>2.6.2 The Experimental Technique</li> <li>2.6.3 Employing the PCFC as a Flammability Testing Tool</li> <li>2.7 Conclusions</li> </ul>	34 35 38 <b>43</b>

## Chapter 3.

**Reaction to Fire Behaviour of Natural Fibre Reinforced Polymer Composites:** A Feasibility Study

3.1 Introduction51
3.2 Experimental Study
3.2.1 Sample Preparation53
3.2.2 Experimental Detail54
3.3 Results and Discussion
3.3.1 Heat Release Rate (HRR)55
3.3.2 Time to Ignition60
3.3.3 Effect of Irradiance61
3.3.4 Effect of Materials63
3.3.5 Effective Heat of Combustion (EHC)63
3.4 Conclusions
3.5 References

### Chapter 4.

Aluminium Trihydroxide in Combination with Ammonium Polyphosphate as Flame Retardants for Unsaturated Polyester

4.1 Introduction	71
4.2 Experimental Study	
4.2.1 Materials and Specimen Preparation	73
4.2.2 Experimental Procedure	74
4.2.2.1 Cone Calorimetry	74
4.2.1.2 Thermal Analysis	74
4.3 Results and Discussion	
4.3.1 Cone Calorimetry	75
4.3.2 Thermal Analysis	
4.4 Conclusions	88
4.5 References	

## Chapter 5.

Multiwall Carbon Nanotubes and Nanoclays as Flame Retardants for Unsaturated Polyester

5.1 Introduction	93
5.2 Experimental Detail	
5.2.1 Materials	96
5.2.2 Experimental Methods	
5.3 Results and Discussion	
5.3.1 Thermogravimetric Analysis	
5.3.3 Microcalorimetry	101
5.3.4 Cone Calorimetery and Surface Morphology	
5.4 Conclusions	110
5.5 References	111

## Chapter 6.

Multiwall Carbon Nanotubes and Nanoclays as Flame Retardants for Polypropylene

6.1. Introduction	115
6.2. Experimental	
6.2.1. Materials	
6.2.2. Compounding	119
6.2.3. Characterisation	
6.3. Results and Discussion	
6.3.1. Thermogravimetric Analysis	
6.3.1.1. Polypropylene	
6.3.1.2. PP/MWNT	
6.3.1.3. PP/Sepiolite	
6.3.1.4. PP/MWNT/Sepiolite	127
6.3.2. Microcalorimetry	
6.3.3. Cone Calorimetry	133
6.4. Conclusions	136
6.5 References	136

#### Chapter 7.

Multiwall Carbon Nanotubes and Nanoclays as Flame Retardants for Polylactide and its Natural Fibre Reinforced Composites

7.1. Introduction	
7.2. Experimental Procedure	
7.2.1 Materials	
7.2.2 Processing	148
7.2.3 Characterisation	
7.3 Results and Discussion	
7.3.1 Screening using TGA	151
7.3.1.1 PLA/MWNTs	151

7.5 References	164
7.4. Conclusions	
7.3.3 Cone Calorimetery	
7.3.2 Microcalorimetry	
7.3.1.2 PLA/Sepiolite	153

## Chapter 8.

Predicting the Performance of an Optimised Bio-based Composite in the Single Burning Item Test

8.1 Introduction	172
8.2 The Construction Product Directive and Euroclass Classification	173
8.3 Fire Modelling	174
8.3.1 Mathematical Models	174
8.3.2 Zone Models and Field Models	175
8.3.2.1 Stochastic Model	175
8.3.2.2 Deterministic Models	175
8.3.2.3 Field Model	176
8.3.2.4 Zone Model	176
8.4 Scale of Reaction to Fire Tests	177
8.4.1 The Single Burning Item Test (SBI)	178
8.5 Prediction of Bio-based Composite Performance in Single Burning I	tem
Performance Using Cone Calorimeter Data	
8.5.1 Introduction	180
8.5.2 The FIGRA Classification	
8.5.3 The Model	184
8.6 Results from the ConeTools Software Package	
8.7 Conclusions	189
8.8 References	186

## <u>Chapter 9.</u>

Summary and Future Work	
9.1 Summary	
9.2 Future Work	

## **List of Tables**

**Table 2.1.** Properties of glass and cellulose natural fibres. Source from-15-Food and Agriculture Organization of the United Nations.

**Table 2.2.** Parameters measured in the cone calorimeter. Table from -23-Babrauskas and Grayson 1992.

<b>Table 3.1.</b> List of materials tested in the cone calorimeter.	-53-
---	------

**Table 4.1.** UP formulations studied in this investigation.-74-

**Table 4.2.** The delay in the time to ignition (TTI) for the FR UP specimens.
 -75 

**Table 4.3.** The peak heat release rate (PHRR) and total heat release (THR)-77-of the FR UP specimens.

**Table 4.4.** The delay in time to peak effective heat of combustion (EHC)-80-and the reduction in average EHC of the FR UP specimens.

**Table 4.5.** The delay in the time to peak specific extinction area (SEA) for-80-the FR UP specimens.

**Table 4.6.** The total smoke release (TSR) total smoke production (TSP)-82-and carbon monoxide yield (COY) measurements.

**Table 4.7.** The peak mass loss rate (MLR), residual mass (RM) and -83-average specific mass loss for the FR UP specimens from the conecalorimeter.

 Table 5.1. Specimen formulations studied these include binary and ternary systems.
 -96 

 Table 5.2.
 PHRR for the nanocomposites obtained from the -101 

 microcalorimeter.

 Table 5.3. PHRR results for the binary and ternary nanocomposite
 -104 

 formulations in the cone calorimeter.

**Table 6.2.** Parameters obtained for PP and its sepiolite nanocomposite from-127-TGA.

**Table 6.3.** The effect of different CNT grades on peak heat release rate -129-(PHRR), total heat release (THR) and heat release capacity (HRC) of PP nanocomposite. Compounding time 15 minutes, (1 wt.% MWNTs).

**Table 6.4.** The effect of CNT loading on peak heat release rate (PHRR), -129-total heat release (THR) and heat release capacity (HRC) of PP/CNT(Nanocyl 3100).

**Table 6.5.** The effect of sepiolite loading on peak heat release rate (PHRR), -130-total heat release (THR) and heat release capacity (HRC) of PP.

**Table 6.6.** The effect of mixed MWNT plus sepiolite nanofiller loading on-130-peak heat release rate (PHRR), total heat release (THR) and heat releasecapacity (HRC) of PP.

**Table 6.7.** The effect of using convential flame retardant fillers in the -131-microcalorimeter on peak heat release rate (PHRR), total heat release(THR) and heat release capacity (HRC) of PP.

**Table 6.8.** The effect of the burn type in the PCFC on peak heat release-132-rate (PHRR), total heat release (THR) and heat release capacity (HRC).

**Table 6.9.** Cone calorimeter data of PP and its ternary nanocomposite.
 -133 

**Table 7.1.** Parameters obtained for the PLA nanocomposites from the -156-TGA.

**Table 7.2.** The effect of CNT on the heat release capacity of PLA.-157-

**Table 7.3.** The effect of sepiolite clay on the heat release capacity of PLA.
 -157

**Table 7.4.** The effect of ternary nanocompoiste formulations on the heat-157-release capacity of PLA.

 

 Table 7.5. Parameters obtained from the cone calorimeter for the PLA -159composites.

**Table 8.1.** Cone calorimeter data from the specimens below were put into-181-the ConeTools software.

**Table 8.2.** Classes of reaction to fire performance for construction products-183-excluding floorings. Source Council Directive 89/106/EEC 2000.

<b>Table 8.3.</b> Some typical classification for some construction products.         -	183-
---	------

**Table 8.4.** Results from ConeTools software.-188-

# **List of Figures**

**Figure 1.1.** Graphical and computer representation of a SWNT and MWNT -4respectively. Images from <u>http://neurophilosophy.wordpress.com/</u>

**Figure 1.2.** (a) Computed tomography (CT) scanner and (b) a USAF F22 -5-Raptor. Sources <u>http://bryanking.net/</u> and <u>http://www.time.com/</u> respectively.

**Figure 1.3.** (a) Photograph of Easton EA90 SLX wheels and (b) Babolat -6-Aerostorm tennis rackets. Both use CNTs in their structure to improve stiffness without adding weight. Images from <u>http://www.eastonbike.com/</u> and <u>http://www.babolat.com/</u> respectively.

**Figure 1.4.** The oxygen framework of smectite clay nanolayers. Image -7from Zammarano (2007).

**Figure 1.5.** (a) Schematic representation of a single sepiolite fibre, (b) -9-SEM image of pristine sepiolite. Images from Bilotti PhD thesis 2008.

**Figure 2.1.** (a) Photograph showing a Lotus Elise Eco. The rear wing, front -16clamshell and the roof reinforced by hemp fibre and (b) Shows the interior is also composed of natural fibre. Images from Lotus Group PLC.

**Figure 2.2.** Photograph showing flashover in a domestic room (a) before -19and (c) after. Images from <u>www.azobuild.com</u>

**Figure 2.3.** The course of a well-ventilated compartment fire. Image from -19-Friedman, 1975. **Figure 2.4.** (a) General view of the cone calorimeter during a test, (i) -24-Radiant heater (ii) Load cell (iii) Specimen holder (iv) Spark igniter and (b) A full fire scale calorimeter, image from <u>www.azobuild.com.</u>

**Figure 2.5.** FIGRA<sup>\*</sup> curve for PP and of the PP/flax composite vs. time -26-(heat flux 50kw/m<sup>2</sup>) (source from Le Brasa, 2005). (The fire growth index (FIGRA) is the ratio of the rate of heat release rate on time HRR/t<sub>i</sub>).

**Figure 2.6.** Morphologies of polymer/clay nanocomposites: (a) -29conventional miscible microcomposites, (b) partially intercalated and exfoliated, (c) fully intercalated and dispersed and (d) fully exfoliated and dispersed. Source from Usuki et al., 1993.

**Figure. 2.7.** (a) Cross sectional representation of the formation of islands -34and a structured continuous network layer (Image from Cipiriano et al., 2007) (b) Electron micrograph of protective char (Source form Dasari et al., 2009).

**Figure 2.8.** Schematic showing the PCFC setup and how it relates to a real -36life scenario. Image modified from Lyon et al., 2006.

**Figure 2.9.** (a) The PCFC unit (b) sampling stage (c) schematic of the -37-PCFC pyrolyser and combustor setup. Schematic courtesy of FTT UK.

**Figure 2.10.** An example PCFC plot of a research polymer. Image from -41-Lyon and Walters, 2004.

**Figure 3.1**. Specimen before testing with aluminum foil as stated by -54-ASTM E1354.

Figure 3.2. General view of the cone calorimeter during a test. -54-

**Figure 3.3.** HRR curves for FR NFSMC and FR SMC at  $25 \text{ kW/m}^2$ . -56-

Figure 3.4. HRR curves for non-FR NFSMC and non-FR SMC at 25 -56- kW/m<sup>2</sup>.

**Figure 3.5.** HRR curves for FR NFSMC and FR SMC at  $50 \text{ kW/m}^2$ . -57-

Figure 3.6. HRR curves for non-FR NFSMC and non-FR SMC at 50  $-57-kW/m^2$ .

**Figure 3.7.** HRR curves glass vinyl ester, plywood and gypsum board at 25 -58- kW/m<sup>2</sup>.

**Figure 3.8.** HRR curves glass vinyl ester, plywood and gypsum board at 50 -59- kW/m<sup>2</sup>.

**Figure 3.9.** Time to Ignition (TTI) values of materials tested ant both -60-irradiances.

Figure 3.10. Peak heat release rate of materials tested ant both irradiances. -62-

**Figure 3.11.** EHC curves for FR NFSMC and FR SMC at  $25 \text{ kW/m}^2$ . -64-

**Figure 3.12.** HRR curves for non-FR NFSMC and non-FR SMC at 25  $-64-kW/m^2$ .

**Figure 3.13.** EHC curves for FR NFSMC and FR SMC at  $50 \text{ kW/m}^2$ . -65-

**Figure 3.14.** HRR curves for non-FR NFSMC and non-FR SMC at 50 -65- kW/m<sup>2</sup>.

**Figure 3.15.** EHC curves glass vinyl ester, plywood and gypsum board at  $-66-25 \text{ kW/m}^2$ .

**Figure 3.16.** EHC curves glass vinyl ester, plywood and gypsum board at  $-66-25 \text{ kW/m}^2$ .

**Figure 4.1.** The reduction in heat release rate profile for the FR UP -77-specimens.

**Figure 4.2.** The effect on the smoke production release (SPR) of the FR UP -81-specimens.

**Figure 4.3.** The TGA thermogram of fillers used in the UP formulations. -84-

**Figure 4.4a.** The effect of the various fillers and their combination on -84improving the thermal stability and residual mass of UP.

**Figure 4.4b.** The effect of the various fillers and their combination on -85improving the thermal stability and residual mass of UP tested in nitrogen.

**Figure 4.5.** DSC thermogram of the unfilled fillers on their own. -87-

Figure 4.6. DSC thermogram of the FR UP formulations. -87-

**Figure 5.1.** Mass loss vs. temperature, showing the onset of thermal -98-degradation increases with addition of MWNTs.

**Figure 5.2.** Mass loss vs. temperature, showing that the residual char as -99well as the onset temperature have been improved with the addition of sepiolite clay.

Figure 5.3. TGA curve illustrating the thermal degradation behavior of the -100-1Sep:2CNT based ternary system.

**Figure 5.4.** TGA curve, showing improved thermal behaviour and a larger -100-residual mass for the 10Sep:0.5CNT based ternary system.

**Figure 5.5.** HRR vs. time, depicting the lowering of the HRR of the -104nanocomposite specimens.

Figure 5.6. Shows photographs of the specimens post cone calorimetery. -106-

**Figure 5.7.** Mass Loss Rate (MLR) vs. time profile obtained from the cone -108-calorimeter for the nanocomposite specimens.

**Figure 5.8.** Total heat release rate (THR) in the cone calorimeter for the -108-nanocomposite specimens.

**Figure 6.1.** (a) Mini extruder unit (b) conical twin screws (c) twin screw -119extruder (d) tape extrusion.

**Figure 6.2.** (a) Schematic and microcalorimeter setup and how it relates to -121a real life scenario (b) Photograph of FTT's microcalorimeter. Schematic modified from (Lyon and Walters 2004) and photograph courtesy of Fire Testing Technology Ltd.

**Figure 6.3.** (a) Thermogravimetric analysis (TGA) and (b) differential -122thermal analysis (DTA) scans of PP in air and nitrogen, showing the effect of testing PP in different atmospheres. There is an onset decomposition shift of 100 °C when tested in nitrogen rather than air.

**Figure 6.4.** TGA scans of PP with MWNTs in (a) air and (b) nitrogen, -123-showing the effect of CNTs on the decomposition behaviour of PP.

**Figure 6.5.** TGA analysis of PP with sepiolite in (a) air and (b) nitrogen, -125-showing the effect of sepiolite clay on the decomposition behaviour of PP.

**Figure 6.6.** TGA analysis of PP ternary system (10 wt.%Sep+2wt.%CNT) -128in (a) air and (b) nitrogen, showing the increase in residual char and improved thermal stability in air compared to binary nanocomposite systems and neat PP resin.

**Figure 6.7.** Heat release rate vs. time for unfilled PP and ternary PP -134nanocomposite (10 wt.% sepiolite + 2 wt.% MWNT). **Figure 7.1.** Flow diagram of manufacturing and testing procedure involved -149in developing flame retardant natural fibre composite.

**Figure 7.2.** Thermal gravimetric analysis scans of PLA in air and nitrogen, -151-showing the onset decomposition temperature.

**Figure 7.3.** Thermal gravimetric analysis scans of PLA with CNTs in (a) -152air and (b) nitrogen showing the effect of an aerobic and anaerobic environment to the decomposition behaviour of the PLA nanocomposites.

**Figure 7.4.** Thermal gravimetric analysis scans of PLA with sepiolite clay -154in (a) air and (b) nitrogen.

**Figure 7.5.** Thermal gravimetric analysis scans of PLA ternary -155nanocomposite systems in air, showing the increased residual char.

**Figure 7.6.** Heat release rate profile of the specimens tested on the cone -158-calorimeter.

**Figure 7.7.** Photographs taken during cone calorimetery testing (a) unfilled -160-PLA and (b) PLA ternary nanocomposite system, showing the resistance to melting.

**Figure. 7.8.** HRR profile and photographs of (a) PLA/hemp composite -161during testing (b) PLA ternary nanocomposite post testing (c) PLA ternary hemp composite post testing.

**Figure. 7.9.** SEM micrographs of PLA nanocomposite specimens after -162being exposure to 325 °C (a) PLA+CNT (b) PLA+Sep (c) PLA ternary system.

**Figure 8.1.** Schematic diagram for typical two-zone model. Image from -177-Cadorin and Franssen 2003.

**Figure 8.2.** (a) Schematic of the single burning item test (b) Photograph of -179-SBI in progress. Images from EN 13823:2002 standards and Exova Warringtonfire, respectively.

**Figure 8.3.** Graphical representation of lines with a constant FIGRA value -182of 120,250,750. Image from Federation of European Rigid Polyurethane Foam Associations report "Figra Report".

**Figure 8.4.** Suggestion of three different routes for development of the -184effective heat releasing area in the SBI test. Image from Hansen 2002.

**Figure 8.5.** Screen shot of ConeTools input and data generation screen. -187-Image courtesy of Interscience Communications.

# **List of Author's Publications**

- Hapuarachchi. T.D, Ren. G, Fan. M, Hogg. P.J and Peijs. T: *Fire Retardancy* of Natural Fibre Reinforced Sheet Moulding Compound. Applied Composite Materials. 2007.14: p. 251-264.
- 2. Hapuarachchi. T.D and Peijs. T: Aluminium trihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin. Express Polymer Letters. 2009. **3**. No 11. p. 743-751.
- Hapuarachchi. T.D, Bilotti. E, Reynolds. C.T and Peijs. T: Multiwalled Carbon Nanotubes and Sepiolite Nanoclay as Flame Retardants for Unsaturated Polyester. Submitted to Fire and Materials.
- T.Dhanushka. Hapuarachchi, Emiliano. Bilotti, Ton. Peijs: Thermal degradation and flammability behaviour of polypropylene / clay / carbon nanotube nanocomposite systems. Submitted to Polymers for Advanced Technologies.
- 5. T. Dhanushka. Hapuarachchi and Ton. Peijs : *Multiwalled carbon nanotubes and sepiolite nanoclays as flame retardants for polylactide and its natural fibre reinforced composites*. Submitted to Composites Part A: Applied Science and Manufacturing.

# 1

## Introduction

The combination of natural fibres with other materials to form composites is not an original concept. The ancient Egyptians were one of the first documented civilisations to use the first natural composites systems for housing; clay and straw were used to build walls. During the early part of the 20<sup>th</sup> Century, the use of natural fibre materials fell due to the development of stiffer, tougher and lighter synthetic materials. The success and tremendous growth of the petrochemical industry in the 20<sup>th</sup> Century slowed the growth of bio-based products. However, environmental as well as economic factors are now the driving force towards greater utilisation of bio-based polymers and materials. The challenge to the scientific community is to develop the technology needed to make the bio-based materials revolution a reality.

The production of chemicals and materials from bio-based feedstock is expected to increase from today's 5 % level to ~12 % in 2010, 18 % in 2020 and 25 % in 2030 (Wedin, 2004). Expectations are that two-thirds of the \$1.4 trillion global chemical industry can eventually be based on renewable resources. Petroleum transitioned from a single product (kerosene in the early 1900's) to a multiproduct industry (petrol, jet fuel, diesel fuel, asphalt and polymeric materials) between the late 19<sup>th</sup> and the middle of the 20<sup>th</sup> Century. Research conducted from the 1990's to the present has led to many new bio-based products (Drumright *et al.*, 2000; Thomas, 2001; Peijs, 2002; Metha *et al.*, 2004).

Some examples include polylactic acid (PLA) from corn; lubricants from vegetable oil and polyurethane products from soy oil to name but a few. The persistence of plastics in the environment, the shortage of landfill space, concerns over emissions during incineration, and entrapment and ingestion hazards from these materials have spurred efforts to develop biodegradable plastics. Several of the world's largest chemical companies, including DuPont, Monsanto and Cargill have announced a major shift in their base science and technology from traditional petrochemical processing to life sciences (Thayer, 1999). DuPont and Monsanto have invested \$12.5 billion to acquire expertise in agricultural biotechnology (Thayer, 1999). Biocomposites are now starting to migrate into the mainstream and bio-based polymers may soon be competing with commodity plastics. Composite materials, especially green composites fit well into this new concept shift. Simply stated, bio-based materials include industrial products for durable goods applications, made from renewable agricultural and forestry feed stocks, including wood, agricultural waste, grasses and natural fibres.

With numerous advantages that polymeric materials provide to society in everyday life, there is one obvious disadvantage related to the high flammability of many polymers. Fire hazard is a combination of many factors, including; ignitability, ease of extinction, flammability of the volatile products generated, rate of heat released, flame spread, smoke obstruction and smoke toxicity (Hirschler, 2001; Purser, 2000; Irvine *et al.*, 2000). According to fire statistics, more than 12 million fires break out every year in the United States, Europe, Russia and China killing some 300,000 people and injuring several hundreds of thousands. Calculating the direct worldwide losses and costs is difficult and \$500 million is an estimate based on some national data (Manor and Georlette, 2005). Therefore, in the pursuit of improved approached to flame retarding polymers, a wide variety of concerns must be addressed. The low cost of polymers requires that the flame retardant (FR) approach be of low cost. This limits the solutions to the problem primarily to additive type approaches.

These additives must be easily processed with the polymer, must not excessively degrade the other performance properties, and must not create environmental problems in terms of recycling or disposal. Conventional systems such as brominated polymers prevent flame spread but have the significant disadvantage of producing dense smoke and corrosive combustion by-products. Another filler commonly used is hydrated alumina or aluminium trihydrate (ATH), which is looked upon as a greener FR. The effectiveness of this flame retardant tends to be limited since large amounts of the filler is needed for adequate flame retardancy (>50 wt.%), which has a the detrimental effect on processability and mechanical properties. The field of nanotechnology has also made its presence in the discipline of fire science. Since the early 1990's, the subject of polymer nanocomposites has expanded greatly to its current status as a major field of polymer materials research. It is now released that polymer nanocomposites, as a class of materials, were in use long before this field of research was officially named in the early 1990's. Indeed, work published as early as 1961, and patents going back to the 1940's, have shown that layered silicates (or clays) can be combined with polymers in small amounts (typically 2-10 wt.%) to produce new materials with greatly improved thermal properties and flame retardancy. More recent work has looked into using carbon nanotubes to reduce the flame retardancy of polymers. However these concepts are still in its infancy and need to be researched further to be considered advantageous in commercial ventures.

#### **1.2 Nano Materials**

#### 1.2.1 Carbon Nanotubes (CNTs)

The reader is advised to read further material about CNTs (Thostenson *et al.*, 2001) as this is only a brief introduction. The morphology of a carbon nanotube is defined by the orientation and magnitude of the chiral vector in a graphene sheet, which is wrapped up to form the single-walled carbon nanotube (SWNT) (Thostenson *et al.*, 2005).

The density of a SWNT is about 1.33-1.40 g/cm<sup>3</sup>, which is just one-half of the density of aluminum. The elastic modulus of SWNT is comparable to that of diamond (1 TPa). The reported tensile strength of SWNT is much higher than that of high-strength carbon fibre (~ 80 GPa). The thermal conductivity of SWNT is predicted to be 6000 W/(m·K) at room temperature; this is nearly double the thermal conductivity of diamond of 3320 W/(m·K). SWNTs are stable up to 2800 °C in vacuum and 750 °C in air, whereas metal wires in microchips melt at 600-1000 °C. Multi-walled nanotubes (MWNT) consist of several layers of graphite rolled in on themselves to form a tube shape which improves their chemical and thermal resistance.





*Figure 1.1. Graphical and computer representation of a SWNT and MWNT respectively. Images from <u>http://neurophilosophy.wordpress.com/</u>* 

#### 1.2.2 Current Applications

The special nature of carbon combined with the molecular perfection of CNTs endow them with exceptionally high material properties such as electrical and thermal conductivity, strength, stiffness, and toughness. The high-frequency carbon-carbon bond vibrations provide an intrinsic thermal conductivity higher than even diamond. In most materials, however, notably MWNTs the actual observed material properties - strength, electrical conductivity, etc - are degraded very substantially by the occurrence of defects in their structure. For example, high strength steel typically fails at about 1% of its theoretical breaking strength.

The SWNTs, however, achieve values very close to their theoretical limits because of their perfection of structure and their molecular perfection. This aspect is part of the unique story of CNTs. Much of the history of plastics over the last half century has been as a replacement for metal. For structural applications, plastics have made tremendous headway, but not where electrical conductivity is required, plastics being famously good electrical insulators. This deficiency is overcome by loading plastics up with conductive fillers, such as carbon black and graphite fibres (the larger ones used to make golf clubs and tennis racquets). The loading required to provide the necessary conductivity is typically high (> 10 wt.%) resulting in heavier parts, and more importantly, plastic parts whose structural properties (ductility) are highly degraded. It is well established that higher aspect ratio fillers require lower loadings to achieve a given level of conductivity. Nanotubes are ideal in developing conductive polymer composites (CPC), since they have the highest aspect ratio of any carbon based filler. In addition, their natural tendency to form ropes provides inherently very long conductive pathways even at ultralow loadings. Applications that exploit this behaviour of CNTs include EMI/RFI shielding composites and coatings for enclosures, gaskets, and other uses; electrostatic dissipation (ESD), and anti-static materials and (even transparent) coatings; and radarabsorbing materials.



*Figure 1.2.* (a) Computed tomography (CT) scanner and (b) a USAF F22 Raptor. Images from <u>http://bryanking.net/</u> and <u>http://www.time.com/</u> respectively.

The ultimate properties of CNTs are not limited to electrical and thermal conductivities, but also include mechanical properties, such as stiffness, toughness, and strength which make them ideal for **structural application**. Current functions are: combat jackets that use CNTs in ultra-strong fibres and to monitor the condition of the wearer (ISN, 2008).



*Figure 1.3.* (a) Photograph of Easton EA90 SLX wheels and (b) Babolat Aerostorm tennis rackets. Both use CNTs in their structure to improve stiffness without adding weight. Images from <u>http://www.eastonbike.com/</u> and <u>http://www.babolat.com/</u> respectively.

The exploration of CNTs in **biomedical applications** is just underway and has significant potential. However, there has been a numerous amount of research papers published about the potential health implications of handling carbon nanotubes. Ma-Hock *et al* (2009) carried out experiments which composed of exposing laboratory rodents to MWNTs and concluded no systemic toxicity. On the other hand, other researchers have concluded that exposure to SWNTs caused pulmonary lesions (Chiuwing *et al.*, 2006; Lam *et al.*, 2004; Warheit *et al.*, 2004; Walters *et al.*, 2001; Maynard *et al.*, 2004). Journeay *et al* (2008) carried out a study on effects of CNTs aspect ratio on the toxicity effect to lung tissue.

It was discovered that the aspect ratio has implications for clearance from the lungs and for phagocytic cells such as the macrophage. Therefore particularly care must be taken when studying the health implications of CNTs.

#### 1.2.3 Nanoclays

As mentioned previously, nanocomposites usually exhibit improved performance properties compared to conventional composites owing to their unique phase morphology and improved interfacial properties. For these reasons, nanostructured organic-inorganic composites have attracted considerable attention from both fundamental research and an applications point of view. The structure of a typically smectite clay nanolayer is presented in Figure 1.4.



*Figure 1.4.* The oxygen framework of smectite clay nanolayers. Image from Zammarano (2007).

Silica is the dominant constituent of clays, with alumina being essential, as well. See the structure in Figure 1.4. Clays have a layered structure consisting of two types of sheets, the silica tetrahedral and alumina octahedral sheets. The silica tetrahedral sheet consists of  $SiO_4$  groups linked together to form a hexagonal network of the repeating units of composition  $Si_4O_{10}$ . The alumina sheet consists of two planes of closely packed oxygen's or hydroxyl's between which octahedrally coordinated aluminum atoms are imbedded in such a position that they are equidistant from six oxygen's or hydroxyl's. The two tetrahedral sheets sandwich the octahedral, sharing their apex oxygen's with the latter.

Montmorillonite is a type of clay and is classified as magnesium aluminum silicate which has a sheet morphology, and can be used to make a new class of polymer/clay nanocomposites. The total surface area of montmorillonite can be as large as  $750 \text{ m}^2/\text{g}$ and the high aspect ratio (70-150) contributes to its rheological benefits. In order to make the clay into organoclay it is reacted them with organ-cationic surfactants. The modified clays then change from hydrophilic to organophilic. The organically modified clays are able to impart various rheological characteristics to organic polymer. When a small amount of the organoclay like 4 wt.% is added into a polymer, there can be a significant increase in mechanical properties including tensile strength, Young's and flexural moduli. Therefore, composites can be made lighter and maintain transparency because the filler is in the nanometer range. Moreover, the heat resistant property of organoclay can increase the heat distortion temperature of the composites by making them more dimensionally stable and flame retardant. On the other hand, the high aspect ratio of the organoclay provides a tortuous path which makes difficulty for gas and vapour passing through. Therefore, barrier properties of polymer can be greatly improved.

Another type of nanoclay is **sepiolite**. It is non-swelling, lightweight and absorbent clay with a large specific surface area. Sepiolite has a needle-like morphology unlike other clays. It is an important material for a wide range of applications due to its extraordinary particle shape, porosity, and high surface area and for its outstanding sorption capacity and colloidal properties.



*Figure 1.5.* (a) Schematic representation of a single sepiolite fibre and (b) SEM image of pristine sepiolite. Images from Bilotti PhD thesis 2008.

Sepiolite has a formula  $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4.8H_2O$  and is a hydrated magnesium silicate. It is not a layered phyllosilicate like other clays. Quincunx can be used to describe the structure of sepiolite (five object arranged such as, one occupies the centre of a rectangle or square and the other four occupy the corners) that are separated by parallel channels as shown in Figure 1.5. Unlike other clays, which produce plate-like particles for their structures, sepiolite produces needle-like particles. From the range of clay minerals available, sepiolite has the highest surface area (BET, N<sub>2</sub>), about 300 m<sup>2</sup>/g (*Bilotti, 2009*).

The hydophilicity of sepiolite is marked by the high density of silanol groups (-SiOH). The cation exchange capacity is very low as the silicate lattice does not have a significant negative charge. The particles of sepiolite have a width of 0.01  $\mu$ m and an average length of 1  $\mu$ m to 2  $\mu$ m. They include open channels with dimensions of 3.6 Å × 10.6 Å, consecutively along the length of the axis of the particle. Sepiolite has a high porosity due its extensive capillary network and its light-weight since it has a vast empty space.

#### 1.2.4 Current Applications

The outstanding sorptive and colloidal properties of sepiolite provide specific solutions for a wide variety of industrial applications. **Industrial absorbents:** Sepiolite absorbs liquid spills and leaks keeping work and transit areas dry and safe. Sepiolite is a nonflammable material with high liquid absorbing capacity, suitable mechanical strength of the granules even in wet conditions, and chemical inertness which avoids reaction with absorbed liquids. **Polymers and Elastomers:** The use of sepiolite fillers improve processing, dimensional stability, mechanical strength and thermal resistance. **Rheological additives for organic systems:** Organically modified sepiolite allows controlling the rheological behaviour of different solvent-based systems as paints, greases, resins and inks enhancing their stability under a wide temperature range and making for easier application.

#### **1.3 Scope of the Thesis**

The aim of this thesis is to develop and characterise a flame retardant bio-based polymer composite utilising both CNTs and sepiolite as flame retardant additives. Encompassed within this envelope is; (**Chapter 3**) which is a feasibility study of using cellulose based fibres to reinforce a thermoset polymer in relation to its flammability.
(Chapter 4) possible improvements to the flammability of the thermoset polymer using conventional flame retardant additives; (Chapter 5) a shift towards nano-sized filler solutions for reducing the flammability of a thermoset polymer; (Chapter 6) shifting from a thermoset to thermoplastic base resin with nanofillers, (Chapter 7) moving to a fully bio-based nanocomposite system and (Chapter 8) finally carrying out some fire simulation work to show the predictive performances of the optimised composite if taken to full scale application use.

# **1.4 References**

Bilotti. E: Polymer/Sepiolite Clay Nanocomposites. Thesis (PhD), Queen Mary University of London, 2008.

Drumright. R. E, Gruber. P.R and Henton. D.E: *Polylactic acid technology*. Advanced Materials. 2000. **12**(23): p. 1841-1846.

Hirschler. M: *Fire performance of organic polymers, thermal decomposition, and chemical composition*, in: G.L. Nelson and C.A. Wilkie, Eds. Fire and Polymers: Materials and Solutions for Hazard Prevention. ACS Symposium Series, Vol. 797. American Chemical Society, Washington, DC, (2001): p. 293-306.

Irvine. D. J, McCluskey. J.A and Robinson. I.M: *Fire hazards and some common Polymers*. Polymer Degradation and Stability. 2000. **67**: p. 383-396.

Institute for Soldier Nanotechnologies (ISN), Massachusetts Institute of Technology, Cambridge, MA, USA, <u>http://web.mit.edu/isn/.</u>

Journeay. W.S, Suri. S.S, Fenniri. H and Singh. B: *High-aspect ratio nanoparticles in nanotoxicology*. Integrated Environmental Assessment and Management. January 2008. **4**(1): p. 128-9.

Lam. C.W, James. J.T, McCluskey. R and Hunter. R.L: *Pulmonary toxicity of singlewall carbon nanotubes in mice 7 and 90 days after intratracheal instillation*. Toxicological Sciences. 2004. **77**: p. 126-134.

Lam. C.W, James. J.T, McCluskey. R, Sivaram. A and Hunter. R.L: A Review of Carbon Nanotube Toxicity and Assessment of Potential Occupational and Environmental Health Risks. Critical Reviews in Toxicology. 2006. **36**(3): p. 189-217.

Manor. O and Georlette. P: *Flame retardants and the environment*. Speciality Chemicals Magazine. 2005. **25**(7): p. 36-39.

Maynard. A. D, Baron. P. A, Foley. M, Shvedova. A. A, Kisin. E. R and Castranova. V: *Exposure to carbon nanotube material I: Aerosol release during the handling of unrefined single walled carbon nanotube material.* Journal of Toxicology and Environmental Health, Part A. 9<sup>th</sup> January 2004. **67**(1): p. 87-107.

Ma-Hock. L, Treumann. S, Strauss. V, Brill. S, Luizi. F, Mertler. M, Wiench. K, O. Gamer. A, Van Ravenzwaay. B and Landsiedel. R: *Inhalation toxicity of multi-wall carbon nanotubes in rats exposed for three months*. Toxicological Sciences. 2009. **112**(2): p. 468-481

Metha. G, Mohanty. A.K, Misra. M and Drzal. L.T: *Biobased resin as a toughening agent for biocomposites*. Composites Part A: Applied Science and Manufacturing. 2004.
35: p. 363-370.

Peijs. T: Composites turn green. e-Polymers (2002): p. 1-12 n. T\_002.

Purser. D. A: *Toxic product yield and hazard assessment for fully enclosed design fires*. Polymer International. 2000. **49**: p. 1232-1255.

Thayer. A. M: *Chasing the Innovation Wave*. Chemical Engineering News. 8<sup>th</sup> February 1999. **77**: p. 17-22.

Thomas. S. M: *Biomass Grass makes for composite Cars*. Materials World. 2001. **9**: p. 24.

Thostenson. E. T, Ren. Z. F and Chou T.W: *Advances in the science and technology of carbon nanotubes and their composites: a review*. Composite Science Technology. 2001. **61**(13): p. 1899-1912.

Thostenson. E. T, Li. C and Chou. Tsu-Wei: *Nanocomposites in context (review)*. Composites Science and Technology. 2005. **65**: p. 491-516.

Walters. D.A, Casavant. M. J, Qin. X. C, Huffman. C. B, Boul. P. J, Ericson. L. M, Haroz/ E. H, O'Connell. M. J, Smith. K and Colbert, D. T: *In-plane-aligned membranes of carbon nanotubes*. Chemical Physics Letters. 2001. **338**: p. 14-20.

Warheit. D.B, Laurence. B. R, Reed. K. L, Roach. D.H, Reynolds. G. A. M and Webb, T. R: *Comparative Pulmonary Toxicity Assessment of Single-wall Carbon Nanotubes in Rats.* Toxicological Sciences. 2004. **77**: p.117-125.

Wedin. R: Chemistry on a High Carb Diet. American Chemical Society. Spring 2004. p. 30-35.

Zammarano. M. *Thermoset Fire Retardant Nanocomposites*. In: Morgan A.B and Wilkie C.A, Editors. Flame retardant polymer nanocomposites. Wiley-Interscience (2007).

# **Literature Review**

### 2.1 Prologue

This chapter gives a broad overview of the field which then focuses into the experimental chapters hereafter. In order to familiarise the reader with this work, particular topics have been brought forward and discussed. This is the duty of the literature survey which tries to encompass; the relevant background, fundamental theories, experimental procedures and current research in this field of research.

# 2.2 Natural Fibre Reinforced Composites (NFCs)

#### 2.2.1 Background

Classic fibre reinforced composites often cause considerable problems in terms of reuse, recycling and disposal at the end of their lifetimes. This is primarily because the compound consists of miscellaneous and usually very stable fibres such as carbon and glass fibres. A simple landfill disposal is not an option, since increased environmental sensitivity has resulted in tighter laws and regulations (e.g. Regulation for the Prevention of Packaging Waste, Recycling and Waste Management Law) (CIWM). Eco-friendly alternatives are now being explored and examined, such as the recovery of raw materials, CO<sub>2</sub> neutral thermal utilization, or biodegradation.

An interesting option to meet these demands may be provided by natural fibre reinforced polymer composites (NFCs). This technology utilises the high stiffness and strength of filamentary materials, of which cellulose is only one example. Cellulose composites include everything from straw reinforced clay materials to cellulose fibres in radial tyres. In a way, many paper and board materials may be conceived as a type of composite, but the usual reference is a reinforced matrix material. As early as the beginning of the  $20^{\rm th}$  century (Baekeland), composite materials were applied for the fabrication of large quantities of sheets, tubes and pipes for electric purposes, usually fibre reinforced phenol or melamine-formaldehyde resins. The industrial use of biocomposites in the manufacturing industry was promulgated by Henry Ford in the late 1930's. There is also a long history of reinforced composite materials derived from fibres such as jute, flax, sisal and hemp. The interest in using cellulosic materials in composites is derived from a combination of favourable economics, the fact that cellulosics are a renewable resource and the high modulus of crystalline cellulose (~ 138 GPa).

Fibre					
	E-glass	Hemp	Sisal	Jute	
Density (g/cm <sup>3</sup> )	2.55	1.48	1.33	1.46	
Tensile strength <sup>*</sup> (10E <sup>6</sup> N/m)	2400	400-900	220	400-800	
E-modulus (GPa)	73	70	6	10-30	
Elongation at failure (%)	3	1.6	2-3	1.8	
Moisture absorption (%)	-	8	10	12	

**Table 2.1.** Properties of glass and cellulose natural fibres. Source from Food andAgriculture Organization of the United Nations.

<sup>\*</sup> Tensile strength strongly depends on type of fibre, being a bundle or a single filament

Economically and ecological accepted manufacturing technologies are involved as well. The use of natural fibre composites will also have an effect on the reduction of usage of wood, which causes deforestation and impacts the environment. Due to their lighter weight, high stiffness to weight ratio, corrosion resistance and other advantages, natural fibre based composites are becoming important composite materials in building and civil engineering fields. In the case of synthetic fibre based composites, despite their usefulness in service, these materials are difficult to be recycled after their service life. However, natural fibre based composites are recognised as a realistic alternative to conventional glass reinforced composites.







*Figure 2.1.* (a) Photograph showing a Lotus Elise Eco. The rear wing, front clamshell and the roof reinforced by hemp fibre and (b) Shows the interior is also composed of natural fibre. Images from Lotus Group PLC  $\mathbb{R}$ .

#### 2.2.2 Manufacturing Processes

At the present time, practically all natural fibre composites are manufactured using press moulded technology, thermoplastic or thermoset. However the trend is now towards thermoplastic matrix systems. The reason for this change lie in the easier processing and recycling possibilities of thermoplastics. Injection moulding can also be used for the production of NFCs. In general, injection moulding is the preferred route to manufacturing the more complicated shaped panels that are difficult, if not impossible, to make by single press-moulded, methods; composite panel manufacturers expect that injection moulding will become increasingly important.

#### 2.2.3 Thermoplastic Manufacturing

In this process one of either two methods of blending NFs with thermoplastic fibres such as polypropylene (PP) is used. The fibres are first cut to lengths of between 80 and 120 mm and then these fibres are blended as uniformly as is practicable before being carded and made into felt by a needle punching process, or separate NFs and thermoplastic needle felts are made. These are then built up into as many layers as necessary and are then placed in the moulding presses under heat to achieve the panels required. In order to improve the NFs and thermoplastic fibre bonding a small amount of a compatibilizer such as malic anhydride (MA-g-PP) is sometimes used as an interface between the fibre and the matrix (Peijs *et al.*, 1998). Another technique is to impregnate the NFs with a polymer melt. Compatibilisation must be taken into consideration due to the polar and non-polar nature of the polymer and fibre. This mismatch can result in lower composite properties e.g. mechanical properties (Garkhail *et al.*, 2000).

#### 2.2.4 Thermoset Manufacturing

The NF felts are sprayed with or soaked in synthetic binders such as epoxy resins or polyurethane and then moulded to the desired shape. Concerning the fibres used, it has been found helpful to blend the finer fibres (flax, jute) with a proportion of the coarser fibres (hemp, sisal, kenaf) as the finer fibres impart stability to the blend but may prevent their complete permeation by the binder if used on their own.

#### 2.2.5 Current Limitations

Traditional biocomposites, like paper and board materials, are attractive because of the low environmental impact of their product life cycle. Yet composites, based on synthetic polymers, are often more competitive from an economic point of view. There is also a difficulty of these new composites to break into mature artificial composites markets. The performance of biocomposites must generally be improved, for instance with respect to their moisture sensitivity and low toughness. In general there is a delicate balance between product performance and the rate and degradation of biocomposites, which must be solved. Finally, there has been a lack of suitable processing methods to manufacture new biocomposites. However one of the limitations of using natural fibre composites is their poor inherent flammability resistance. A number of researchers (Schartel *et al.*, 2003; Le Brasa *et al.*, 2005) have tried to improve the reaction to fire performance of these materials. These studies confirm that with adequate modification of the resin system, natural fibre composites can have improved reaction to fire properties and can really be a viable alternative to synthetic polymer composites.

# **2.3 Introduction to Fire**

Few discoveries have had as much influence on the development of mankind as the skill of generating fire. This capability is a basic requirement of all civilizations, since it enabled man to reduce his dependences on a hostile environment. Archaeology indicates that ancestors of modern humans such as Homo erectus seem to have been using controlled fire as early as some 790,000 years ago. The Cradle of Humankind site located 50 kilometres northwest of Johannesburg South Africa has evidence for controlled fire a million years ago. Today, the applications of fire are numerous. In its broadest sense, fire is used by nearly every human being on earth in a controlled setting every day. Owners of internal combustion engines use fire in vehicles every time they drive. Thermal power stations provide electricity for a large percentage of humanity.

The self-sustaining nature of fire makes it extremely dangerous if uncontrolled. Fire has been described as a "living entity consuming both oxygen and matter in order to survive" (Adams, 2004). Even with its numerous uses, uncontrolled it can be very disastrous. Every year about 5,000 people are killed by fires in Europe and more than 4,000 people in USA. Direct property loss through fire is roughly 0.2 % of the gross domestic product and the total cost of fires is around 1 % of the gross domestic product (Beyer, 2005). This is the driving force for scientists and safety bodies to develop new materials to tackle this problem.



*Figure 2.2. Photograph showing flashover in a domestic room (a) before and (c) after. Images from <u>www.azobuild.com</u>.* 



Figure 2.3. The course of a well-ventilated compartment fire. Image from Friedman, 1975.

Once a fire starts in a room containing flammable materials; it will generate heat, which can heat up and ignite additional combustible materials. As a consequence the rate at which the fire progresses speeds up because more and more heat is released and a progressive increase in the room temperature is observed. The radiant heat and temperature can rise to such an extent that all materials within the room are ignited very easily, resulting in an extremely high rate of fire spread. This point in time is called flashover and leads to a fully developed fire. Flashover normally occurs at around 500 °C and an incident heat flux at floor level of 20 kW/m<sup>2</sup>. Escape from the room will then be virtually impossible and the spread of the fire to other rooms is highly likely. When a fire reaches flashover, every polymer will release roughly 20 % of its weight as carbon monoxide, resulting in excess toxic smoke. Consequently, most people die in big fires and 90 % of fire deaths are the result of fires becoming "too big", resulting in too much toxic smoke.

#### 2.3.1 The Establishment of Fire Test Methods

The 1988 edition of the compilation of fire tests by the American Society for Testing and Materials (ASTM) alone lists some 77 tests. ASTM is only one of many US and international organisations publishing fire test standards; the actual number of fire tests in use is at least in the hundreds. It is customary to divide the actual fire test standards into two broad categories: (i) reaction to fire, or flammability, and (ii) fire endurance, or fire resistance. Reaction to fire is how a material or product responds to heating or to a fire. This includes ignitability, flame spread, heat release rate, and the production of various toxic, obstructing, corrosive etc, products of combustion. Reaction to fire largely concerns the emission of undesired components, e.g. how much heat is emitted, how much smoke, or how fast does the first emission start (ignitability). A reaction to fire test is typically performed on combustibles. Fire endurance, by contrast, asks the questions: how well does a product prevent the spread of fire beyond the confines of the room? Such a test is performed on barriers to fire and load bearing elements, such as walls, floors, ceilings, doors, windows and related items. Manufactures of resins, flame retardants, and plastic products are accustomed to describing reaction to fire performance according to two tests: the UL 94 vertical Bunsen burner test and limiting oxygen index (LOI) test. The LOI test determines how low of an oxygen fraction the test specimens can continue burning in a candle-like configuration. It has never been correlated to any aspect of full scale fires. The UL 94 test was developed to determine the resistance to ignition of small plastic parts, such as may be found inside electrical switches. For this purpose, it is an accurate simulation of a real fire source.

#### 2.3.2 The Necessity for Heat Release Rate Tests

Heat release rate (HRR) is the driving force of a fire. This happens as a means of positive feedback in that heat produces more heat. This occurrence does not happen for all variables, for instance, with carbon monoxide. Carbon monoxide does not produce more carbon monoxide. Most other variables in the fire are correlated to HRR. The generation of most other undesirable fire products tend to increase with increasing HRR. Smoke, toxic gases, room temperature and other fire hazard variables generally progress to increase with HRR, as HRR intensifies. Furthermore a high HRR indicates a high threat to life. Some fire hazard variables do not relate to threats to life. An example could be, a product shows easy ignitability or flame spread rates, however this does not necessarily mean that the fire conditions are expected to be dangerous. Such behaviour may merely suggest a predisposition to nuisance fires. However high HRR is intrinsically dangerous. This is because high HRR causes high temperatures and high heat flux environments, which may prove lethal to occupants.

#### 2.3.3 The Vision of the Cone Calorimeter

The cone calorimeter is the most significant dynamic bench scale instrument in the field of fire testing. Heat release rate is the key measurement required to assess the fire severity and development for materials and products. The cone calorimeter was first announced in 1982 by workers at the National Institute of Standards and Technology (NIST) formerly NBS, in the USA, with input predominantly from Vytenis Babrauskas (1982). However ISO 5660-1 standard was only published in its final form in 1993 and the smoke evolution measurement was supplemented later in 2001 ISO 5660 part 2 (2002). The American Society for Testing and Materials has also recognised the cone calorimeter as a certified reaction to fire apparatus in ASTM 1354 (2004). The two cone calorimeter standards are identical, except for the fact that the ISO standard does not include the smoke measurement. As a result, heat release rate research using the cone calorimeter started from that point on. It was decided to produce an improved bench scale heat release rate test which would overcome the deficiencies of existing small scale heat release rate tests which relied upon the measurement of the outflow enthalpy of enclosed systems. Oxygen consumption calorimetery was identified as the best measurement method. In 1917, Thornton showed that for a large number of organic liquids and gases, a relatively constant net amount of heat is released per unit mass of oxygen consumed for complete combustion. Huggett (1980) found that this was also true for organic solids and obtained an average value for this constant of 13 MJ/kg of O<sub>2</sub>. This value may be used for practical applications and is accurate with very few exceptions to within  $\pm$  5 %. Thornton's rule implies that it is sufficient to measure the oxygen consumed in a combustion system in order to determine the net heat release. Therefore, for example, in compartment fires, the oxygen consumption technique is much more accurate and easier to implement than methods based on measuring all the terms in a heat balance of the compartment.

The cone calorimeter is designed to investigate "reaction to fire" of materials and products intended for industrial or commercial market use. This test allows an estimation of parameters such as shown in Table 2.2.

Parameter	Unit
Heat Release Rate (HRR):	kW/m <sup>2</sup>
Average Heat Release Rate:	kW/m <sup>2</sup>
Total Heat Released (THR):	MJ/m <sup>2</sup>
Effective Heat of Combustion (EHC):	MJ/kg
Specific Extinction Area (SEA):	m²/kg
Exhaust Flow Rate	m <sup>3</sup> /s
Mass Loss Rate (MLR):	g/s
Final Sample Mass:	g
Time to Sustained Ignition:	S
CO/CO <sub>2</sub> Production (optional):	g/s

*Table 2.2.* Parameters measured in the cone calorimeter. Table from Babrauskas and Grayson 1992.

Reaction to fire tests ascertain whether the material takes part in the fire, their contribution to flame spread and their tendency to propagate and expand the fire by altering the thermal environment (preheating). The main importance in looking at the reaction to fire is to study the behaviour of the material before flashover as seen in Figures 2.2; this is the phenomenon in which the furniture and other materials in the room ignite virtually simultaneously. The intention is to study the smouldering to combustion performance of the material before full scale fire transpires, as this is the interim before the fire can be controlled and resultantly extinguished. According to the ISO concept, the phenomenon accompanying the fire such as ignitability, flame spread and heat release rate can be grouped into the primary effects of fire.

The secondary fire effects, smoke and toxic fire gases, occur alongside these phenomena, particularly as the rate of flame spread increases. Together with the radiant heat release and lack of oxygen they represent the greatest danger to people. The principal result of using the cone calorimeter is a heat release rate curve over the duration of the test. The HRR due to combustion is determined using oxygen consumption methodology. The overwhelming importance of the role of HRR in fires must be made apparent. Heat release rate is not just one of many variables used to describe a fire. It is, in fact, the single most important variable in describing fire hazards. The information gathered from the cone calorimetery tests can be used in computer modelling to evaluate what would happen in a large scale fire.



**Figure 2.4.** (a) General view of the cone calorimeter during a test, (i) Radiant heater (ii) Load cell (iii) Specimen holder (iv) Spark igniter and (b) A full fire scale calorimeter, image from <u>www.azobuild.com</u>.

# **2.4 Flame Retardancy of Natural Fibre Composites by** means of Conventional Fillers

Several works have been published in the field of fire testing of natural fibre composites. Schartel *et al.*, (2003) looked into improving the fire retardancy of flax fibre polypropylene (PP) composites. The group studied the effects of adding ammonium polyphosphate (APP) and expandable graphite (EG) into the polymer composite, as a flame retardant (FR) additive. Thermal analysis was achieved using Thermogravimetric-Fourier Transform Infrared Spectrometry (TGA-FTIR) to assess the mass loss in relation to temperature and the composition of the gases evolved. A narrow group of tests were selected to evaluate the steady state heat release, which was achieved by cone calorimetery. Flammability properties were assessed by using limited oxygen index (LOI) (which measures the percentage of oxygen that is needed to sustain combustion, normal  $O_2$  in the atmosphere is ~20.95 %), UL94 (flame spread), GMI 60261 which assesses the surface flammability of interior trim materials used in motor vehicles (similar to FMVSS.302), and the glow wire test, which is used by the electrical industry to simulate electrical overloads on their end products.

The materials performed in similar fashion when tested in the TGA, they all decomposed at the same temperature ~ 220 °C, and this was thought to be due to the thermal characteristics of PP and flax. The results from the cone calorimeter test showed that the 30 wt.% flax fibre composite showed a peak heat release rate (PHRR) of 167 kW/m<sup>2</sup>, which was further improved to a PHRR of 35 kW/m<sup>2</sup>. This was achieved with a composition of 30 wt.% flax fibre and the addition of 25 wt.% of expandable graphite (EG) additive. There was also a decrease in the smoke and CO evolved with the increasing addition of EG. The addition of 25 wt.% of ammonium polyphosphate (APP) did not make any significant improvements.

From the other flammability tests, the NFC without FR additive achieved a LOI of 21 %, UL94 HB; conversely the NFC with 25 wt.% EG achieved a LOI of 30 % and a V1 UL94 classification (the higher the LOI percentage the more  $O_2$  needed therefore providing better resistance to flaming). A later study by Le Brasa *et al* (2005) also looked into the flammability properties of flax/PP composite systems. However the team looked into different intumescence systems to help improve the materials fire susceptibility by increasing the efficiency of the swelling and charring of the FR system.



**Figure 2.5.** FIGRA<sup>\*</sup> curve for PP and of the PP/flax composite vs. time (heat flux  $50 \text{kw/m}^2$ ) (source from Le Brasa, 2005). (The fire growth index (FIGRA) is the ratio of the rate of heat release rate on time HRR/t<sub>i</sub>).

They evaluated a system similar to that of Schartel *et al* (2003), this time with the addition of pentaerythritol and melamine which aids to the intumescence. They carried out fire tests which included UL94 and cone calorimeter. The team noticed an improvement in the FR system compared to the non-FR PP/flax system. The former gained a V0 rating (self-extinguishing), the highest in the UL94 as well as a reduced PHRR and mass loss rate.

De Chirico et al (2003) studied the flame retardant effects of adding lignin into an isotactic polypropylene. Lignin is a constitute found in plants of which it represents 20-30 wt.%. It has an amorphous polyphenolic structure. It has been noticed that lignin degrades at high temperatures and forms a char which acts as a barrier at the surface to the oxygen in the atmosphere. The team used lignin alone and in synergism with some phosphorus compounds and ATH. In carrying out cone calorimeter tests, a 71 % reduction in PHRR was observed in a combination of PP with 15 wt.% lignin compared to pure PP. The combination of PP with lignin 14 wt.% and 6 wt.% APP showed a further reduction in the PHRR. There has also been some minor work done on fully biodegradable flame retardant composites by Matkó et al (2005). Here the team looked into PP, polyurethane (PU) and starch matrices with cotton fibre, wood flake (as saw dust) and corn shell as reinforcing fibres. The flame retardant additive was APP. In terms of flammability properties, they looked at LOI and UL94 tests. It was seen that when the LOI values were measured for polyurethane/wood flake and polyurethane/corn shell that the addition of 20 % APP showed an increase from 23 to 31 and 20 to 27 (v/v %) respectively. A V0 rating was achieved for the flame retarded systems. The PU composition showed a better flame retardancy over PP as a consequence of the char forming tendency. The starch based composite showed a 60 (v/v %) value when loaded with 30 wt.% APP, which also gained a V0 rating.

The Institute of Natural Fibres in Poznan Poland, conducts extensive work into natural fibres and its polymer composites. Helwig and Paukszta (2000) presented initial studies on the flammability of polypropylene and flax based composites. The composites were manufactured by compression moulding. Reaction to fire tests on the composites were carried out to observe the effects of fibre content. The cone calorimeter was used with a heat flux of 35 kW/m<sup>2</sup>. Samples tested varied in fibre content in the following: pure polypropylene, 12.5, 20, 30 and 40 wt.% flax fibre. It was concluded that for samples of 20 wt.% fibre content the PHRR was 50 % lower than that of pure polypropylene.

This advantageous effect became more prevalent when the flax fibre content was increased to 30 and 40 wt.%. This resulted in a lowering of total heat released (THR) and average heat of combustion (Av HOC). This may have been due to the increasing charring effect of the organic fibres, which improves the poor flammability of the pure polypropylene. However, there were two shortcomings in raising the fibre content. The time to ignition (TTI) became shorter and smoke production increased. However, there are some disadvantages when using traditional flame retardant fillers. The most significant is embrittlement of the composite due to the high FR loading levels needed to create adequate flame retardancy.

#### **2.5 Nanofillers as Flame Retardant Additives**

The applications of traditional FRs such as aluminum trihydroxide and magnesium hydroxide require a very high filler loading to be deployed within the polymer matrix; filling levels of more than 50 wt.% are necessary to achieve suitable flame retardancy, for example in cables and wires. Clear disadvantages of these high filler levels are the high density and lack of flexibility of end products, the low mechanical properties and the problematic processing, compounding and extrusion steps. Moreover, in Europe there are reservations about the general use of brominated compounds as flame retardants. A new class of materials, called nanocomposites, can avoid the disadvantages of traditional flame retardant systems. Especially promising in terms of flame retardancy has been the discovery that polymer nanocomposites, in particular nanoclays, have distinct advantages over traditional fire retardants in production, such as; the relatively small amount of additive needed (only 2-5 wt.% compared to 40-70 wt.%) and as a result the improved recycling. In addition, concurrent work will enhance the flame retardancy and reduce fuel formation by promoting char formation using traditional fire retardants together with nanocomposites. There are two possible forms of nanodispersion.

The intercalated structure is generated if the nanodispersed filler is still ordered; while if the filler is homogenously dispersed an exfoliated structure is generated (Figure 2.6). The most important fillers that can be used for the generation of these structures at a nanometre level are layered silicates. The first step in achieving nanoscale dispersion of clays in a polymer is to open the galleries between the layers and to match the polarity of the polymer or monomer so that it will intercalate between the layers. This is done by exchanging an organic cation for an inorganic cation. The larger organic cations swell the layers and increase the hydrophobic properties of the clay, resulting in organically modified clay (Usuki *et al.*, 1993). The organically modified clay can then be intercalated with polymer by several routes. Solution processing involves dispersion of both the organically modified clay and polymer in a common solution.



*Figure 2.6.* Morphologies of polymer/clay nanocomposites: (a) conventional miscible microcomposites, (b) partially intercalated and exfoliated, (c) fully intercalated and dispersed and (d) fully exfoliated and dispersed. Images from Usuki et al., 1993.

Unfortunately, not all organoclays can be nanodispersed in all polymers. There has been a significant amount of research material published indicating that a polar polymer matrix is very helpful and that also the length and the chemical structure of the quaternary organic ammonium compound play an important role in the successful production of a nanocomposite. The ability to disperse the nanoclay in the polymer is dependent on the type of polymer, as well as the process. In general, it is easier to disperse and exfoliate nanoclays in polar polymers. Toyota, however, successfully demonstrated that the clays and hydrophobic polymers could be compounded, provided the system is compatibilized by the replacement of the exchange cations in the galleries of the native clay by alkyl ammonium surfactants (Usuki et al., 2003; Okada et al., 1990, 1995; Ray and Okamoto, 2003; Alexandre and Dubois 2000). There are a number of reviews discussing approaches to the fabrication of nanocomposites, including: intercalation of polymers or pre-polymers from solution, in situ intercalation polymerization methods, and melt interaction methods (Le Baron and Wang, 1999; Cao and Mallouk, 1991). At this stage, polymer or pre-polymer from solution and in situ polymerization methods are the primary methods (Giannelis et al., 1992; Burnside and Giannelis, 1995). Therefore, polymers like ethylene-vinyl acetate (EVA) and polyamide (PA) easily form nanocomposites, while it is considerably more difficult for non-polar polymers such as polyethylene (PE) and polypropylene (PP). For the non-polar polymer PE it is reported that a blend of PE and MA-g-PE can be used to create a nanocomposite (Durmus *et al.*, 2007).

The first indications that nanoclays could increase the thermal stability of polymers was demonstrated in 1965 for montmorillonite/PMMA composites. The decomposition temperature (defined as 50 % mass loss) increased about 50 °C for a composite with only 10 wt.% filler (Blumstein, 1965). More recently, the decomposition temperature of polydimethylsiloxane (PDMS) was found to increase about 140 °C with 10 wt.% montmorillonite for a delaminated nanocomposite (Kuchta *et al.*, 1999). A 50 °C increase was found for intercalated clay/PE composites (Lee and Jang, 1998). The dispersion of clays is critical to increase the decomposition temperature. Exfoliated composites have significantly higher decomposition temperatures than intercalated nanocomposites or traditional clay composites (Agag *et al.*, 2001).

Some speculate that this increase in stability is due to the improved barrier properties of the composites. If oxygen cannot penetrate, then it cannot cause oxidation of the resin (Kuchta *et al.*, 1999). In addition, the inorganic phase acts as a radical sink to prevent polymer chains from decomposing. The improved thermal stability of some composites may be limited by the lower thermal stability of alkylammonium ions. For example, in intercalated clay/polystyrene composites, the intercalating agent decomposes at about 250 °C. Bonding the intercalating ions to the polystyrene matrix noticeably improved the thermal stability. Polyimide (Agag *et al.*, 2001) and polymethylmethacrylate (Salahuddin and Shehata 2001) also become more thermally stable with the addition of organomodified montmorillonite (OMMT).

Gilman (1999) carried out some flammability studies on Nylon 6/clay nanocomposites. There was a significant improvement in terms of HRR using only 5 wt.% clay. The HRR increases at a lower temperature for the nanocomposite, but levels off quickly. Clay nanocomposites showed a 60 % reduction in PHRR relative to unfilled polymer. In addition, the mass loss rate is the same for the two materials until a char forms, and then the nanocomposite exhibits a significantly lower mass loss rate. Observations of the char suggest that the layered structure acts to reinforce the char and reduce the permeability of the char, reducing the rate of volatile products released. The flammability resistance of clay-filled polymers indicates that their ablation resistance might also be improved. As a material is heated during ablation, the surface of the material reacts and forms a tough char. If the char is not reinforced, it fails and is removed from the surface, exposing more material (Vaia et al., 1999). Traditional composites require a significant weight fraction of filler (more than 30 wt.%) to achieve significant ablation resistance. On the other hand, 2-5 wt.% nanoclay-filled Nylon 6 exposed to a mock solid rocket motor firing rig formed a layer of char on the surface that was tough and significantly retarded further erosion (Fong, 2001). In addition, oxygen plasma forms a passivation layer on Nylon 6/layered silicate nanocomposites, which significantly retards further erosion of the composite surface (Beyer, 2001).

This behaviour is not a strong function of the organic molecules used to modify the clay or the strength of the clay/polymer interaction (Beyer, 2001), but is a function of the degree of exfoliation (Fong, 2001). Of particular importance to the industry is the fact that often very similar reductions in heat release rates are observed for both intercalated and exfoliated structures. In practice, the flame retardancy of polymers is currently achieved using different traditional additives. Halogen-free flame retardants, which are most important for Europe is achieved through aluminum trihydroxide (ATH) and to a lesser degree by magnesium hydroxide. Nitrogen and phosphorus based flame retardants are also used. The proportion of ATH needed can be very high, up to 60 wt.% for adequate flame retardancy. The low flexibility of such compounds, moderate mechanical properties and difficulties during compounding and extrusion or injection moulding are frequently reported. Alternatively, the amount of halogen based flame retardants for polymers is lower, but particularly in Europe customers and legislators are demanding the development of non-halogen flame retardants. Therefore, the aim of an innovative flame retardant solution for Europe would be a significant reduction in the amount of traditional halogen-free flame retardants for compounds, while still maintaining a high level of flame retardancy, nanocomposites offer a solution. Organoclays alone do not exhibit sufficient flame retardancy in a polymer matrix. However, a combination of ATH or magnesium hydroxide with organoclay produces sufficient flame retardancy and simultaneously allows the reduction of the total filler content. Schartel et al (2006) evaluated the combination of ATH, phosphonium modified montmorillonite silicate and organic flame retardants containing phosphorus, in an epoxy resin system.

The silicate worked as inert filler, induced limited additional residue formation of the polymer matrix, which resulted in a small effect on the effective heat of combustion of the volatile decomposition products, and showed a pronounced barrier effect. The comparison between adding phosphonium-modified montmorillonite, ATH and adding both additives revealed that the combination of these two additives showed superposition or even synergistic behaviour for nearly all flame retardancy properties.

Antagonistic behaviour was found only for some characteristics. The investigated combination of layered silicate and phosphorus flame retardants is not a promising approach. The combination of layered silicate and phosphorus flame retardants results in deteriorating interaction at least for the investigated system. The concept of using nanoclays in conjunction with traditional micro-sized flame retardants was explored by Nazare et al (2002). Different organically modified clays were with customary flame retardants in the polyester resin such as; ammonium polyphosphate, aluminum trihydrate, and melamine phosphate. The objective was to study the various combinations of these hybrid composites in terms of thermal and fire retardancy. The TGA data indicated an increase in residual mass with increasing clay loading. This was thought to be caused by the clay forming a strong char during the decomposition process. The samples with clay and 20 wt.% APP also showed an increased char, however for the clay and 30 wt.% loaded samples there was a slight decrease. This was thought to be attributed to the high filler content reducing the crosslinking efficiency which results in a less char formation. In terms of flame retardance, the PHRR dropped for samples loaded with 10 wt.% clay from 1115 to 705 kW/m<sup>2</sup>.

The higher clay loading resulted in the formation of a thicker insulating layer on the surface of the burning polymer, thus providing a potential barrier to both mass and energy transport (Gilman *et al.*, 2005). The less processable samples of 10 wt.% clay with 20 or 30 wt.% APP showed a significant reduction in PHRR value of 417 kW/m<sup>2</sup> and this was lower than for samples only containing APP. Thus combinations of clay-APP showed better fire performance even if crosslinking is reduced. The significant conclusion was that the presents of nanoclays with conventional flame retardants can reduce the values of the polyester as much as 40-70 %.



*Figure.* 2.7. (a) Cross sectional representation of the formation of islands and a structured continuous network layer, image from Cipiriano et al (2007) and (b) Electron micrograph of protective char, image from Dasari et al., 2009.

# 2.6 Pyrolysis Combustion Flow Calorimeter (PCFC)/ Microcalorimeter

#### 2.6.1 Introduction

To fully assess the fire behaviour of polymers, it was essential to develop some standardised tests for assessing the flammability and other combustion related properties of polymers. Most countries have standards and codes for the classification of materials with respect to their combustion behaviour, but the experiments used in existing standard tests vary considerably according to the nature, shape and size of the polymeric materials to be tested. The rank order of the fire performance of many pure polymers has been assessed by some small scale flammability tests, such as limiting oxygen index (LOI) and cone calorimetery.

However, all these tests still require replicate samples on the order of 100 grams each, and the results are determined not only by the characteristic of the materials involved in fire but also by a multitude of conditions and factors including ignition source (Scudamore *et al.*, 1991), sample thickness (Babrauskas, 1986), sample orientation (Kashiwagi and Cleary 1993), ventilation (Tewarson, 1995) and edge conditions (Pearce *et al.*, 1981), all of which combine to make the test data configuration dependent and to obscure the effect of material properties and composition on burning behaviour. Thus, it would be a great improvement to establish a relatively low cost, convenient and quantitative test to set up another evaluation standard. The present method of pyrolysis-combustion flow calorimetery (PCFC) also known as the microcalorimeter (see Figure 2.8) seeks to improve upon laboratory pyrolysis-combustion methods by providing dynamic capability for solids without the need to measure mass loss rate during the test.

#### 2.6.2 The Experimental Technique

A sample weighing no more that 5 mg is placed into an alumina crucible (6.4 mm  $\emptyset$ ). The quartz tube containing the crucible and sample is inserted into the heating coil of the pyrolysis probe and the probe is inserted into the pyrolysis chamber and sealed. The pyrolysis chamber is equilibrated at a temperature which is a few degrees below decomposition which is determined by a separate TGA experiment. A constant rate of temperature rise (ramp) is used to heat the sample to a hold temperature (soak) which is well above the thermal decomposition range of typical combustible solids. The ramp and high temperature soak program forces complete thermal decomposition of most combustible solids. Selecting a hold temperature which corresponds to a particular fire environment (heat flux), but which is within the normal temperature range of the polymer thermal decomposition, discriminates between materials with regard to heat resistance but not fire resistance, in general, the heat flux is not known.

Therefore, in order to obtain an unambiguous measure of the heat capacity of a combustible material to release heat in a fire, the standard pyrolysis combustion heat release rate test involves heating the sample at a constant rate (260 K/min) to a maximum temperature of 930 °C and holding the sample at the maximum temperature for 10 to 120 seconds to reach complete pyrolysis. The volatile pyrolysis products are generated during the temperature ramp and are swept from the pyrolyser by nitrogen gas flowing at 82 cm<sup>3</sup>/min to which is added 18 cm<sup>3</sup>/min of pure oxygen at the inlet to the combustor (Figure 2.8 and 2.9). Combustion gases are scrubbed to remove carbon dioxide, water, acid gases and the gas stream passes through the flow meter and oxygen analyser. Deconvolution of oxygen consumption signal is performed during the test, and the heat release rate, heat release capacity, and total heat of combustion are calculated and displayed. The crucible is weighed after the test to determine the mass of the sample.



*Figure 2.8.* Schematic showing the PCFC setup and how it relates to a real life scenario. Image from Lyon et al., 2006.



*Figure 2.9.* (a) The PCFC unit (b) sampling stage (c) schematic of the PCFC pyrolyser and combustor setup. Schematic courtesy of FTT UK.

#### 2.6.3 Employing the PCFC as a Flammability Testing Tool

Lyon (2000) and Walters (2003) developed this technique with co-workers at the Federal Aviation Authority (FAA) laboratories and were first to publish information about their experimental results. Their work entitled *Pyrolysis combustion flow calorimetery* was published in 2004. Polymer samples were unfilled, natural or pure commercial grades obtained from Aldrich Chemical Company. The commonly used polymers consisted of; polyethylene, polystyrene, ABS, PMMA, PET, PEEK and PBI. The first parameter attained was the heat release rate in terms of W/g (see Figure 2.10). Data for generic polymers from different sources were averaged to obtain values. Polymers were listed in descending order of heat release capacities ( $\eta$ ) which span the entire range measured to date for polymeric solids which showed that polyethylene had the highest  $\eta$  value of 1600 J g<sup>-1</sup> K<sup>-1</sup> and polyimide the lowest 23 J g<sup>-1</sup> K<sup>-1</sup>. Heat release capacities can vary by  $\pm$  20 % which was said to probably reflect differences in thermal stability, chemical backbone structure, molecular weight, chain defects, end groups, thermal processing history, and additive package between polymers from different sources.

Total heat release  $h_{c,s}^{0}$  is the heat of complete combustion of the pyrolysis gases per unit initial mass of polymer. Low total heat release relative to the heat of complete combustion measured by oxygen bomb calorimetery indicates that a fraction of the pyrolysis products were not oxidized in the PCFC test (e.g. acid gases or char). The theoretical relationship between heat release capacity and flammability is an active area of research that is being driven by empirical data showing that low heat release capacity is a good predictor of ignition resistance and low heat release rate in flaming combustion (Babrauskas, 1992). Polycarbonate of bisphenol-A (PC), comprises of a single heat release rate peak and forms 20-25 % char when pyrolysed under anaerobic conditions. The total oxygen consumed in the experiment is proportional to the net heat of combustion of the polymer as determined in an oxygen bomb calorimeter. The net heat of complete combustion of PC calculated from oxygen consumption is the time integrated heat release rate. The net heats of complete combustion measured by the PCFC are within 2 % of the literature based on the cone calorimeter (Babrauskas 1992; Walters *et al.*, 2000) values on average for the ten polymers listed in their work.

Wilkie et al (2006) looked at high-throughput (HT) techniques for rapidly assessing combinations of nanocomposites with conventional fire retardant additives using the PCFC. This becomes valuable if one has only two components, in addition to the polymer, and these could be used at amounts of 5, 10, 15 or 20 %, then it would require more than 20 experiments to evaluate this set of data. Since any experiment must be replicated, the number of experiments is significantly increased. Pyrolysis combustion flow calorimetery was performed using a TGA equipped with an auto-sampler and a custom designed evolved gas analysis attachment capable of combusting the pyrolysis gases from the TGA in excess oxygen. These heat release rate tests are performed automatically at the rate of 2-3 samples per hour, using only a few milligrams of sample. The heat release capacity (HRC) is calculated as well as the heat of combustion of the pyrolysis gases and the heat release temperature  $T_{max}$ . The repeatability, relative efficiency and data quality of the various HT and conventional flammability measurements were calculated. It was shown that the HT methods were more efficient at gathering data than UL94 and cone calorimetery, the HT data are quantitative and more repeatable than UL94 data. The PCFC was shown to be the best at repeatability as well as efficiency. Together with all these benefits the PCFC has the additional advantage of small (mg) sample size, for these reasons the PCFC is being considered as a new ASTM standard testing method ASTM D20 (2006).

Lyon et al (2003) attempted formulating and characterising ultra fire resistant elastomers for commercial aircraft cabins using thermal gravimetric analysis, cone calorimetery and the PCFC. The assumption was based on altering the chemical composition of the polymer from which it is made. Hydrocarbon rubbers, such as polyurethane, styrenebutadiene (SBR), polyisoprene, and rubbers from ethylene-propylene-diene monomers (EPDM) are the most flammable because they ignite easily and have high-fuel value and heat release. Replacing carbon and hydrogen atoms in the polymer with inorganic atoms, such as chlorine, silicon, nitrogen, sulphur, or phosphorus, results in a polymer with reduced flammability because of increased heat resistance and lower fuel value. The FAA's Fire Resistant Materials research program is focusing on semi-inorganic rubbers for seat cushions. The objective was to develop cost effective FR elastomers by means of rapid screening processes. The TGA indicates the onset time and temperature for decompostion however this does not specify the fire hazards of the material. The heat release capacity which is calculated from the PCFC is the molecular-level response of a polymer to an imposed heat flux (heating rate) and is proportional to the heat release rate in steady-flaming combustion. Consequently, low values of  $\eta_c$  are indicative of low flammability in the FAA seat cushion test and low full-scale fire hazard. Thus the molecular design of polysilphenylene-siloxane and polyphosphazene has yielded flexible elastomers having the fire resistance of high-temperature engineering plastics like e.g. polyetherimides, polyetherketones, and polyphenylsulfones based on the results from PCFC data.

In another piece of research Walters and Lyon (2003) studied the cure chemistry; thermal stability and fire behaviour of fire resistant cyanate ester-epoxy blends. A PCFC was used as the first test to screen the materials for flammability. An Ohio State University (OSU) fire calorimeter was used to evaluate the flammability of the polymer blends under standard conditions (FAR 25.53, 2000). Trends in the measured heat release rates of the blends were observed.

The heat release capacity measured in the non-flaming test showed a decrease in the heat release capacity with an increasing cyanate concentration. However, the char yields from the two flammability tests did not correlate well due to the different sample environments. Pyrolysis in the microcalorimeter is completely anaerobic. Conditions in the OSU are only anaerobic at the sample surface when the sample is burning.



Figure 2.10. An example PCFC plot of a research polymer. Image from Lyon and Walters, 2004.

If the sample does not ignite or ceases to burn, it is subjected to the radiant heat flux and an impinging flame for the duration of the test. The high volumetric flow rate of air sweeping over the sample surface at elevated temperatures causes oxidative pyrolysis and a lower char yield. Zhang *et al* (2002) also used the PCFC technique to characterise new fire retardant polyarylates. Thermal decomposition behaviour and flammability of three polyarylates based on bisphenol A (BPA), 1, 1-dichloro-2, 2-bis (4-hydroxyphenyl) ethylene (BPC II) and 4, 40-dihydroxy-3-ethoxy benzylidenoacetophenone (Chalcon II), their copolymers and blends were investigated by pyrolysis GC/MS, simultaneous thermal analysis and pyrolysis combustion flow calorimetry. The heat release capacity which is obtained by dividing maximum heat release rate by the sample weight and heat rate indicates the fire hazard of the material. Direct integration of the heat release rate versus time gives the total heat of combustion of the fuel gases per unit sample mass.

As well as the conclusions about the formulations, this study showed that the correlations between PCFC and some standard tests, such as oxygen bomb calorimeter, cone calorimeter at 50 kW/m<sup>2</sup> incident heat flux and Underwriter Laboratories Test for Flammability of Plastic Materials (UL-94), are all comparatively good (Walters, 2001). Therefore, the PCFC is an efficient screening tool for newly synthesized fire resistant materials. One of the most recent pieces of research work undertaken on the PCFC was carried out to assess its potential as a flammability screening tool for polymers. The findings led to the belief that the heat release capacity (HRC) and heat release rate (HRR) values can be used for an initial screening in terms of intrinsic fire hazards of materials. Schartel et al (2007) also commented on the fact that performance in fire tests can be estimated, but identifying precisely the materials ability to pass or fail a specific test from the investigated set of materials with similar performance is clearly limited. Several effects determining the fire behaviour of the material such as wicking, dripping, intumescence, to name but a few are not covered by the PCFC. The PCFC screening performs better for materials that show large differences in char yield or effective heat of combustion of the pyrolysis gases are compared. The well defined conditions of the combustion in the PCFC differ essentially from the ones of real fires and fire tests in which the fire behaviour of the specimen also crucially controls the fire scenario. The complete combustion used in the PCFC rules out an assessment of the influence of flame inhibition for the polymeric specimens.

Therefore, combing the quasi-equilibrium characteristics of TGA and PCFC and cone calorimetery make a useful approach for investigating the behaviour on milligram samples. However, PCFC does not account for important physical effects thus other fire tests must be undertaken for final quality assurance.

## **2.7 Conclusions**

This chapter presented an overview into topics which concern this thesis and the reason for future investigations. Typical issues covered were the progression into biodegradable polymer composites and their inferior flame retardancy. Also an introduction into nanofillers and how their superior chemical and physical properties may assist in reducing the inherent heat release rate of polymers. Finally, an introduction into the testing methods used to asses the flammability of polymeric materials was given. The evolution of material synthesis and screening turnaround has required scientist and engineers to develop the pyrolysis combustion calorimeter (PCFC). Still in its infancy in terms of being used solely for flammability testing, it has not yet been granted international standardisation by any governing bodies. Nevertheless this apparatus is ideal for testing new polymer nanocomposites in terms of academic research.

## 2.8 References

Adams. C: *What exactly is fire*? (The Straight Dope) Chicago Reader, Inc, Chicago, IL. 2004. <u>http://www.straightdope.com/columns/021122.html.</u>

Agag. T, Koga. T and Takeichi. T: *Studies on thermal and mechanical properties of Polyimide-clay nanocomposites*. Polymer. 2001. **42**(8): p. 3399-3408.

Alexandre. M and Dubois. P: *Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials.* Materials Science and Engineering: Reports. 15<sup>th</sup> June 2000. **28**(1-2): p. 1-63.

ASTM D 1354:2004. Standard test method for heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter. ASTM, Conshohocken, Pa, USA.

ASTM D 20:2006, Proposed standard for the Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry. The proposed standard, ASTM WK9492. ASTM WK9492 is under the jurisdiction of Subcommittee D20.30 on Thermal Properties. ASTM Int'l Develops Microscale Combustion Calorimetry Standard. 24<sup>th</sup> October 2006.

Babrauskas. V: Comparative Rates of Heat Release from Five Different Types of Test Apparatuses. Journal of Fire Sciences. 1986. **4**(2): p. 148-158.

Babrauskas. V: *From Bunsen burner to heat release rate calorimeter*. In: Heat Release in Fires (Ed.): Babrauskas. V and Grayson S, Elsevier, New York (1992), p. 7-29.

Beyer. G: *Flame retardant properties of EVA-nanocomposites and improvements by combination of nanofillers with aluminium trihydrate.* Fire and Materials. September/October 2001. **25**(5): p. 193-197.

Beyer. G: *Nanocomposites offer new way forward for flame retardants*. Plastics, Additives and Compounding. September-October 2005. **7**(5): p. 32-35.

Blumstein. A: Polymerization of absorbed monolayers Π. Thermal degradation of the inserted polymer. Journal of Polymer Science Part A: General Papers, 1965. **3**(7): p. 2665-2672.

Burnside. S.D and Giannelis. E. P: *Synthesis and properties of new poly* (*dimethylsiloxane*) nanocomposites. Chemistry of Materials. 1995. **7**(9): p. 1597-600.

Cao. G and Mallouk. T. E: *Topochemical Solid State Diacetylene Polymerization in Layered Metal Phosphonate Salts*. Journal of Solid State Chemistry. 1991. **94**: p. 59-71.

Cipiriano. B.H, Kashiwagi. T, Raghavan. S.R, Yang. Y, Grulke. E.A, Yamamoto. K, Shields. J.R. and Douglas. J.F: *Effects of aspect ratio of MWNT on the flammability properties of polymer nanocomposites*. Polymer. 2007. **48**: p. 6086- 6096.

(CIWM) Chartered Institution of Wastes Management: *Plastics recycling information sheet*. <u>http://www.wasteonline.org.uk/resources/InformationSheets/Plastics.htm.</u>

De Chirico. A, De Armanini. P, Chini. P, Cioccolo. G, Provasoli. F and Audisio. G: *Flame retardants for polypropylene based on lignin*. Polymer Degradation and Stability. 2003. **79**: p. 139-145.

Dasari. A, Yu. Z.Z, Mai. Y.W, Cai. G and Song. H: *Roles of graphite oxide, clay and POSS during the combustion of polyamide* 6. Polymer. 2009. **50**(6): p. 1577-1587.

Durmus. A, Kasgoz. A and Macosko. C.W: *Linear low density polyethylene* (*LLDPE*)/clay nanocomposites. Part I: Structural characterization and quantifying clay dispersion by melt rheology. Polymer. 2007. **48**: p. 4492-4502.

FAR 25.53:2000, *Heat release test for cabin materials*, Aircraft Materials Fire Test Handbook. DOT/FAA/AR-00/12.

Fong. H: *Self-passivation of polymer-layered silicate nanocomposites*. Chemistry of Materials. 2001. **13**(11): p. 4123-4129.

Garkhail. S.K, Heijenrath. R.W.H and Peijs. T: *Mechanical properties of natural-fibremat-reinforced thermoplastics based on flax fibres and polypropylene*. Applied Composite Materials. November 2000. **7**(5-6): p. 351-372. Giannelis. E.P, Mehrotra. V, Tse. O, Vaia. R.A and Sung. T.C: *Intercalated twodimensional ceramic nanocomposites*. In: Rhine, W. E. Shaw, T. M., Gottshall, R.J., Chen, Y. (Eds.), Synthesis and Processing of Ceramics: Scientific Issues, MRS Proceeding. Pittsburgh, PA. (1992): p. 547-548.

Gilman. J.W: *Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites.* Applied Clay Science. 1999. **15**: p. 31-49.

Gilman. J.W, Bourbigot. S, Bellayer. S, Stretz. H and Paul. D.R: In Fire Retardancy of Polymers New Application of Mineral Fillers: Le Bras. M, Wilkie. C. A, Bourbigot. S, Duquesne. S, Jama. C (eds). The Royal Society of Chemistry: Cambridge, UK, (2005), p. 177-186.

Helwig. M and Paukszta. D: *Flammability of Composites Based on Polypropylene and Flax Fibers*. Molecular Crystals and Liquid Crystals. (2000): **354**: p. 373-380.

Huggett. C: *Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements*. Fire and Materials. 1980. **4**(2): p. 61-65.

ISO 5660 Part 1:1993, *Reaction-to-fire tests Heat release, smoke production and mass loss rate (Cone Calorimeter Method)*, International Organization for Standardization, Geneva, Switzerland.

ISO 5660 Part 2:2002, Fire Tests-Reaction to Fire- Rate of Heat Release from Building Products (Cone Calorimeter Method), Intern. Organization for Standardization, Geneva, Switzerland.

Kashiwagi. T and Cleary. T.G: *Effects of Sample Mounting on Flammability Properties of Intumescent Polymers*. Fire Safety Journal. 1993. **20**: p. 203-225.
Kuchta. F.D, Lemstra. P.J, Keller. A, Batenburg. L.F and Fischer. H.R: In Organic/Inorganic Hybrid Materials II, edited by Klein. L.C, Francis L, DeGuire. M.R, Mark J.E, Mater. Materials Research Society Symposia Proceedings. **576**: Warrendale, PA, 1999. p.363-368.

Kojima. Y, Usuki. A, Kawasumi. M, Okada. A, Kurauchi. T and Kamigaito. O: *Synthesis of nylon 6-clay hybrid by montmorillonite intercalated with E-caprolactam.* Journal of Polymer Science Part A: Polymer Chemistry. 1993. **31**(4): p. 983-986.

Le Baron. P.C, Pinnavaia. T.J and Wang. Z: *Polymer-Layered Silicate Nanocomposites: an Overview*. Applied Clay Science. 1999. **15**: p. 11-29.

Le Brasa. M, Duquesnea. S, Foisb M, Griselb. M and Poutch. F: *Intumescent polypropylene/flax blends: a preliminary study.* Polymer Degradation and Stability. 2005. **88**: p. 80-84.

Lee. D.C and Jang. L.W: *Characterization of epoxy-clay hybrid composite prepared by emulsion polymerization*. Journal of Applied Polymer Science. 1998. **68**(12): p. 1997-2005.

Lyon. R.E: Heat Release Kinetics. Fire and Materials. 2000. 24: p. 179-186.

Lyon R.E, Speitel. L, Walters. R.N and Crowley. S: *Fire-resistant elastomers*. Fire and Materials. 2003. **27**(4): p. 195-208.

Lyon R.E and Walters. R.N: *Pyrolysis combustion flow calorimetry*. Journal of Analytical and Applied Pyrolysis. March 2004. **71**(1): p. 27-46.

Lyon. R.E, Walters. R.N and Stoliarov. S: Thermal analysis of flammability, In: Flame Retardants 2006 Proceedings.

Matkó. Sz. A, Toldy. S, Keszei. P, Anna, Bertalan. Gy and Marosi. Gy: *Flame retardancy of biodegradable polymers and biocomposites*. *Polymer Degradation and Stability*. April 2005. **88**(1): p. 138-145.

National Bureau of Standards: Development of the Cone Calorimeter - A Bench-Scale Heat Release Rate Apparatus Based on Oxygen Consumption, (NBSIR 82-2611), Babrauskas. V, US, 1982.

Nazare. S, Kandola. B and Horrocks. A.R: *Use of cone calorimetry to quantify the burning hazard of apparel fabrics*. Fire and Materials. 2002. **26**: p. 191-199.

Okada. A.K, Usuki. A, Kojima. Y, Kurauchi. T and Kamigaito. O: *Polymer-Based Molecular Composites*, Schaefer. D.W, Mark. J.E, Eds. Materials Research Society, Pittsburgh 1990, **171**: p. 45.

Okada. A.K and Usuki. A: *The chemistry of polymer-clay hybrids*. Materials Science and Engineering: C. November 1995. **3**(2): p. 109-115.

Pearce. E.M, Khanna. Y.P and Raucher. D: *Thermal Analysis of Polymer Flammability*. In: Thermal Characterization of Polymeric Materials, (Eds) E.A. Turi, Academic Press, Orlando, FL, p. 793-843, 1981.

Peijs. T, Garkhail. S, Heijenrath. R, Van den Oever. M and Bos. H: *Thermoplastic composites based on flax fibres and polypropylene: Influence of fibre length and fibre volume fraction on mechanical properties.* Macromol Symposium. 1998. **127**: p.193-203.

Ray. S and Okamoto. M: *Polymer/layered silicate nanocomposites: a review from preparation to processing.* Progress in Polymer Science. November 2003. **28**(11): p. 1539-1641.

Schartel. B, Braun. U, Schwarz. U and Reinemann. S: *Fire retardancy of polypropylene/flax blends*. Polymer. September 2003. **44**(20): p. 6241-6250.

Schartel. B, Knoll. U, Hartwig. A and Pütz. D: *Phosphonium-modified layered silicate epoxy resins nanocomposites and their combinations with ATH and organo-phosphorus fire retardant*. Polymers for Advanced Technologies. 2006. **17**(4): p. 281-293.

Schartel. B, Pawlowski. K.H and Lyon R.E: *Pyrolysis combustion flow calorimeter: A tool to assess flame retarded PC/ABS materials*? Journal of Thermoanalytical and Calorimetric Methods. 15<sup>th</sup> October 2007. **462**(1-2): p. 1-14.

Salahuddin. N and Shehata. M: *Polymethylmethacrylate-montmorillonite composites: preparation, characterization and properties.* Polymer. September 2001. **42**(20): p. 8379-8385.

Scudamore. M. J, Briggs. P.J and Prager. F.H: *Cone Calorimetry-A Review of Tests Carried out on Plastics for the Association of Plastic Manufacturers in Europe*. Fire and Materials. 1991. **15**: p. 65-84.

Tewarson. A: *Generation of Heat and Chemical Compounds in Fires*, In SFPE Handbook of Fire Protection Engineering, 2nd Edition, Chapters 3-4, Society of Fire Protection Engineers, Boston, MA, 1995.

Thornton. W.M: *The relation of oxygen to the heat of combustion of organic compounds*, Philosophical Magazine, 1917. **33**: p. 196-203.

Usuki. A, Kojima. Y, Kawasumi. M, Okada. A, Fukushima.Y, Kurauchi. T and Kamigaito. O: *Synthesis of nylon 6-clay hybrid*. Journal of Materials Research. 1993. **8**: p. 1179-1184.

Usuki. A, Kojima. Y, Kawasumi. M, Okada A, Kurauchi. T and Kamigaito. O: *Interaction of nylon 6-clay surface and mechanical properties of nylon 6-clay hybrid*. Journal of Applied Polymer Science. 2003. **55**: p. 119-123.

Vaia. R.A, Patrick. G. P, Ruth. N, Hieu. T, Lichtenhan Nguyen and Joseph: *Polymer/layered silicate nanocomposites as high performance ablative materials*. Applied Clay Science, September 1999. **15**(1-2): p. 67-92.

Walters. R.N, Hackett. S.M and Lyon. R.E: *Heats of Combustion of High-Temperature Polymers*. Fire and Materials. 2000. **24**(5): p. 245-252.

Walters. R.N and Lyon. R.E: *Molar group contributions to polymer flammability*. Journal of Applied Polymers and Science. 2003. **87**(3): p. 548-563.

Walters. R.N: *Proceedings of the Third Triennial International Aircraft Fire and Cabin Safety Research Conference*. Atlantic City, NJ. 22-25October 2001.

Wilkie. C.A, Chigwada. G, Gilman. J. W and Lyon. R. E: *High throughput techniques for the evaluation of fire retardancy*. Journal of Materials Chemistry. 2006. **16**: p. 2023-2030.

Zhang. H, Westmoreland. P.R, Farris. R.J, Coughlin. E.B, Plichta. A and Brzozowski. Z. K.: *Thermal decomposition and flammability of fire-resistant, UV/visible-sensitive polyarylates, copolymers and blends*. Polymer. September 2002. **43**(20): p. 5463-5472.

# 3

# Reaction to Fire Behaviour of Natural Fibre Reinforced Polymer Composites: A Feasibility Study

# **3.1 Introduction**

The use of natural fibres have been documented since their use by the Egyptians 3,000 years ago, but since the seventies a number of high tech synthetic fibres such as glass, aramid and carbon fibres have entered and dominated the composite market due to their exceptional mechanical and thermal properties. With increasing environmental concerns natural fibres are once again being considered as reinforcements for polymer composites. The development and application of natural fibre polymer composites have been extensively reviewed (Garkhail *et al.*, 2000; Mohanty *et al.*, 2000; Joshia *et al.*, 2004; Schneider *et al.*, 1995; Peijs *et al.*, 2002). Joshia *et al* (2004) discussed whether natural fibres are environmentally superior to glass fibres by comparing their characteristics such as mechanical performance in relation to their environmental impact. However, the properties which make these composites ideal in terms of recyclability, disposability and cost are disadvantageous in terms of their reaction to fire.

The contribution of a material to a fire can be assessed using the cone calorimeter which determines the heat release rate in terms of heat evolved per meter squared ( $kW/m^2$ ) by oxygen consumption theory (Babrauskas, 1982). A small number of studies have looked into the fire performance of natural fibre polymer composites. Schartel and Braun (2003) prepared and characterised polypropylene (PP) reinforced with flax fibres in terms of mechanical, thermal and fire behaviour. The composite was manufactured in small quantities by twin screw extrusion; the formulations included the flame retardants; ammonium polyphosphate (NH<sub>4</sub>PO<sub>3</sub>) and expandable graphite. A marked difference was noticed in the ignition times and peak heat release rate values which were attributed to the flame retarding mechanisms of the additives. Helwig and Paukszta (2000) also looked into PP with flax fibres, but no flame retardants were used, instead the fibre volume fraction was varied.

The results establish that when the fibre content was increased the ignition time was delayed and the peak heat release rate value was decreased. The explanation was that the fibres charred when exposed to the radiant heat source and protected the material by forming a carbonous barrier. Sain et al (2004) studied the flammability of PP filled with sawdust and rice husk and made a composite using magnesium hydroxide  $Mg(OH)_2$  as the flame retardant additive. The tests conducted were an ASTM D635 horizontal burning test and an ASTM D2863 limiting oxygen index test. These tests were inadequate for extensive reaction to fire characterisation, although improvements were noticed with the magnesium hydroxide additive. The objective of this study is to formulate, develop and characterise a natural fibre sheet moulding compound (NFSMC) using a standard SMC manufacturing route. In order to improve the flame retardancy an industrial formulation containing aluminum trihydroxide (ATH) was used in the unsaturated polyester paste. A non-fire retardant formulation containing calcium carbonate (CaCO<sub>3</sub>) was also manufactured to eradicate dilution effects. This fire retarded hemp fibre based SMC was assessed and compared to a range of alternative building materials in terms of its reaction to fire.

# **3.2 Experimental Study**

#### 3.2.1 Sample Preparation

The NFSMC was manufactured at Menzolit UK, two batches were produced, a fire retardant (FR) and a non-fire retardant (non-FR) NFSMC. The resin formulation used for the glass fibre SMC (SMC) and NFSMC were the same. The constitute reinforcements were 25 mm long chopped glass or hemp fibres. Unsaturated polyester resin (P17 ortho resin) consisted of 20 wt.% of the overall paste formulation, 40 wt.% of filler (CaCO<sub>3</sub> or Al(OH)<sub>3</sub>), 25 wt.% hemp fibre (800 g/m<sup>2</sup>) fibre length 25 mm and the rest of the formulation consisted of catalysts, inhibitors and pigments. The building materials consisted of: woven glass (0/90°) vinyl ester laminate, plywood and gypsum board. The NFSMC and SMC composite panels were produced by hand lay-up method. The semi-finished plies were placed in a mild steel mold (400 × 400 mm). The moulding pressure was 16 kg/cm<sup>2</sup> (200 lbs/in<sup>2</sup>) for a dwell time of 7 minutes at 140 °C. The glass winyl ester laminate was manufactured by the vacuum infusion route. After the glass mats had been wetted out by the vinyl ester resin, the panel was cured at room temperature for 15 minutes and then post cured at 80°C for 3 hours.

Identification	Mass (g)	Thickness (mm)
FR NFSMC	92	5
non-FR NFSMC	97	5
FR SMC	66	5
non-FR SMC	74	5
Glass Vinyl ester	51	5
Plywood	79	17
Gypsum board	87	12

 Table 3.1. List of materials tested in the cone calorimeter.

### 3.2.2 Experimental Detail

Samples were cut on a table saw to the dimensions of  $100 \times 100$  mm. All materials were conditioned at  $23 \pm 3$  °C and a relative humidity of  $50 \pm 5$  % for 24 hours prior testing. The samples were wrapped with aluminum foil around the back and edges (Figure 3.1) before placing the specimen onto the holder and then into the cone calorimeter. This was carried out to prevent any molten material dripping from the sample onto the load cell. The samples were then backed with a non-combustible insulating refractory material. All tests were carried out in accordance with ASTM E1354 unless stated otherwise. All the tests were conducted on the cone calorimeter (Figure 3.2) assembled by Fire Testing Technology Ltd, (East Grinstead, UK) in accordance to ASTM E1354 specifications which is located at the Interscience Communications Laboratories, Watford. The specimens were orientated horizontally and exposed to irradiances of 25 and 50 kW/m<sup>2</sup> which approximate to 600 and 772 °C respectively. The specimens were pilot ignited and run in triplicate.



*Figure 3.1.* Specimen before testing with aluminum foil as stated by *ASTM E1354.* 



*Figure 3.2. General view of the cone calorimeter during a test.* 

# **3.3 Results and Discussion**

The results of cone calorimeter investigations are a comprehensive characterisation of the performance of the tested specimens in a relatively well defined fire test scenario. Since the cone calorimeter was developed in order to approximate an ideal performance based bench scale fire testing method, some of the results even allow for an accurate description of the materials properties, such as the heat release rate, peak heat release rate value, ignition times and effective heat of combustion, to name but a few.

#### 3.3.1 Heat Release Rate (HRR)

Heat release rate (HRR) sometimes referred to as rate of heat release (RHR) as measured by the cone calorimeter is the heat generated per unit time during burning of the sample divided by the surface area of the sample. The HRR is a measure of the rate of heat release to the surrounding per unit surface area of burning material. The graphs in Figures 3.3 to 3.8 show the change of HRR with time for all the specimens tested. A sharp peak is seen for glass vinyl ester (Figures 3.7 and 3.8). The FR and non-FR NFSMC have a much lower peak HRR value and broader appearance at both heat fluxes (Figures 3.3 to 3.6). The plywood specimen follows this trend as well. The gypsum board shows the lowest profile out of all the tested materials (Figures 3.7 and 3.8). The peak heat release rate values were also recorded and illustrated in Figure 3.10. These graphs show the general shape of a typical heat release rate curve for the NFSMC and other building materials which included; glass vinyl ester, plywood and gypsum board. The plywood profile (Figures 3.7 and 3.8) consisted of a sharp maximum that appears soon after ignition as a result of the surface being consumed. After that, a char layer gradually builds up as the pyrolysis front moves inwards. The char layer forms an increasing thermal insulation between the exposed surface and the pyrolysis front resulting in a continuously decreasing rate of heat release after the first maximum.

After that a second maximum appears which is said to be attributed to the pyrolysis front encountering unburnt material and refueling the fire Karlsson (1992), Hakkarainen and Kokkala (2001). The specimens were backed by a low density ceramic fibre insulation blanket, as recommended by the cone calorimeter standard.



*Figure 3.3. HRR curves for FR NFSMC and FR SMC at 25 kW/m*<sup>2</sup>.



*Figure 3.4. HRR curves for non-FR NFSMC and non-FR SMC at 25 kW/m<sup>2</sup>.* 



*Figure 3.5. HRR curves for FR NFSMC and FR SMC at 50 kW/m*<sup>2</sup>.



*Figure 3.6. HRR curves for non-FR NFSMC and non-FR SMC at 50 kW/m*<sup>2</sup>.

This char layer causes a barrier for heat transfer into the material and the process of pyrolysis is slowed down. The heat is transferred to the material predominantly from one side (top surface) therefore it behaves as a pseudo one-dimensional heat transfer model and the quasi-steady burning can be observed after the char layer is formed (middle part of the curve). The material then burns gradually through the thickness. This results in an increase in heat release rate which reaches a plateau after about 200 seconds of combustion. The second peak in the heat release rate curve represents the rear edge effects. The last part of the curve after the knee of the heat release rate profile which is less than 50 kW/m<sup>2</sup> represents the glowing combustion of the char residue at solid gas interface (when volatiles had been already burnt out). From the point of view of reaction to fire, the most important part of the burning process is the burning of volatiles, which gives a much higher heat release rate than the combustion of char residue. The heat release rate curve for the plywood is slightly dissimilar to the other specimens. The progressional region from the initial peak to the second peak has a 'fluctuating' appearance unlike the others which have a smooth progression. This can be attributed to the different layers burning in the plywood, which is made up of sheets of veneer.



*Figure 3.7. HRR curves glass vinyl ester, plywood and gypsum board at 25*  $kW/m^2$ .



*Figure 3.8.* HRR curves glass vinyl ester, plywood and gypsum board at  $50 \text{ kW/m}^2$ .

It was interesting to observe that the FR NFSMC showed a broad double HRR peak (Figures 3.3 and 3.5), which was similar to those of the plywood specimen. This broad peak is indicative of the slower release of combustibles whereas the sharp peak of the glass vinyl ester laminate (Figures 3.7 and 3.8) is attributable to the higher rate of gasification of the resin (Brown *et al.*, 1988; Scudamore, 1994). The non-FR NFSMC showed a single HRR peak suggesting that the lower layers decomposed and produced combustible volatiles at the same time as the upper layer. The time from the start of the experiment to the base of the first peak corresponds to the time to ignition (these match ignition values). The sudden decrease in the heat release rate with time is due to the formation of char, which was also witnessed with the plywood specimen. This char acts as a thermal insulator for the bulk of the material and acts as a passive fire retardant mechanism which impedes the heat transfer from the surface to the underlying virgin material, which reduces the rate of pyrolysis and the supply of combustible gases to the flame from (Madorsky, 1965).

## 3.3.2 Time to Ignition

Time to ignition for the specimens at the different irradiance levels was measured with the cone calorimeter by using the 'CONCAL' software. The results for the NFSMC's and other construction materials tested at 25 and 50 kW/m<sup>2</sup> irradiance are graphically represented in Figure 3.9.



*Figure 3.9. Time to Ignition (TTI) values of materials tested ant both irradiances.* 

Figures 3.3 to 3.6 indicate that there is a noticeable difference in the FR and non-FR NFSMC profiles at both heat fluxes. Firstly, it can be clearly seen from the HRR curves that the ignition times for the non-FR NFSMC and FR have been delayed from 185 to 290 seconds at 25 kW/m<sup>2</sup> and 54 to 78 seconds at 50 kW/m<sup>2</sup> irradiance. Ignition time for a material exposed to a given heat flux depends on many material factors. The most important of these are thickness, density and particularly for thin materials, thermal conductivity and the substrate used in the test.

For composites the thermal inertia,  $k\rho c$ , where k refers to the bulk thermal conductivity of units(W m<sup>-1</sup> K<sup>-1</sup>),  $\rho$  is the bulk density (kg m<sup>-3</sup>) and C is the specific heat capacity (J kg<sup>-1</sup> K<sup>-1</sup>) has a major effect on the ignitability of the surface lining. As many of these factors were different for the various materials tested in this study, a comparison in terms of ignitability characteristics alone must be treated with caution. Therefore merely ignitability data cannot be used to assess the fire hazard of material; as much more information is usually required. There are instances, however, where ignition characteristics can provide a guide to quality deviations in the product.

This type of information can be obtained from the much cheaper ISO 5657 ignitability test, which measures piloted ignition delay times as a function of external flux. Essentially one of the most significant parameter had been reduced. The peak heat release rate fell from 290 to 159 kW/m<sup>2</sup> at 25 kW/m<sup>2</sup> and 362 kW/m<sup>2</sup> fell to 180 kW/m<sup>2</sup> at 50 kW/m<sup>2</sup> (Figure 3.10) with the FR paste consisting of ATH in the NFSMC. The addition of ATH to the SMC polyester system reduced the peak heat release rate to the surroundings between 44 and 50 % depending on the irradiances used. The glass vinyl ester laminate performed the worst in terms of peak heat release rate of which it emitted the highest at both 25 and 50 kW/m<sup>2</sup> which were 373 and 467 kW/m<sup>2</sup> respectively. This specimen showed a narrow HRR curve, with high sharp peak after ignition. This was believed to occur due to the presence of a resin rich top surface layer (Scudamore, 1994).

#### 3.3.3 Effect of Irradiance

Measurement of the heat release for the materials was done through the cone calorimetery method which is based on oxygen consumption principle. Figure 3.9 illustrates that irradiance has an apparent effect on the time to ignition. The gypsum board did not ignite at 25 kW/m<sup>2</sup>. The paper covering the gypsum board charred and smoldered.

However at 50 kW/m<sup>2</sup> the paper face of the gypsum did ignite for 15 seconds. The plywood ignited the quickest in 59 seconds at 25 kW/m<sup>2</sup> which was reduced to 8 seconds at 50 kW/m<sup>2</sup>. The glass vinyl ester laminate was the third quickest to ignite at 25 kW/m<sup>2</sup> of which it took 132 seconds which was reduced to 40 seconds at 50 kW/m<sup>2</sup>. The FR NFSMC performed the best with respects to ignition time delay behavior. Ignition at 25 kW/m<sup>2</sup> was 290 seconds and 78 seconds at 50 kW/m<sup>2</sup>. Comparing these values with the glass reinforced FR SMC which demonstrated 227 seconds at 25 kW/m<sup>2</sup> and 52 seconds at 50 kW/m<sup>2</sup> shows very favourable properties for FR NFSMC. The non-FR NFSMC also showed a similar improvement over the glass fibre SMC with ignition times of 130 seconds and 68 seconds at 25 kW/m<sup>2</sup> and 50 kW/m<sup>2</sup> respectively. The non-FR NFSMC showed 185 seconds at 25 kW/m<sup>2</sup> and 54 seconds at 50 kW/m<sup>2</sup> ignition delay time.



Figure 3.10. Peak heat release rate of materials tested at both irradiances.

#### 3.3.4 Effect of Materials

Unlike synthetic polymers, wood is an inhomogeneous material which is also anisotropic. It is a complex mixture of natural polymers of high molecular weight, the most important of which are cellulose (~ 50%), hemicellulose (~ 25%) and lignin (~ 25%) (Madorsky, 1965), although these proportions vary from species to species. Moreover, it normally contains absorbed moisture, the amount of which will vary according to the relative humidity and conditions of exposure. The rate of heat transfer in a hygroscopic material is significantly influenced by the evaporation of any physically or chemically entrapped moisture (Davies, 1993). During the heating of a hygroscopic material, a complex process of dissociation (dehydration), vaporisation and migration of moisture takes place. Therefore when analysing the results obtained from the cone calorimeter, discrepancies may occur due to different levels of moisture in the cellulose based materials.

### 3.3.5 Effective Heat of Combustion (EHC)

The effective heat of combustion (EHC) is the heat released per gram of mass lost (Figures 3.11 to 3.16). It has a constant value at the beginning of combustion but starts to fluctuate in the latter part of the testing. As the heat of combustion is determined by the heat of emission and mass loss, the rate of mass loss multiplied by the EHC will approximately give the heat release rate (because the effective enthalpy of combustion varies during the combustion cycle).



*Figure 3.11. EHC curves for FR NFSMC and FR SMC at 25 kW/m<sup>2</sup>.* 



Figure 3.12. HRR curves for non-FR NFSMC and non-FR SMC at 25 kW/m<sup>2</sup>.



*Figure 3.13. EHC curves for FR NFSMC and FR SMC at 50 kW/m*<sup>2</sup>.



*Figure 3.14. HRR curves for non-FR NFSMC and non-FR SMC at 50 kW/m<sup>2</sup>.* 



*Figure 3.15. EHC curves glass vinyl ester, plywood and gypsum board at 25 kW/m<sup>2</sup>.* 



*Figure 3.16. EHC curves glass vinyl ester, plywood and gypsum board at 50 \text{ kW/m}^2.* 

The heat of combustion profiles (Figures 3.11 to 3.16) show almost constant values throughout the test for all the specimens tested, but they appear to change during the final stages of the burn. This indicates that the composition of the substrate is changing with time due to charring (Davies et al., 1993). The effective heat of combustion during 300 seconds for the NFSMC (EHC<sub>300</sub>) was moderately reduced from 18 to 11 MJ/kg. This indicates that the combustion mechanism is being interfered with, which was most likely to do with the ATH decomposing in the vapour phase. However when considering the total heat of combustion (THC) during the burning process, the THC value for the non-FR NFSMC was 5221 MJ/kg and 7496 MJ/kg for the FR system at 25 kW/m<sup>2</sup>. The values are as expected high at 50 kW/m<sup>2</sup> due to the higher energy input into the system thus breaking the chemical bonds quicker which in turn emits a higher energy. The values were 4880 MJ/kg and 8193 MJ/kg for the non-FR NFSMC and FR system, respectively. These values suggest that the CaCO<sub>3</sub> filled systems behaved in a much more endothermic mode than the ATH system at absorbing the heat. However the ATH is far better at interfering and suppressing the combustion process than the  $CaCO_3$ . The addition of aluminum trihydroxide is added to polymers to reduce flammability and reduce cost.

The flame retardant mechanism of ATH requires a reaction temperature in excess of 220 °C, at which point it decomposes thus causing the release of water vapour. This has the resulting effect of absorbing heat from the system consequently acting as a heat sink and prolonging ignition time. These dilute and displace flammable gases from the propagation zone. Together with charring products, an aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) protective layer is formed on the surface of the substrate. Thermodynamic data of aluminum trihydroxide shows it absorbing as high as 1.20 MJ/kg of thermal energy by the following reaction:  $2Al(OH)_3 \xrightarrow{\Lambda} Al_2O_3 + 3H_2O + 1.20MJ/kg$  (Roberts, 1971).

Therefore the two functions of the ATH of which the release of water of hydration in tandem with absorbing heat is far better than the inert heat sink behavior of the  $CaCO_3$  with respect to reaction to fire performance, this is evident from the ignition times, peak heat release rate values and the overall HRR profile.

# **3.4 Conclusions**

This work assed the feasibility of using natural fibres in SMC type material for use in the construction industry such as floor coverings which are currently not controlled in terms of reaction to fire properties. Internal wall linings where adequate performance under British standard reaction to fire tests can be applied may allow the material to compete with commonly used plasterboard linings. The incorporation of aluminum trihydroxide into the unsaturated polyester resin system did have a significant effect on the reaction to fire behavior of the composite. The ignition delay times were prolonged and the peak heat release rate values were reduced at both radiant heat fluxes. The findings indicated that with adequate flame retardant additives being incorporated into the SMC system the NFSMC can compete with some alternative building materials in terms of reaction to fire performance.

# **3.5 References**

ASTM E-1354; Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using the Oxygen Consumption Calorimeter. The American Society for Testing and Materials. 1992.

Babrauskas. V: *Development of the Cone Calorimeter, A Bench-Scale Heat Release Rate Apparatus Based on Oxygen Consumption*. Report (NBSIR 82-2611). [U.S.] National Bureau of Standards. (1982). Brown. J.E, Braun. E and Twilley. W.H: *Cone calorimetric evaluation of the flammability of composite materials*. Report (NBSIR 88-3733). [U.S.] National Bureau of Standards. (1988).

Davies. J.M, Hakmi. R and Wang. H.B: *Numerical temperature analysis of hygroscopic panels exposed to fire*. In: Proceedings of eighth international conference on numerical methods in thermal problems. Swansea (1993).

Garkhail. S. K, Heijenrath. R.W.H and Peijs, T: *Mechanical properties of natural-fibremat-reinforced thermoplastics based on flax fibres and polypropylene*. Applied Composite Materials. 2000.7: p. 5-6.

Hakkarainen. T and Kokkala. M: *Application of a one-dimensional thermal flame spread model on predicting the rate of heat release in the SBI test.* Fire and Materials. 2001. **25**: p. 61-70.

Joshia. S.V, Drzal. L.T, Mohanty. K and Arora. S: *Are natural fiber composites environmentally superior to glass fiber reinforced composites*? Composites: Part A. 2004. **35**: p. 371-376.

Karlsson. B: *Modelling fire growth on combustible lining materials in enclosures*. 1992. Report TVBB-1009, Lund University, Lund, Sweden.

Madorsky. S.L: *Thermal degradation of organic polymers*. Clothing and Textiles Research Journal. 1965. **35**: p. 289-290.

Malgorzata. H and Paukszta. D: *Flammability of composites based on polypropylene and flax fibres*. Molecular Crystals and Liquid Crystals. 2000. **354**: p. 373-380.

Mohanty. K, Misraa. M and Hinrichsen. G: *Biofibres, biodegradable polymers and biocomposites: An overview*. Macromolecular Materials and Engineering. 2000. **276/277**: p.1-24.

Peijs. T: Composites turn green, e-Polymers. 2002. no. T\_002.

Roberts. A.F: *Problems associated with the theoretical analysis of the burning of wood*. In: 13<sup>th</sup> international symposium on combustion, p. 893-903. The Combustion Institute, Pittsburgh. (1971).

Sain. M, Park. S.H, Suhara. F and Law. S: *Flame retardant and mechanical properties of natural fibre-PP composites containing magnesium hydroxide*. Polymer Degradation and Stability. 2004. **83**: p. 363-367.

Schartel. B. (ed) and Braun U.: Fourteenth Annual BCC Conference on Flame Retardancy, *Fire Retarded Polypropylene/Flax Biocomposites*. August 2003. p. 219-228.

Schneider. J.P, Myers. G.E, Clemons. C.M and English, B.W: *Biofibers as reinforcing fillers in thermoplastic composites*. Journal of Vinyl and Additive Technology. 1995. **1**(2): p. 103-108.

Scudamore. M.J: *Fire performance studies on glass reinforced plastic laminates*. Fire and Materials. 1994. **18**: p. 323-325.

# 4

# Aluminium Trihydroxide in Combination with Ammonium Polyphosphate as Flame Retardants for Unsaturated Polyester

# **4.1 Introduction**

Unsaturated polyester resins (UP) are extremely versatile in terms of their properties and applications and have been a popular thermosetting resin for glass-fibre reinforced plastics (GRP) (Heger and Sharff, 2001). This matrix material has been used for many years in broad technology fields such as naval, offshore applications, automotive and construction industries. The reinforcement of polyesters has been traditionally with glass fibres. Recent studies replacing the traditional fibres with various cellulosic fibre reinforcements have shown promising results. These systems meet the environmental credentials without losing the characteristic properties of composite materials (Aziz *et al.*, 2005; Goutianos *et al.*, 2006; Hapuarachchi *et al.*, 2007).

However despite the numerous advantages that polymeric materials provide to society in everyday life, there is an obvious disadvantage related to the high flammability of many polymers. Fire can be broken down into their constituent fire hazards: ignitability, ease of extinction, heat release rate, flame spread, smoke obstruction and smoke toxicity (Hirschler, 2001; Purser, 2000; Babrauskas, 1988). According to fire statistics, more than 12 million fires break out every year in the United States, Europe, Russia and China killing some 166,000 people and injuring several hundreds of thousands. Calculating the direct losses and costs for these countries is difficult, but \$500 million per annum is an estimate based on some national data (Manor and Georlette, 2005). Therefore, in the pursuit of improved approaches to flame retardants (FR) of polymers, a wide variety of concerns must be addressed. Competing with expensive flame retardant polymers as well as reducing the overall cost of the final product demands that the FR's are kept at a reasonable cost. This limits the solutions to the problem primarily to additive type approaches. These additives must be easily processable with the polymer, must not excessively degrade the other performance properties, and must not create environmental problems in terms of recycling or disposal.

Traditional systems such as brominated FR's (e.g. Hexabromocyclododecane (HBCD)) which has been used in many polymers including unsaturated polyester to prevent flame spread but have significant disadvantages of producing dense smoke and corrosive combustion by-products which can have a negative impact on the environment. Another commonly used filler is aluminum trihydroxide (ATH), which is looked upon as a greener FR. The effectiveness of this flame retardant tends to be limited since relatively large amounts of the filler are needed for adequate flame retardancy (>60 wt.%), which has a detrimental effect on the processing and as well as possible alterations to the mechanical properties of the final product. Some previous studies have shown improved flame retardancy of thermoplastic systems based on improving the effect of ATH in

combination with other FR fillers such as nitrogen rich melamine (Zilberman *et al.*, 2000).

Also, there has been some research carried out using combinations of aluminum trihydroxide together with ammonium polyphosphate (APP) in different polymer systems (Castrovinci *et al.*, 2005). These studies resulted in some synergistic and antagonistic behaviour with respect to reducing the flammability of the polymer. To date, these two fillers have not been used together in a UP system. Therefore the purpose of this work is to carry out thermal and cone calorimetry studies on unsaturated polyester resin with ATH in combination with APP to create a flame retardant ternary system.

# 4.2 Experimental Study

#### 4.2.1 Materials and Specimen Preparation

This study consisted of bench scale fire testing a set of flame retardant unsaturated polyester specimens. The unsaturated polyester resin (UP) used was a P17 (ortho resin) from Reichhold Organic Chemicals Ltd. A non-flame retardant specimen consisting of 50 wt.% calcium carbonate (CaCO<sub>3</sub>) (~ 200 phr) supplied by Omya UK was prepared. The flame retardant fillers used were aluminum trihydroxide (OL104) from Albemarle Corporation and Exolit<sup>TM</sup> ammonium polyphosphate from Clariant. An unfilled unsaturated polyester specimen was also produced as a control specimen. To prepare the specimens, the fillers were dispersed in the UP under excessive shear mixing using a High Speed Mechanical Mixing (HSMM) Citenco, FHP Motors LC9 with four blades. The formulation was mixed for 5 minutes at 3000 rpm. The specimens were cured in an open steel mould with dimensions of 100×100 mm. The formulations (Table 4.1) were prepared and cured for 10 minutes at 140 °C in an air circulated oven.

Specimens (Weight percentage)		
Unsaturated Polyester Resin (UP)		
+ 50 wt.% Calcium Carbonate (CaCO <sub>3</sub> )		
+ 30 wt.% ATH		
+ 40 wt.% ATH		
+ 50 wt.% ATH		
+ 50 wt.% ATH + 5 wt.% APP		
+ 50 wt.% ATH + 10 wt.% APP		
+ 50 wt.% ATH + 15 wt.% APP		

Table 4.1. UP formulations studied in this investigation.

# 4.2.2 Experimental Procedures

## 4.2.2.1 Cone Calorimetry

All the tests for this study were conducted in the horizontal orientation. An irradiance of  $50 \text{ kW/m}^2$  was used. Ignition was spark induced; specimens were run without a retainer frame and in triplicate and averaged.

# 4.2.2.2 Thermal Analysis

Thermogravimetric analysis (TGA) was carried out using TA Instruments Q500 TGA at a heating rate of 10 °C/min under air and nitrogen rich atmospheres; with a gas flow rate of 20 ml/min. In each case, specimens of approximately 5 mg were positioned in a platinum pan. Differential scanning calorimetry (DSC) analysis was carried out using Mettler Toledo DSC822e and closed aluminum pans with a pierced hole in the cover. Thermal scans were run from 30-350 °C at 10 °C/min with specimen masses averaging 5 mg, in air.

### 4.3 Results and Discussion

#### 4.3.1 Cone Calorimetry

Inorganic hydroxide flame retardant additives decompose when heated, releasing water in the vapour phase of combustion (pyrolysis stage). As this elimination of water results in an endothermic reaction, heat is removed from the substrate. This removal of heat slows down the decomposition of the substrate, which is indicated by the delay in time to ignition (TTI) (Table 4.2) and also the reduction in heat release rate (Figure 4.1).

Specimens	TTI (s)
UP	7
+50 wt.% CaCO3	8
+30 wt.% ATH	20
+40 wt.% ATH	22
+50 wt.%ATH	24
+50 wt.% ATH+5 wt.% APP	26
+50 wt.% ATH+10 wt.APP	27
+50 wt.% ATH+15 wt.% APP	30

Table 4.2. The delay in the time to ignition (TTI) for the FR UP specimens.

This phenomenon allows the substrate to remain below its ignition temperature for the duration of the hydroxide decomposition process. Literature reports that the largest of the commercially used inorganic hydroxides absorbs between 1000 and 1500 J/g of energy during decomposition (Lyons, 1987). Although other references may cite different values for this parameter, the apparent discrepancies should not be of great concern, as they are relative.

The values obtained depend on the type of equipment used to measure the endothermic response, the heating rate used, the sample size, particle size, crystal morphology, the method of sample preparation and the temperature range used in the determination. The addition of the fillers within the UP shows a delay in ignition times. Interference of the flame is due to the decomposition mechanisms of the individual fillers which are shown by the TGA and DSC thermograms, which will be discussed later. Cone calorimeter tests have been performed to estimate the reaction to fire of the flame retardant UP systems. Many reactions to fire parameters were determined, such as the time to ignition, the heat release rate, mass loss behaviour and the smoke production over time. In this study, tests were carried out at 50 kW/m<sup>2</sup> heat flux, which in the cone calorimeter is considered to represent a well developed fire (Schartel *et al.*, 2005).

The time to ignition data for the tested UP formulations is shown in Table 4.2. A marked improvement can be seen in the ATH filled formulations compared to unfilled with respect to delaying the ignition time. The UP had a TTI of 7 seconds and combusted violently with a large flame during testing. As the loading of ATH increases the TTI was prolonged. The ATH starts to break down in the temperature range of 180-200 °C, conversion to aluminium oxide taking place in an endothermic reaction with release of water vapour. As a result of the endothermic breakdown, the UP is cooled, and thus fewer pyrolysis products are formed. The water vapour liberated has a diluting effect in the gas phase and forms an oxygen displacing protecting layer over the condensed phase (Sobolev and Woycheshin, 1987).



Figure 4.1. The reduction in heat release rate profile for the FR UP specimens.

Table 4.3 reports a PHRR of 836 kW/m<sup>2</sup> for the unfilled UP. This was reduced to 289 kW/m<sup>2</sup> with the introduction of CaCO<sub>3</sub>, which is thought to occur for two reason; (i) more of the UP volume had been replaced by the filler, thus simply reducing the amount of combustible material present and (ii) when CaCO<sub>3</sub> decomposes it releases CO<sub>2</sub> which is thought to form around the flame front and thus diluting the combustion mixture (Deodhar *et al.*, 2006).

Specimens	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )
UP	836	80
+50 wt.% CaCO <sub>3</sub>	289	85
+30 wt.% ATH	337	116
+40 wt.% ATH	319	113
+50 wt.% ATH	244	107
+50 wt.% ATH+5 wt.% APP	240	105
+50 wt.% ATH+10 wt.% APP	230	93
+50 wt.%ATH+15 wt.%APP	221	90

*Table 4.3.* The peak heat release rate (PHRR) and total heat release (THR) of the FR UP specimens.

As the ATH loading increased from 30 to 50 wt.% the PHRR decreased from 337 to 244  $kW/m^2$ , respectively. Inorganic hydroxides are generally used at levels of 50 wt.% or more to attain the flame retardant results required. In this study 50 wt.% was the maximum loading that could be achieved due to very high shear forces needed to disperse the highly viscous mixture. The results show that the calcium carbonate had a positive effect in reducing the PHRR. This was thought to be due to fuel replacement. The ATH reduced the PHRR further, the endothermic and water liberating effect reduced the combustion of the specimen. This was evident from PHRR for 50 wt.% ATH and 50 wt.% CaCO<sub>3</sub> loaded UP specimens, which were 224 and 289  $kW/m^2$  respectively. The addition of APP also reduced the PHRR. A formulation with the maximum ATH loading of 50 wt.% was chosen to formulate three specimens with 5, 10 and 15 wt.% APP, the PHRR were 240, 230 and 221  $kW/m^2$ , respectively. Again the explanation for this reduction could be due to more inorganic filler being introduced into the resin thus less UP being available for combustion.

However research by Levchik *et al* (1995) and Shen *et al* (1969) have shown a reaction between ATH and APP. Ammonium polyphosphate, a well known component of intumescent flame retardants is considered a shield coating precursor because of the formation of a continuous cross linked vitreous phase called ultraphosphate during thermal decomposition (Camino and Luda, 1998). Whereas aluminum trihydroxide on thermal decomposition undergoes endothermic dehydration releasing water to the gas phase with the in situ formation of a thermally stable ceramic material alumina (Al<sub>2</sub>O<sub>3</sub>).

The formation of an Al<sub>2</sub>O<sub>3</sub> surface layer acts in a similar way to an intumescent flame retardant whereby it shields the heat and mass transfer between the unsaturated polyester and the flame. The flame retardant effectiveness of ATH is however detrimental to the mechanical properties (not tested here), i.e. high loadings generally  $\geq$  50 wt.% are necessary to reach a suitable flame retardant effect but results in a dense and brittle material (Hippi *et al.*, 2003; Liauw *et al.*, 1995).

The combined use of ATH and APP was studied aiming at a more thermally stable P-Al-O surface coating instead of the P-O, bringing together film forming action of ultraphosphate with thermal stability of  $Al_2O_3$  to improve high temperature surface protection of the polymer. Table 4.3 shows the total heat release (THR). Unfilled UP had a THR of 80 MJ/m<sup>2</sup>, which increased for the specimen with the addition of ATH and APP. The total heat release is calculated by integrating the area underneath the HRR vs time curve. Due to the FRs prolonging the burn time for the specimen's results in the slight increase in THR. Zhang *et al* (2004) proposed a correction factor based on theoretical analysis of taking account of the effective heat of combustion of the filler and polymer separately then multiple it with the individual mass loss rates. They suggested that if this correction factor was taken into consideration in their study, then the THR for a PP specimen loaded with 70 wt. % ATH would have a 6.5 % lower.

Nevertheless the most significant predictor of fire hazard is the heat release rate; therefore the rate at which heat is released is of more interest than the total amount (Babrauskas and Grayson, 1992; Babrauskas and Peacock, 1992). An increasing burn time is indicative of the FR additive impeding or hindering the combustion process. Also in general the most important factor in evaluating a material is the peak heat release rate (PHRR) as this signifies the time at which the material evolves the maximum amount of heat into the surrounding, this can give a crude indication of the time available to escape the fire before flashover (the near simultaneous ignition of all combustible material in an enclosed area). The unfilled UP reaches its PHRR of 836 kW/m<sup>2</sup> in 96 seconds and the 50 wt.% ATH+15 wt.% APP system reached its PHRR in 76 seconds but this was only 221 kW/m<sup>2</sup> which is almost 4 times lower than the unfilled UP.

Specimens	Time to Peak EHC	Average EHC
	<b>(s)</b>	(MJ/kg)
UP	236	20.79
+50 wt.% CaCO3	470	20.86
+30 wt.% ATH	600	19.92
+40 wt.% ATH	639	19.44
+50 wt.% ATH	652	19.28
+50 wt.% ATH+5 wt.% APP	672	19.08
+50 wt.% ATH+10 wt.% APP	728	18.91
+50 wt.%ATH+15 wt.%APP	874	18.81

**Table 4.4.** The delay in time to peak effective heat of combustion (EHC) and the reduction in average EHC of the FR UP specimens.

Table 4.4 shows the time to peak effective heat of combustion (EHC) and average EHC for the specimens tested. The EHC is calculated from the THR and total mass loss, which was reduced from an overall average of 20.79 to 18.81 MJ/kg for the unfilled UP and 50 wt.% ATH+15 wt.% APP system, respectively. This is an indication of the combustion mechanism being interfered with, most likely in the vapour phase by the FR mechanisms of the aluminum trihydroxide and ammonium polyphosphate. Also, the time to peak EHC was delayed, which shows that the combustion is being hindered by the flame retardant mechanisms. The results of the smoke parameter measurements made in the cone calorimeter can be expressed in a number of different forms. Table 4.5 displays the time to peak specific extinction area (SEA), which is the total obstruction area of smoke produced, divided by the total mass loss during the burn.

**Table 4.5.** The delay in the time to peak specific extinction area (SEA) for the FR UP specimens.

Specimens	Time to Peak SEA (s)
UP	136
+50 wt.% CaCO <sub>3</sub>	420
+30 wt.% ATH	645
+40 wt.% ATH	668
+50 wt.% ATH	680
+50 wt.% ATH+ 5wt.% APP	712
+50 wt.% ATH+10 wt.% APP	720
+50 wt.% ATH+15 wt.% APP	730

The shift in the time to peak is most likely to be due to the FR formulations generating a protective charred layer which prevents volatiles and smoke evolving from the specimen's surface. Another important smoke measurement is the average smoke production release (SPR). The SPR is the area of obscuration produced per second. Figure 4.2 illustrates the effect of FR fillers on reducing the average SPR from 0.06 to 0.04 m<sup>2</sup>/s for the unfilled UP and 50 wt.% ATH+15 wt.% APP specimens, respectively. Table 4.6 lists the total smoke release (TSR) and total smoke production (TSP). The rise in these two properties is indicative of incomplete combustion. This smouldering (flameless combustion) effect results in a longer burn time which, allows for more smoke and soot debris to accumulate which is especially important here due to the high degree of aromatic content (especially the styrene) in the unsaturated polyester resin (Troitzsch, 1990).



Figure 4.2. The effect on the smoke production release (SPR) of the FR UP specimens.

The gas products released by a decomposing polymer substrate depend on the chemical nature of the organic constituents, oxygen availability, and temperature of the fire. Table 4.6 also displays the mean carbon monoxide yield (COY) in kg/kg. The mean COY is seen to be inversely proportional to the TSR and TSP. The theory behind this is that more carbon monoxide is liberated at a higher decomposition temperature in the UP (Cunliffe *et al.*, 2003). Cunliffe's group carried out this work on the pyrolysis behaviour of various polymers including unsaturated polyester. The generation of carbon oxides would be expected from the breakdown of ester bonds within the resin. The higher pyrolysis temperatures caused by the higher PHRR of the UP would result in more carbon monoxide to be evolved due to further cracking of the polyester chains. While the types and amounts can vary between materials, all polymers release carbon monoxide is a major safety concern because it is lethal at a relatively low concentration, with human death occurring within one hour at a concentration of about 1500 ppm (Hirschler, 2001).
**Table 4.6.** The total smoke release (TSR) total smoke production (TSP) and carbonmonoxide yield (COY) measurements.

Specimens	TSR	TSP	Mean COY
	$(m^2/m^2)$	( <b>m</b> <sup>2</sup> )	(kg/kg)
UP	2172	21.7	0.0311
+50 wt.% CaCO <sub>3</sub>	3209	32.1	0.0243
+30 wt.% ATH	3442	34.4	0.0237
+40 wt.% ATH	3546	35.5	0.0232
+50 wt.% ATH	3811	38.1	0.0216
+50 wt.% ATH+5 wt.% APP	3838	38.4	0.0215
+50 wt.% ATH+10 wt.% APP	3914	39.1	0.0213
+50 wt.% ATH+15 wt.% APP	3996	39.5	0.0212

**Table 4.7.** The peak mass loss rate (MLR), residual mass (RM) and average specific mass loss for the FR UP specimens from the cone calorimeter.

Specimens	Peak MLR	RM (%)	Average specific
	(g/s)		ML
			$(\mathbf{g/s \cdot m}^2)$
UP	0.42	6.8	34.4
+50 wt.% CaCO <sub>3</sub>	0.22	36.7	11.1
+30 wt.% ATH	0.21	17.7	14.4
+40 wt.% ATH	0.17	18.7	13.7
+50 wt.% ATH	0.165	25.1	10.9
+50 wt.% ATH+5 wt.% APP	0.164	26.7	9.7
+50 wt.%ATH+10 wt.% APP	0.162	28.4	9.3
+50 wt.%ATH+15 wt.% APP	0.161	28.8	9.3

#### 4.3.2 Thermal Analysis

To examine the effect of FRs on the thermal stability and the decomposition behaviour, TGA data under nitrogen and air atmospheres were determined and analysed. The TGA curve of aluminum trihydroxide (ATH) (Figure 4.3) which was heated to 900 °C shows one main weight loss step at about 240 °C which is due to endothermic release of its 35 % water of crystallisation into the gas phase, this leads to the in-situ formation of a ceramic layer of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Both the endothermic dehydration and the formation of the ceramic layer are responsible for the FR mechanism of inorganic hydroxides (Bourbigot *et al.*, 1999).



Figure 4.3. The TGA thermogram of fillers used in the UP formulations.



*Figure 4.4a.* The effect of the various fillers and their combination on improving the thermal stability and residual mass of UP.



*Figure 4.4b.* The effect of the various fillers and their combination on improving the thermal stability and residual mass of UP tested in nitrogen.

The TGA analysis carried out on ammonium polyphosphate (APP) shows that the elimination of ammonia and water starts at 190 °C (maximum rate of weight loss at 370 °C) with transformation of linear crystalline APP into a vitreous crosslinked ultraphosphate) which undergoes fragmentation to volatile P<sub>2</sub>O<sub>5</sub>. Ammonia evolution from APP is related to acidic sites formation involved in the intumescence phenomenon. Calcium carbonate ( $CaCO_3$ ) thermally decomposes at a much higher temperature than the other two fillers. The single decomposition step occurred at 800 °C which indicates a higher thermal stability. Calcium carbonate does not combust; it thermally decomposes and converts through the following mechanism;  $CaCO_3 \rightarrow CaO + CO_2$ . When  $CaCO_3$  is heated to 800 °C it liberates CO<sub>2</sub> and will thus become CaO. Figure 4.4a and 4.4b show the results of the UP formulations test in the TGA under air and nitrogen respectively. The formulations started to decompose at around 250 °C due to the decomposition of the resin system. The unsaturated polyester started to decompose at 250 °C, whereas the main weight loss occurred between 300 °C and 400 °C. During thermal decomposition, it is thought that the polystyrene cross-links started to decompose first which was followed by volatilisation of the styrene. The linear polyester portion undergoes scission. Ferreira et al., 2006 have shown that during thermal decomposition, volatiles are lost up to 400 °C while above 400 °C; it is solid phase oxidation reactions that predominate. The 50 wt.% CaCO<sub>3</sub> specimen demonstrated the best performance in terms of thermal stability when tested in air. The ATH loaded specimens showed a marked improvement in residual weight retention at temperatures above 600 °C as the loading level increase. This is thought to be due to the conversion of  $Al(OH)_3$  to  $Al_2O_3$  which is a thermally stable engineering ceramic which possesses a melting temperature of 2054 °C. The addition of APP to the formulation also increased the residual mass, which was also observed for the cone calorimeter specimens (Table 4.7). It has been well documented that as APP decomposes it dehydrates and converts into an intumescent char; this could be the reason for the extra residual mass. The ATH+APP specimens which were run under nitrogen (Figure 4.4b) showed no major differences to those which were tested in air.

Since the pyrolysis of polymers during fires are characterised by anaerobe decomposition, it was important to conduct the TGA tests in nitrogen as well as thermooxidative conditions. With respect to char yields, the pure UP comprised of slight more at the end of the run. However the most significant difference was with the CaCO<sub>3</sub> specimen. There was rapid decomposition after 400 °C and had only a 22 % char yield whereas when tested in air it held stable up to 800 °C in which it ended with a 55 % char yield. The specimen not being able to form a protective skin in the presence of a nitrogen rich atmosphere was thought to be attributed to this difference (Krämer et al., 2007). Figure 4.5 shows the energy absorption profile investigated by differential scanning calorimetry (DSC) on the fillers. The aluminum trihydroxide absorbed the most significant amount of thermal energy out of all the fillers. The ATH underwent endothermic decomposition and absorbed 978 J/g of thermal energy. However, the other two fillers did not show any significant endothermic effects. The DSC scan of APP showed an endothermic process between 240 and 260 °C which corresponds to polymorphic transitions of residual APP crystal structure form APP I to APP form II, above which ammonia and water elimination begins at low rates as seen from TGA (Figure 4.6).



Figure 4.5. DSC thermogram of the unfilled fillers on their own.



Figure 4.6. DSC thermogram of the FR UP formulations.

This process decreases the concentration of fuel available for combustion and limits the amount of heat being fed back into the surrounding polymer. The result is a decrease in the mass burning rate for the polymer. Figure 4.6 shows the heat sink effect caused upon by the introduction of ATH into the UP resin. The direct result of this and the evolution of water vapour can be witnessed in Table 4.2 which shows TTI data. As the ATH loading increases so too does the time to combustion.

# **4.4 Conclusions**

The purpose of this study was to observe any possible flame retardant improvements to commercial unsaturated polyester resin using "greener" non-toxic flame retardants. The use of ATH in combination with APP was expected to impart an improved flame retardant effect in the UP system. A combination of both FRs showed an improved ignition delay time as well as decreases in the peak heat release rate and carbon monoxide yield. However, synergistic behaviour was not witnessed but instead a mere fuel replacement effect on the role of the fillers is more plausible.

In general, synergism can be defined as two or more components working together to produce a result not obtainable by any of the components independently. The polymer used plays an important part in the effectiveness of these two FR fillers and their combination does not work with all polymers as shown in the literature. The additional reduction in the PHRR with the addition of APP does not justify its use due to the resultant difficulties with increased viscosity, which will result in major processing difficulties in adopting these materials in potential fibre reinforced composites.

## **4.5 References**

Aziz. S.H, Ansell. M.P, Clarke. S.J and Panteny. S.R: *Modified polyester resins for natural fibre composites*. Composites Science and Technology. 2005. **1**: p.525-535.

Babrauskas. V: Effective measurement techniques for heat, smoke and toxic fire gases. In Fire: Control the Heat, Reduce the Hazard. QMC Fire & Materials Centre, London, UK, p. 4.1-4.10, (1988).

Babrauskas. V and Grayson. S. J: *Heat Release in Fires*, E & FN Spon (Chapman and Hall), London (1992).

Babrauskas. V and Peacock. R. D: *The Single Most Important Variable in Fire Hazard*. Fire Safety Journal. 1992. **18**: p. 255-272.

Bourbigot. S, Le Bras. M, Leeuwendal. R, Shen. K.K and Schubert. D: *Recent advances in the use of zinc borates in flame retardancy of EVA*. Polymer Degradation and Stability. 1999. **64**(3): p. 419-425.

Camino. G and Luda. M. P: *Mechanistic study on intumescence*. In *Fire retardancy of Polymers: The use of intumescence*; Le Bras. M, Camino. G, Bourbigot. S, Delobel. R, Eds; Special Publication-Royal Society of Chemistry. **224**. Royal Society of Chemistry: Cambridge. p. 48-63 (1998).

Castrovinci. A, Camino. G, Drevelle. C, Duquesne. S, Magniez. C and Vouters. M: *Ammonium polyphosphate-aluminum trihydroxide antagonism in fire retarded butadiene-styrene block copolymer*. European Polymer Journal. September 2005. **41**(9). p. 2023-2033.

Cunliffe. A.M, Jones. N and P.T. Williams: *Recycling of fibre-reinforced polymeric waste by pyrolysis: thermo-gravimetric and bench-scale investigations*. Journal of Analytical and Applied Pyrolysis. December 2003.**70**(2): p. 315-338.

Deodhar. S, Shanmuganathan. K, Patra. P, Fan. Q, Calvert. P and Warner. S: *Polypropylene based novel flame retardant nanocomposite compositions*. In: Technical Papers in Composites 2006 Convention and Trade Show American Composite Manufacturers Association. St Louis, MO USA; October 18-20, 2006.

Ferreira. J.M, Errajhi. O.A.Z and Richardson. M.O.W: *Thermogravimetric analysis of aluminised E-glass fibre reinforced unsaturated polyester composites*. Polymer Testing. December 2006. **25**(8): p. 1091-1094.

Goutianos. S, Peijs. T, Nystrom. B and Skrifvars. M: *Development of Flax Fibre based Textile Reinforcements for Composite Applications*. Applied Composite Materials. 2006. **13**: p. 199-215.

Hapuarachchi. T.D, Ren. G, Fan. M, Hogg. P.J and Peijs. T: *Fire Retardancy of Natural Fibre Reinforced Sheet Moulding Compound*. Applied Composite Materials. 2007. **14**: p. 251-264.

Heger. F.J and Sharff. P.A: *Buildings: Plastics and Composites, Encyclopaedia of Materials: Science and Technology*. p. 833-841. Pergamon Press. UK. (19 Sept 2001).

Hirschler. M.M: Fire performance of organic polymers, thermal decomposition, and chemical composition, in: Fire and Polymers: Materials and Solutions for Hazard Prevention (eds.: G.L. Nelson and C.A. Wilkie). American Chemical Society (ACS Symposium Series), Washington, DC, **797**: p. 214-227, (2001).

Hippi. U, Mattila. J, Korhonen. M and Seppala. J: *Compatibilization of polyethylene/aluminum hydroxide (PE/ATH) and polyethylene/magnesium hydroxide (PE/MH) composites with functionalized polyethylenes*. Polymer. 2003. **74**: p.1193-1201.

Hume. J: Assessing the fire performance characteristics of GRP composites. In: International conference on materials and design against fire. London. (1992): p.11-15.

Krämer. R.H, Raza. M.A and Gedde. U.W: *Degradation of poly(ethylene-co-methacrylic acid)-calcium carbonate nanocomposites*. Polymer Degradation and Stability. 2007. **92**: p.1795-1802.

Levchik. S.V, Camino. G and Costa. L: *Mechanism of action of phosphorous-based flame retardants in Nylon 6. I: Ammonium polyphosphate.* Journal of Fire Sciences. 1995. **13**(1): p. 43-58.

Liauw. C.M, Lees. G.C and Hurst. S.J: *The effect of surface modification of aluminium hydroxide on the crystallisation behaviour of aluminium hydroxide filled polypropylenes*. Macromolecular Materials and Engineering. 1995. **235**(1): p. 193-203.

Manor. O and Georlette. P: *Flame retardants and the environment*. Speciality Chemicals. 2005. **25**(9): p. 36-39.

Lyons. J.W: *The Chemistry and Uses of Fire Retardants*. John Wiley and Sons Ltd, Florida, USA, (1987).

Purser. D.A: *Toxic product yield and hazard assessment for fully enclosed design fires*. Polymer International. 2000. **49**: p.1232-1255.

Sastri. S.B, Armistead. J.P, Keller. T.M and Sorathia. U: *Flammability characteristics of phthalonitrile composites*, In: *Evolving technologies for the competitive edge*: Proceedings of the 42nd International SAMPE Symposium", Anaheim, California, 1032 (May 4-8, 1997).

Schartel. B, Bartholmai. M and Knoll. U: *Some comments on the use of cone calorimeter data*. Polymer Degradation and Stability. June 2005. **88**(3): p. 540-547.

Shen. C.Y, Stahlheber. N.E and Dyroff. D.R: *Preparation and characterization of crystalline long-chain ammonium polyphosphate*. Journal of the American Chemical Society. 1969. **1**(91): p. 62-67.

Sobolev. I and Woycheshin. E.A: *Alumina trihydrate*. In: Katz. H.S and Milewski. J.V (Editors), Handbook of fillers for plastics, Van Nostrand Reinhold, New York, p. 292-310, (1987).

Troitzsch. J: International plastics flammability handbook. Hanser Publishers, New York (1990).

Zhang. J, Wang. X, Zhang. F and Horrocks. A. R: *Estimation of heat release rate for polymer-filler composites by cone calorimetry*. Polymer Testing. April 2004. **23**(2): p. 225-230.

Zilberman. J, Hull. R.T, Price. D, Milnes. G.J & Keen F: *Flame retardancy of some ethylene-vinyl acetate copolymer-based formulations*. Fire Materials. 2000. **24**: p. 159-164.

# 5

# Multiwall Carbon Nanotubes and Nanoclays as Flame Retardants for Unsaturated Polyester

# **5.1 Introduction**

The purpose of this chapter was to continue the work from previous investigations in this thesis. Overcoming the issue of flammability in conjunction with reducing the filler loading was the prime objective of this investigation. This study used the same resin as previous chapters, however this time with the addition of nano-sized fillers such as carbon nanotubes and nanoclays. The initial discovery by Kojima *et al* (1993) within the Toyota group showed that a polyamide-6 clay nanocomposite, containing 5 % clay could lead to an increase of 40 % in tensile strength, while at the same time increasing the heat distortion temperature while maintaining impact strength. Due to the silicates fundamental unit thickness of 1 nm and high aspect ratio in combination with their high stiffness, these nanofillers when dispersed well will reinforce polymers far better than conventional fillers like calcium carbonate or glass fibres.

This has beneficial effects on the processability of the polymer due to a decrease in viscosity and a lower density of the material and more importantly less embrittlement. After the early work of Kojima et al (1993) in which various nylon-6 clay hybrids were investigated to determine their mechanical properties, Morgan et al (2005, 2006) contributed by carrying out a literature review into polymer layered silicate nanocomposites. Schartel et al (2006) studied the thermal and flame retarding effects of phosphonium modified silicates in epoxy resins. The mechanism is thought to be due to the clay acting as a barrier to the flame trying to penetrate the unconsumed polymer underneath the protective char layer. Layered clays have performed well in retarding the flame due to their excellent barrier properties. A recent addition to the nanoclay group is sepiolite which is a natural hydrous magnesium silicate. As a clay mineral, structurally it consists of two sheets of SiO<sub>4</sub> tetrahedra bonded via oxygen atoms to a central sheet of octahedrally arranged magnesium atoms. It has a needle-like profile which helps the flow ability of the polymer when melt produced. Bilotti et al (2008); Marosfoi et al (2008) and Franchini et al (2009) have looked at the dispersion of sepiolite within thermoplastic polymers as well as studying the effect on mechanical and thermal properties of the resulting nanocomposite.

Since the inadvertent discovery of carbon nanotubes (CNTs) by Iijima (1991), there has been a great deal of research into possible applications (Erik *et al.*, 2005; Wang *et al.*, 2007, 2008). Kashiwagi *et al* (2005) was one of the first to introduce CNTs into polypropylene (PP) with the sole purpose of reducing its flammability behaviour. The team reported that a possible mechanism for the reduction in peak heat release rate may have been due to the formation of a structured network layer. Beyer *et al* (2002) has also looked into using crude and purified MWNTs to decrease the flammability of ethylene vinyl acetate (EVA) copolymer. Dubois *et al* (2004) took the concept further and explored the consequences of using both CNTs and nanoclay fillers together in an EVA matrix. A synergic improvement was recorded for this ternary system when compared with the binary base systems. Ma *et al* (2007) also investigated a ternary CNT/nanoclay system with acrylonitrile butadiene styrene (ABS). Both studies recorded a reduction in the PHRR, and suggested that the CNTs acted as a sealing agent to create a network with the clay layers which formed a much tighter char than clay alone. The concept of synergism is often used in the enhancement of flame retardant polymer. By definition, synergism means the enhanced performance of a mixture of two or more components compared to that of a single component at the same concentration. In the field of fire science, this concept helps to limit the amount of volatile gases escaping from the degrading polymer and impedes the oxygen ingress.

Work to improve the flammability of a thermoset unsaturated polyester resin (UP) using multiwalled carbon nanotubes (MWNTs) and sepiolite nanoclay (Sep) was the purpose of this study. The conventional flame retardant (FR) used in glass reinforced plastics (GRP) is hydrated alumina (ATH) (Hapuarachchi *et al.*, 2009). The disadvantage with this FR filler is that a substantial loading level (>50 wt.%) is required to obtain a suitable flame retardancy which results is a highly viscous, porous and brittle materials (Hapuarachchi *et al.*, 2007). The use of nanofillers either on their own or together in a ternary system is anticipated to alleviate some this problem.

# **5.2. Experimental Detail**

#### 5.2.1 Materials

The MWNTs used were grade Nanocyl 3150 which is a short thin (95% purity) nanotube functionalized with amine (NH<sub>2</sub>) supplied by Nanocyl S.A. (Belgium). The nanoclay was an unmodified sepiolite clay (Sep) donated by Tolsa S.A. (Spain). The base resin used was unsaturated polyester (UP) resin (P17 ortho resin) from Reichhold Organic Chemicals Ltd. To prepare the nanocomposites the fillers were dispersed in the UP under excessive shear mixing using a High Speed Mechanical Mixer (HSMM) Citenco, FHP Motors LC9 with four blades. The formulation was mixed for 5 minutes at 3000 rpm. The formulation was poured into an open steel mould and placed into an air assisted oven to cure at 140 °C for 15 minutes.

Table 5.	1. S <sub>l</sub>	pecimen	formulations	s studied	these	include	binary	and	ternary	systems.
----------	-------------------	---------	--------------	-----------	-------	---------	--------	-----	---------	----------

	Binary	Systems	Ternary Systems		
No Filler	MWNT (wt. %)	Sepiolite (wt.%)	MWNT (wt. %)	Sepiolite (wt.%)	
	0.5	1	2	1	
	1	2.5	0.5	10	
Unfilled UP	2	5	-	-	
	-	10	-	-	

#### 5.2.2 Experimental Methods

Thermal gravimetric analysis (TGA) was employed to assess the thermal stability of the polymer nanocomposites. The derivative mass loss rate (DTG) was also provided; this is used to study the rate in change. A TA Instruments Q500 TGA was used, with average specimen weight of 3 mg. The temperature range was from 30 °C to 1000 °C at a ramp rate of 60 °C/min in air.

Fire Testing Technologies (FTT, UK) microcalorimeter measures parameters such as the heat release capacity (HRC) and peak heat release rate (PHRR) by utilising traditional oxygen depletion calorimetry. This is a rapid screening tool which is ideal for experimental polymer nanocomposite samples. Although it is not as well established as the cone calorimeter, it is the perfect tool to be used additionally with the cone calorimeter. The specimens for the microcalorimeter were approximately 5 mg and the test runs were carried out in triplicate and then the averaged values were used. The gas mixture was an [80/20] N<sub>2</sub>/O<sub>2</sub> mix. For each run the pyrolzer was set to a 60 °C/min heating rate to reach 750 °C from room temperature. The combustor was pre-set to 900 °C.

Cone calorimetry was carried out on samples of  $100 \times 100 \times 5$  mm. All these materials were conditioned at  $23 \pm 3$  °C at a relative humidity of  $50\% \pm 5\%$  for 24 hours prior to testing. The samples were wrapped with aluminum foil around the back and edges before placing the specimen into the holder and then into the cone calorimeter. A retainer frame was used to reduce edge burning effects. All these tests were carried out in accordance with ISO 5660 unless stated otherwise. All the cone tests were conducted using the FTT cone calorimeter at the Interscience Communications Laboratories, Watford, UK. The specimens were positioned horizontally and exposed to an irradiance of  $50 \text{ kW/m}^2$ . The specimens were pilot ignited and the tests run were carried out in triplicate and then the average values were used.

## 5.3 Results and Discussion

#### 5.3.1 Thermogravimetric Analysis

The TGA and DTG plots for the unsaturated polyester shows three distinct stages of mass loss (Figure 5.1). The first occurring at around 250 °C, the second over a range of 250 to 400 °C and the third, smaller mass loss, from 400-600 °C. The first loss is thought to be due to the release of styrene and other volatile products. The resin starts to decompose above 200 °C; whereas the main step of mass loss occurs between 200 and 400 °C. Above 400 °C, solid phase oxidation reactions dominate Ferreira *et al* (2006).



*Figure 5.1. Mass loss vs. temperature, showing the onset of thermal degradation increases with addition of MWNTs.* 

During thermal decomposition, the polystyrene cross-links start to decompose first which is followed by volatilisation of the styrene. The linear polyester portion undergoes scission. Ferreira *et al* (2006) have shown that during thermal decomposition, volatiles are lost up to 400  $^{\circ}$ C and, above 400  $^{\circ}$ C; it is solid phase oxidation reactions that predominate.

For the UP nanocomposites, a noteworthy shift in degradation temperature can be observed (Figures 5.1-5.4). For the highest loaded CNT filled specimen, a 20 °C increase in the onset of degradation temperature has been achieved. It is well documented that CNTs are highly resistant to thermal oxidation (Iijima, 1991). This is due to the proposed structure in which each carbon atom is completely bonded to three neighbouring carbon atoms through sp<sup>2</sup> hybridization to form a seamless shell. Furthermore, only the outer layer of the CNT is accessible to oxygen therefore using MWNTs grants extra resistance to its bulk. For sepiolite the onset temperature shifted by 28 °C, which is attributed to the formation of a protective ceramic layer during the reorganization of the silicate layers in the composite structure at high temperatures (Ajayan *et al.*, 1993; Zanetti *et al.*, 2002; Costache *et al.*, 2005).



*Figure 5.2. Mass loss vs. temperature, showing that the residual char as well as the onset temperature have been improved with the addition of sepiolite clay.* 

The significant delay of mass loss in the sepiolite specimens is thought to be due to the barrier effect arising from the dispersion of the sepiolite. Indeed, such morphology induces a decrease of both the volatile thermo-oxidation products by diffusion and oxygen diffusion from the gas phase into the polymer matrix.



*Figure 5.3.* TGA curve illustrating the thermal degradation behavior of the 1Sep:2CNT based ternary system.



*Figure 5.4.* TGA curve, showing improved thermal behaviour and a larger residual mass for the 10Sep:0.5CNT based ternary system.

The ternary mixtures showed a 32 °C and 36 °C delay in the onset temperature for the ternary systems based on 1wt.% sepiolite and 2wt.% MWNT (1Sep:2CNT) and 10wt.% sepiolite and 0.5wt.% MWNT (10Sep:0.5CNT) systems, respectively.

An explanation for this improvement in thermal stability may be found by investigating the residual char after cone testing. The 10Sep:0.5CNT ternary system was the only specimen that left a continuous char at the end of TGA and microcalorimeter testing (11% char@800 °C, see Figure 5.4), indicating a synergistic performance between Sepiolite and MWNTs.

#### 5.3.3 Microcalorimetry

Tables 5.2 and 5.3 show the peak heat release rate values from the microcalorimeter and the cone calorimeter. The peak heat rate for the neat UP in the microcalorimeter was 271 W/g and with the addition of 10 wt. % sepiolite, this value was reduced to 260 W/g and 255 W/g for a loading of 2 wt. % MWNT (Table 5.2).

<b>Table 5.2.</b>	PHRR for the	nanocomposites	obtained from	the microca	lorimeter.
-------------------	--------------	----------------	---------------	-------------	------------

Filler	(wt. %) Peak Heat Release	
		(W/g)
UP	No filler	271
	0.5	264
CNT	1	258
	2	255
	1	267
Sepiolite	2.5	263
	5	261
	10	260
Ternary	1Sep:2CNT	258
Systems	10Sep:0.5CNT	160

Zammarano (2007) has been the only one thus far to have investigated the flame retarding properties of nano-silicate clay filled thermoset systems, specifically epoxy. One of the mechanisms proposed was that the clay accumulates on the surface to create a protective barrier that greatly improves char stability in an oxidative environment. However there seems to be a discrepancy in PHRR value in this work when tested in the cone calorimeter (Table 5.3). This can be down to specimen size and geometrical effects; the microcalorimeter samples are only 5 mg when tested and have an arbitrary shape. The cone samples are of defined size and shape (100 mm<sup>2</sup>) and have a much larger surface area for the nanoclay mechanism to take maximum effect.

Additionally, Zhu *et al* (2001) has also shown that the presence of iron in the silicate clay can lead to some radical trapping reactions which may help to lower the heat release rate. The loading of the clay is also a key factor; at low amounts of clay the paramagmatic radical trapping is effective while the barrier mechanism becomes more important at higher contents of clay. The PHRR for the CNT filled specimens are shown in Table 5.2. The introduction of 2 wt.% MWNT reduced the PHRR from 271 to 255 W/g. There have been many concepts which have been proposed to explain how the introduction of CNTs could reduce the flammability of polymers. These include the formation of a rigid char structure during the combustion rather than a foamed one. Also the CNTs can act as a heat sink and distribute the heat globally throughout the material which reduces localised decomposition.

The authors believe that the percolation threshold had not been reached due to the low CNT content; hence no network was produced throughout this material. Wu *et al* (2006) witnessed for their UP/CNT system an electrical conductivity with a percolation threshold between 2 and 3 wt.%. Testing the 1wt.%Sep:2wt.%CNT ternary system demonstrated no significant change in the PHRR, however the 10wt.%Sep:0.5wt.% CNT ternary system showed an almost 50 % reduction in PHRR in comparison to the unfilled UP specimen.

The rationale behind this was thought to be due to the CNTs acting as a sealing agent which connects the clays to form a much tighter char (Xia *et al.*, 2003) forming a jammed network which impedes melt flow during flaming thus preventing flame spread (Figures 5.6d). This is thought to increase the barrier resistance to the evolved flammable gases which escape into the condensed phase leading to oxygen ingress which would fuel the flame and increase the heat release rate.

#### 5.3.4 Cone Calorimetery and Surface Morphology

Cone calorimetery testing was conducted to confirm the results obtained from the microcalorimeter screening tests. The UP binary systems of (i) 0.5 wt.% MWNT, (ii) 10 wt.% sepiolite and (iii) 10wt.%Sep:0.5wt.%CNT ternary system were brought forward for cone calorimeter testing. Table 5.3 shows the PHRR and Figure 5.5 shows the heat release rate curve from the cone calorimeter in kW/m<sup>2</sup>. A similar synergistic trend as observed in the microcalorimeter tests in which a 40 % reduction in PHRR was documented. In Figure 5.5, the second peak for the 10wt.%Sep:0.5wt.%CNT ternary system had been reduced when compared to the 10 wt.% binary specimen (label A). This indicated that the char had less surface cracks present and an increased stability over time (Beyer, 2004), thus lowering the oxygen ingress and diffusion of the decomposition products by a "labyrinth effect" (Bharadwaj *et al.*, 2002).

*Table 5.3. PHRR results for the binary and ternary nanocomposite formulations in the cone calorimeter.* 

Specimen	Peak Heat Release Rate		
	$(kW/m^2)$		
UP	640		
0.5 wt.% CNT	610		
10 wt.% Sep	477		
10wt.%Sep:0.5wt.%CNT	370		



Figure 5.5. HRR vs. time, depicting the lowering of the HRR of the nanocomposite specimens.

The images in Figure 5.6 illustrate the photographs and scanning electron images of the specimens post cone calorimetery. As expected, the unfilled UP rapidly decomposed which was accompanied by numerous bubbling on the sample surface. At the end of the test, a small amount of residual char was left (Figure 5.6a), indicating poor carbonization.

The sample with CNTs (Figure 5.6b) showed the least amount of residual char, which was thought to be due to the CNTs conducting the heat throughout the material and thus accelerating the decomposition process. The sepiolite filled specimen showed a strong char after testing. However large cracks can be seen permeating its bulk. The final photograph shows the char fragments of the 10wt.%Sep:0.5wt.%CNT ternary specimen, which seems to be smaller and encompassing fewer cracks. The mechanism of the CNTs helping the clay to seal the char can be observed in Figure 5.6d. The introduction of the CNTs to the sepiolite increased the thermal stability of the char. It formed a continuous network-type protective layer that mainly consisted of small fragments without any significant openings or cracks. Bubbling on the sample surface may supply evolved combustible decomposition products to the flame, which in turn compromises the flame retardant effectiveness. Figure 5.6 also illustrates SEM images which may help explain the mechanism of the 10wt.%Sep:0.5wt.%CNT ternary system. The first set of images show the loosely cracked surface of the pure UP with a high area of porosities. The CNT filled samples show a network structure within the char. The char seems slightly tighter with some of the CNTs attempting to bridge the openings. The sepiolite filled specimen shows a much tighter char with some pores in between the needle-like clay layers and micro-cracks in the layer surface. For the ternary system, the char is much denser and has far fewer pores than the individually filled samples.

Chapter 5 | Multiwall Carbon Nanotubes and Nanoclays as Flame Retardants for Unsaturated Polyester



Figure 5.6. Shows photographs of the specimens post cone calorimetery.

Specimen	Peak MLR	Average MLR	<b>Residual Mass</b>
	(g/s)	(g/s)	(%)
UP	0.29	0.09	8.1
0.5 wt.% CNT	0.30	0.15	3.4
10 wt.% Sep	0.22	0.07	16.6
10Sep:0.5CNT system	0.19	0.06	17.3

*Table 5.4.* Peak mass loss rate (MLR), average MLR and residual mass values for the nanocomposites.

Table 5.4 shows the residual mass after calorimetery testing. The CNT filled specimen showed the lowest residual mass. Again, this is thought to be due to the CNTs increasing the thermal conductivity of the specimen, thus not giving adequate protection to the material leading to a more rapid decomposition. The addition of CNTs did not reduce the overall PHRR or the mass loss rate (MLR) (Figure 5.7) which are related to each other. The rate at which the specimen degrades and releases the volatile gases assists the flame intensity which resorts in a higher HRR. The unfilled UP and CNT reinforced specimens showed a peak at around 100 seconds. The other specimens showed a high peak at the start, which is thought to be attributed to the top layer of resin being involved in the combustion. There is a decrease in the rate of mass loss until 370 seconds where the trend rises again. This is thought to be due to a delayed accumulation of thermal energy within the specimen. Another possible reason could be because only now does the rear of the specimen becomes finally involved in the combustion process after being shielded thus far. When sepiolite was introduced the MLR decreased. This is believed to be due to a stable char formation and an increase in the total surface area of the char. A similar trend can be witnessed in the HRR chart (Figure 5.5) where after 300 seconds the HRR is found to increase again.

As established, the most profound effect of using nanofillers was the reduction of the PHRR, peak mass loss rate and residual mass (Table 5.3). These rates and values are correlated with each other, so attention is on the HRR or PHRR since they are the most corresponded parameters.



*Figure 5.7. Mass Loss Rate (MLR) vs. time profile obtained from the cone calorimeter for the nanocomposite specimens.* 



Figure 5.8. Total heat release rate (THR) in the cone calorimeter for the nanocomposite specimens. -109-

The 10wt.%Sep:0.5wt.%CNT ternary specimen tested in this investigation showed the largest reduction in PHRR. However another important parameter measured was the total heat release (THR) (Figure 5.8), which did not change. This suggested that a barrier was formed during combustion which influenced the reaction to fire behaviour. The unchanged initial reaction to fire corresponds to the time period until a barrier was built up. The reduction in HRR without any change in the THR indicates that a physical barrier prolongs the burning times without decreasing the total amount of combustible material. The clay based barrier only slows down the release of fuel; it does not fully prevent it. So polymer nanocomposites will burn slowly until almost all the carbon mass has been pyrolyzed and combusted, which means that the total heat release is unchanged from that of the base polymer, however the peak and average heat release rate is lowered.

### **5.4 Conclusions**

The objective of this investigation was to study the thermal behaviour and flammability of an unsaturated polyester based binary and ternary nanocomposite system. The outcome has shown that the use of CNTs in combination with sepiolite nanoclays can lead to advantageous synergetic behaviour in terms of increasing the thermal stability, residual char and lowering the PHRR. The most important benefit of the 10 wt.% Sep:0.5wt.%CNT ternary system is that it reduces the PHRR, which is the most critical fire hazard, by a synergistic reaction involving the formation of a stable residual char. This char formation reduces the amount of small volatile polymer pyrolysis fragments, or fuel, available for flame. This in turn reduces the amount of heat released and feed back into the polymer surface. The char also insulates the underlying polymer, due to its low thermal conductivity, and reradiates externally impinging energy away from the polymer. The char also functions as a mass transport barrier by physically delaying the volatilisation of decomposition products and or trapping decomposition products through chemical reaction.

# **5.5 References**

Ajayan. P.M, Ichihashi. T and Iijima, S: *Distribution of pentagons and shapes in carbon nano-tubes and nano-particles*. Chemical Physical Letters. 1992. **202**: p. 384-388.

Beyer. G: *Short Communication: Carbon Nanotubes as Flame Retardants for Polymers*. 2002. Fire and Materials. **26**: p. 291-293.

Beyer. G: *Filler blend of carbon nanotubes and organoclays with improved char as a new flame retardant system for polymers and cable applications.* Fire and Materials. 2004. **29**(2): p. 61-69.

Bharadwaj. R.K, Mehrabi. A.R, Hamilton. C, Trujillo. C, Murga. M, Fan. R, Chavira. A and Thompson. A.K: *Structure-property relationships in cross-linked polyester-clay nanocomposites*. Polymer. 2002. **43**(13): p. 3699-3705.

Bilotti. E, Fischer. H.R and Peijs. T: *Polymer nanocomposites based on needle-like sepiolite clays: Effect of functionalized polymers on the dispersion of nanofiller, crystallinity, and mechanical properties.* Journal of Applied Polymer Science. 15<sup>th</sup> January 2008. **107** n2: p. 1116-1123.

Costache. M, Jiang. D.D and Wilkie. C.A: *Thermal degradation of ethylene-vinyl acetate copolymer nanocomposites*. Polymer. 2005. **46**: p. 6947-6958.

Dubois. P, Peeterbroeck. S, Alexandre. M, Nagy. J. B, Pirlot. C, Fonseca. A, Moreau. N, Philippin. G, Delhalle. J, Mekhalif. Z, Sporken. R, Beyer. G and Dubois. P: *Polymer-layered silicate-carbon nanotube nanocomposites: unique nanofiller synergistic effect.* Composites Science and Technology. November 2004. **64**(15): p. 2317-2323.

Erik. T, Li. C and Chou. T.W: *Nanocomposites in context*. Composites Science and Technology. 2005. **65**: p 491-516.

Franchini. E, Jocelyne G and Gerard. J.F: *Sepiolite-based epoxy nanocomposites: Relation between processing, rheology and morphology*: Journal of Colloid and Interface Science. 1<sup>st</sup> January 2009. **329**. No 1: p. 38-47.

Ferreira. J.M, Errajhi. O.A.Z and Richardson. M.O.W: *Thermogravimetric analysis of aluminised E-glass fibre reinforced unsaturated polyester composites*. Polymer Testing. December 2006. **25**(8): p. 1091-1094.

Hapuarachchi. T. D, Ren. G, Fan. M, Hogg. P.J and Peijs. T: *Fire Retardancy of Natural Fibre Reinforced Sheet Moulding Compound*. Applied Composite Materials. 2007. 14: p. 251-264.

Hapuarachchi. T.D and Peijs. T: Aluminium trihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin. Express Polymer Letters. 2009. **3**. No 11: p. 743-751

Iijima. S: Helical micro-tubules of graphitic carbon. Nature. 1991. 345. p. 56.

Kashiwagi. T, F Du. F, Douglas. J.F Winey. K.I, Harris. R.H and Shields J.R: *Nanoparticle networks reduce the flammability of polymer nanocomposites*. Nature Materials. 2005. **4**: p. 928-933.

Kojima. A, Usuki. A, Kawasumi. M, Okada. A, Fukushima. Y, Kurauchi. T and Kamigaito. O: *One-pot synthesis of nylon 6-clay hybrid*. Journal of Polymer Science Part A: Polymer Chemistry. 2003. **31**(7): p. 1755-1758.

Ma. H, Tong. L, Xu. Zhongbin and Fang. Z: *Synergistic effect of carbon nanotube and clay for improving the flame retardancy of ABS resin.* Nanotechnology. 2007. **18**. 375602 (8pp).

Marosfoi. B. B, S. Garas, B. Bodzay, F. Zubonyai and G. Marosi: *Flame retardancy study on magnesium hydroxide associated with clays of different morphology in polypropylene matrix.* Polymers for Advanced Technologies. 2008. **19**: p. 693-700.

Morgan. A. B: *Flame retarded polymer layered silicate nanocomposites: a review of commercial and open literature systems.* Polymers for Advanced Technologies. 2006. **17**(4): p. 206-217.

Morgan. A. B, Chu. L. L and Harris. J. D: *Flammability Performance Comparison Between Synthetic and Natural Clays in Polystyrene Nanocomposites*. Fire and Materials. July/August 2005. **29**. No 4: p. 213-229.

Schartel. B, Uta Knoll, Andreas Hartwig and Dirk Pütz: *Phosphonium-modified layered* silicate epoxy resins nanocomposites and their combinations with ATH and organo-phosphorus fire retardants. Polymers for Advanced Technologies. 2006. **17**(4): p. 281-293.

Wang. W, Ciselli. P, Kuznetsov. E, Peijs. T and Barber. A. H: *Effective reinforcement in carbon nanotube-polymer composites*. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences. 13<sup>th</sup> May 2008. **366**. No 1870: p. 1613-1626.

Wang. Z, Ciselli. P and Peijs. T: *The extraordinary reinforcing efficiency of single-walled carbon nanotubes in oriented poly(vinyl alcohol) tapes*. Nanotechnology. 14<sup>th</sup> November 2007. **18**. No 45: p. 455709 (9pp).

Wu. S.H, Masaharu. I, Natsuki. T and Ni. Q.Q: *Electrical Conduction and Percolation Behavior of Carbon Nanotubes/UPR Nanocomposites*. Journal of Reinforced Plastics and Composites. 2006. **25**: p. 1957-1966.

Xia. H. S, Wang. Q and Qiu G. H: *Polymer-Encapsulated Carbon Nanotubes Prepared through Ultrasonically Initiated In Situ Emulsion Polymerization*. Chemistry of Materials. 2003. **15**: p. 3879- 3886. Zammarano. M, Thermoset Fire Retardant Nanocomposites, Chapter 9 In Morgan. A.B and Wilkie. C.A (Eds): *Flame Retardant Polymer Nanocomposites*, Wiley-Interscience, Hoboken, New Jersey, 2007, p 235-278.

Zanetti. M, Camino. G, Reichert. P and Mülhaupt. R: *Thermal Behaviour of Poly(propylene) Layered Silicate Nanocomposites*. Macromol Rapid Communications. 2001. **22**: p. 176-180.

Zanetti. M, Camino. G, Canavese. D, Morgan. A.B, Lamelas. F.J and Wilkie. C.A: *Fire Retardant Halogen-Antimony-Clay Synergism in Polypropylene Layered Silicate Nanocomposites*. Chemistry of Materials. 2002. **14**: p. 189-193.

# 6

# Multiwall Carbon Nanotubes and Nanoclays as Flame Retardants for Polypropylene

# **6.1 Introduction**

For more than a decade, potential environmental problems associated with organobromine flame retardant systems have motivated the search for non-halogenated based approaches to reduce polymer flammability. Initially, research focused on the development of new phosphorus based flame retardants and numerous publications and patents have been issued in this area (Wang *et al.*, 2007; Liu *et al.*, 2001). Similarly, research also produced non-halogen flame retardant approaches based on other elements such as boron (Wei *et al.*, 2002) and silicon (Park *et al.*, 2002). At the same time, research focused on the use of additives, or fillers with nanometer scale primary particle sizes to produce polymer nanocomposites. These materials exhibit enhancement in a variety of physical properties at typically one-tenth the loading required when micron sized additives are used. Polypropylene (PP) was the first synthetic stereo-regular polymer to achieve industrial importance and it is presently one of the fastest growing polymers for technical end-uses when good mechanical properties coupled with low-cost are essential (Pasquini *et al.*, 2005). Because of its wholly aliphatic hydrocarbon structure, polypropylene by itself burns very rapidly with a relatively smoke-free flame and without leaving a char residue. It has a high self-ignition temperature (570 °C) and a rapid decomposition rate compared with wood and other cellulosic materials and hence has a high flammability (Einsele *et al.*, 1984). In recent years, nanocomposites have become the most widely studied subject of flame retardant research due to attaining similar if not better flame retarding performances to their micron sized counterparts but at much lower loading levels, thus preserving better the characteristics of the unfilled polymer such as good flow, toughness, surface finish and low density.

Blumstein (1965) first reported improved thermal stability of a polymer/clay nanocomposite when poly(methylmethacrylate) was combined with layered montmorillonite clay (MMT). Leszczyńska *et al* (2006, 2007) also reported on the thermal behaviour of PP/MMT composites. Intercalated layered cloisite nanoclays also improved the flammability of PP nanocomposites (Zhang *et al.*, 2006). According to the thermogravimetric analysis, the decomposition temperature increased from 259 °C of PP to 309 °C of the PP/cloisite nanocomposite. Flammability characterisation of polymer/clay nanocomposites, under fire-like conditions using the cone calorimeter revealed improved flammability properties for many different types of polymer/clay nanocomposites (Gilman *et al.*, 1997; NIST 1998). A recent addition to the nanoclay group is sepiolite which is a natural hydrous magnesium silicate. As a clay mineral, structurally it consists of two sheets of SiO<sub>4</sub> tetrahedra bonded via oxygen atoms to a central sheet of octahedrally arranged magnesium atoms. It has a needle-like profile which helps the flowability of the polymer when melt processed.

Bilotti et al (2008, 2009) and Ma et al (2007) have studied the dispersion of sepiolite within thermoplastic polymers as well as their effect on mechanical and thermal properties of the resulting nanocomposites. Due to their typical anisotropic structure and high aspect ratio, carbon nanotubes (CNTs) show characteristic properties. CNTs have shown to improve mechanical (Ciselli et al., 2007; Wang et al., 2007; Deng et al., 2009) and electrical properties of polymers (Zhang et al., 2007,2009; Deng et al., Jul/2009, Nov/2009) but CNTs are also an interesting alternative to the use of conventional flame retardants. Their incorporation at low loadings (<3 wt.%) have been reported to improve the flammability of a large range of polymers, initially ethylene vinyl acetate (EVA) (Peeterbroeck et al., 2007), poly(methyl methacrylate) (PMMA) (Kashiwagi et al., Jan/2005), polyamide 6 (PA-6) (Schartel et al., 2005), and polypropylene (PP) (Kashiwagi et al., May/2005). Kashiwagi (May/2005) studied the effect of nanotube dispersion on the flame retardant properties of PP nanocomposites. They showed that the incorporation of as little as 1 wt.% well dispersed single-walled nanotubes (MWNT) in PP led to a marked decrease in the heat release rate (HRR) measured in the cone calorimeter. Dubois et al (2004) took the concept further and explored the potential of using both CNTs and nanoclay fillers together in an EVA matrix. A synergic improvement was recorded for this ternary system when compared with the binary base systems.

Ma *et al* (2007) also investigated a ternary CNT/nanoclay system with acrylonitrile butadiene styrene (ABS). Previous work from our group reported similar synergistic improvements in flame retardancy for ternary nanocomposite systems based on unsaturated polyester (UP) (Hapuarachchi *et al.*, 2010). All these studies recorded a reduction in the peak heat release rate (PHRR) and suggested that the CNTs acted as a sealing agent to create a network with the clay layers, forming a much tighter char than clay alone. The intention of this research is to develop a thermoplastic polypropylene based nanocomposite system with reduced inherent flammability.

For this the flammability of a number of polypropylene nanocomposites was assessed via a series of thermal and reaction to fire tests. Well established test methods will be used such as thermal gravimetric analysis, cone calorimeter as well as the new microcalorimeter. This is a newly developed apparatus to measure the heat release rate of milligram samples (Lyon and Walters 2004). Previous research has shown that the heat release capacity (HRC) measured by the microcalorimeter or pyrolysis combustion flow calorimeter (PCFC) was proportional to the HRR measured by conventional cone calorimeters and, therefore, be a reasonable estimate of fire hazard, albeit using smaller quantities of samples. This is especially advantageous for the development of nanocomposites, as materials can be screened quickly as well as economically due to the use of small amounts of material.

## **6.2 Experimental Procedure**

#### 6.2.1 Materials

As base polymer an isotactic polypropylene (PP) resin in granular form was used with a melt flow index (MFI) of 44 g/10 min, from Dow Chemical Company. The sepiolite nanoclay (PANGEL<sup>TM</sup>) was supplied by Tolsa S.A. (Spain). Sepiolite (Sep) is a needle-like clay with a bulk density of  $60 \pm 30$  g/L, and a BET surface area of 320 m<sup>2</sup>/g. The characteristic average dimensions of the individual sepiolite fibres are 1-2 mm in length and 20-30 nm in diameter. A number of different CNTs were used; (i) thin multiwalled nanotubes (MWNT) with 95+% purity (Nanocyl<sup>®</sup> 3100); (ii) MWNTs coated with high density polyethylene (HDPE) with 44.8 wt% CNT loading (Nanocyl<sup>®</sup> 9000); (iii) industrial grade MWNTs with 90% purity (Nanocyl<sup>®</sup> 7000); (iv) thin MWNT-COOH (functionalized with carboxylic and hydroxyl acid); and (v) short and thin MWNT-NH<sub>2</sub> with 95+% purity (functionalized with amides). All CNTs were supplied by Nanocyl S.A (Belgium). Conventional micron sized flame retardants were also used for comparison.

These were aluminium trihydroxide (ATH) grade OL104 supplied by Albemarle Corporation (USA) and ammonium polyphosphate (APP) Exolit<sup>TM</sup> from Clariant UK Ltd.

#### 6.2.2 Compounding

The manufacturing of the polymer nanocomposites were carried out on a DSM Xplore micro 15 twin-screw extruder. This mini extruder is equipped with conical co-rotating screws having a length of 150 mm, an L/D ratio of 18 and a net capacity of 15 g. The processing scheme was to compound the polymer composites at 200 °C for 10 minutes at a mixing speed of 200 rpm. After carrying out the bench scale thermal analysis tests using the microcalorimeter, the best performing resin formulation was up-scaled using a Collin ZK25 co-rotating twin-screw extruder with K-Tron gravimetric feeders. Master batches of sepiolite and MWNTs (20 wt.% each) were compounded separately and then diluted with PP to the required filler content (10wt.%Sep+2wt.%CNT). The final batches were pelletized using the Collin CSG/171/1 attachment. A Collin P300E hydraulic hotpress was used at a pressure of 5 bar for 10 minutes at 190 °C to mould the pellets into 220×200 mm<sup>2</sup> plates with a thickness of 6 mm weighing approximately 240 g.



*Figure 6.1.* (a) *Mini extruder unit* (b) *conical twin screws* (c) *twin screw extruder* (d) *tape extrusion.*
### 6.2.3 Characterisation

Thermal gravimetric analysis (TGA) and derivative thermal analysis (DTA) was carried out on a TA Instruments Q500, with specimen size of 5-10 mg. The temperature range was from 30 °C to 1000 °C at a ramp rate of 10 °C/min in air and nitrogen atmosphere. The specimens for the pyrolysis combustion flow calorimeter (PCFC) or microcalorimeter (Figure 6.2) were approximately 5 mg and the tests were carried out in triplicate and results averaged. The gas mixture was an 80:20 N<sub>2</sub>:O<sub>2</sub> mix. For each run, the pyrolzer was set to a 60 °C/min heating rate to reach 750 °C from room temperature. The combustor temperature was pre-set to 900 °C. Cone calorimetry was carried out on samples of  $100 \times 100 \times 5$  mm<sup>3</sup>. All materials were conditioned at  $23 \pm 3$  °C at a relative humidity of  $50 \pm 5\%$  for 24 hours prior to testing. The samples were wrapped with aluminium foil around the back and edges before placing the specimen onto the holder and then into the cone calorimeter. A retainer frame was used to reduce edge burning effects. All the tests were carried out in accordance with ISO 5660 unless stated otherwise. The specimens were positioned horizontally and exposed to an irradiance of  $50 \text{ kW/m}^2$ . The specimens were pilot ignited and run in triplicate.



**Figure 6.2.** (a) Schematic and microcalorimeter setup and how it relates to a real life scenario (b) Photograph of FTT's microcalorimeter. Schematic modified from (Lyon and Walters 2004) and photograph courtesy of Fire Testing Technology Ltd.

# 6.3 Results and Discussion

# 6.3.1 Thermal Gravimetric Analysis

# 6.3.1.1 Polypropylene

Thermogravimetric analysis (TGA) is widely used to characterise the thermal stability of polymers. The 100 °C shift observed when tested in  $N_2$  is due to the thermal oxidative volatilisation of PP (Figure 6.3).



*Figure 6.3.* (a) Thermogravimetric analysis (TGA) and (b) differential thermal analysis (DTA) scans of PP in air and nitrogen, showing the effect of testing PP in different atmospheres. There is an onset decomposition shift of 100 °C when tested in nitrogen rather than air.

Polypropylene volatilizes completely, in two steps beginning at about 250 °C through a radical chain process propagated by carbon centered radicals originated by carbon-carbon bond scission (Marosfoi *et al.*, 2006). Above 200-250 °C oxidative dehydrogenation of PP starts to occur, while depolymerisation and random chain scission by direct thermal cleavage of carbon-carbon bonds becomes possible in air as well as in nitrogen, above 400 °C. In general, the addition of fillers can improve the thermal stability of polymer composite systems to some extent. Numerous studies have reported that polymer/carbon nanotube (CNT) composites can exhibit a higher thermal stability than that of the polymer alone (Gorrasi *et al.*, 2007; Kim *et al.*, 2007). To better understand the effect of MWNT and sepiolite nanoclay on the decomposites in air and N<sub>2</sub> was analysed.

### 6.3.1.2 PP/MWNT

Microcalorimeter tests were carried out first for initial screening of the nanocomposite systems and will be presented later. These test showed that PP with Nanocyl 3100 gave the best performance with respect to PHRR and HRC. Therefore this CNT type was used throughout the thermal degradation studies. The influence of the CNTs on thermal degradation of PP can be seen more clearly when tested in air and with increasing CNT content so does the onset decomposition temperature and residual mass (Figure 6.4). The mechanism is thought to contribute to the delay in thermo-oxidation of PP in presence in air (Levchik *et al.*, 1999; Lánská *et al.*, 1999).



*Figure 6.4.* TGA scans of PP with MWNTs in (a) air and (b) nitrogen, showing the effect of CNTs on the decomposition behaviour of PP.

CNT	Atmosphere	Onset decomposition	<b>Residual mass</b>
(wt.%)		temperature	(%)
		(°C)	
0	Air	279	2
0	$N_2$	392	2
0.5	Air	267	2
0.5	$N_2$	417	1
1	Air	279	2.3
1	$N_2$	414	0.5
2	Air	292	3
2	$N_2$	416	1
5	Air	298	5.3
5	$N_2$	435	4.5
10	Air	332	9.6
10	$N_2$	437	7.5

**Table 6.1.** Parameters obtained for PP and its multiwalled nanotubes nanocompositefrom TGA.

The presence of CNTs may hinder thermo-oxidation of PP in the earlier stages of decomposition, and thus increase the thermal stability of the composite. As mentioned before, the decomposition of PP experiences free radical chain reaction (Zhang *et al.,* 2009) and the CNTs may easily trap a number of free radicals thus enhancing the thermal properties of the polymer. The higher the CNT content, the higher the decomposition temperature, as shown for the PP/MWNT nanocomposites. The unfilled polymer and its composites show single step decomposition in N<sub>2</sub>. However, the degradation trace shows less defined decomposition behaviour when tested in air.

Analogous behaviour, regarding the improvement of thermal stability of PP nanocomposites in an inert atmosphere, has been reported in literature and is attributed to the shielding effect of nanoparticles inhibiting the elimination of the formed volatile by-products (Levchik *et al.*, 1999; Lánská *et al.*, 1999). Unfilled isotactic polypropylene decomposes completely while the residues in the nanocomposite samples with CNTs are almost consistent with the amount of nanotube additive introduced into the polymer.

### 6.3.1.3 PP/Sepiolite

Figure 6.5 shows the thermogram of PP with sepiolite in air and the delay in onset thermal decomposition temperature with increasing nanoclay loading. Previous research established that layered silicate nanostructures create an efficient barrier to oxygen towards the native polymer (Dubois and Alexandre 2006).



*Figure 6.5. TGA analysis of PP with sepiolite in* (*a*) *air and* (*b*) *nitrogen, showing the effect of sepiolite clay on the decomposition behaviour of PP.* 

Polymer molecules trapped within the silicate layers are thus brought into close contact with oxygen and catalyse silicate layers to produce a thermally and oxidative stable carbonized structure. The converse is present when tested in nitrogen. As the sepiolite loading increases the onset temperature decreases. This could be possibly due to catalytic effects of the acidic sites on the clay surface. There is a significant change in thermal behaviour of the nanocomposites when tested in different atmospheres. The decomposition process is delayed in nitrogen compared to air. Table 2 confirms that for a 10 wt.% loaded sepiolite specimen, the onset decomposition temperature in air is 230 °C, whereas it is 343 °C in nitrogen. This can be seen throughout the range of materials studied with respect to peak derivative decomposition temperature and residual mass. The difference between these mass losses suggests that there are two types of carbonaceous materials in the carbon part of the clay-char; a carbonaceous material that can be gasified by heating in nitrogen and a second fraction of material which requires more aggressive conditions; heating in the presence of air which allows for oxidative decomposition and complete removal of the carbonaceous material.

Sepiolite	Atmosphere	Onset decomposition	<b>Residual mass</b>
(wt.%)		temperature	(%)
		(°C)	
0	Air	279	2
0	$N_2$	392	2
1	Air	240	2
1	$N_2$	386	3
2.5	Air	244	2
2.5	$N_2$	380	4
5	Air	233	4
5	$N_2$	379	4
10	Air	230	7
10	$N_2$	343	10

Table 6.2. Parameters obtained for PP and its sepiolite nanocomposite from TGA.

### 6.3.1.4 PP/MWNT/Sepiolite

Figure 6.6 shows the thermogram of the PP, PP/MWNT, PP/sepiolite and a ternary nanocomposite system, again both in air and nitrogen atmospheres. As shown separately in Figure. 6.4 and 6.5, the addition of MWNTs or sepiolite nanoclay improves the thermal stability of PP in air with respect to onset decomposition temperature; again this is thought to be due to the shielding effects of the nanofillers, which reduce the ingress of oxygen which is thought to accelerate decomposition. However, interestingly the formulation of a ternary system based on a combination of MWNTs and sepiolite clay reduces the onset delay in air even further. The rationale behind this is thought to be due to be due to the structure thus altering the rheology.

The ternary system closely followed by the sepiolite based system presented also the highest residual char. The CNTs are thought to aid in creating a tighter char network towards the end of the decomposition process by bridging the clay rich regions together.



*Figure 6.6.* TGA analysis of PP ternary system (10 wt.%Sep+2wt.%CNT) in (a) air and (b) nitrogen, showing the increase in residual char and improved thermal stability in air compared to binary nanocomposite systems and neat PP resin.

### 6.3.2 Microcalorimetery

Various PP nanocomposite formulations were tested in the microcalorimeter. The tablulated microcalorimetry screening test results are presented in Tables 6.3-6.8. All the various formulations did not seem to reduce the heat release capacity (HRC). Table 6.3 shows the effect of various CNT grades on the flame retardancy of PP nanocomposites at 1 wt.% loading. No significant reduction to the HRC was observed. If fact, the HRC increased for one type of CNT having a polyethylene coating (Nanocyl 9000), lowering the thermal stability of this nanocomposite (Ebbesen *et al.*, 1996).

Table 6.4 also shows an increase in HRC in conjunction with filler loading. Carbon nanotubes are known to increase the electrical (Berber *et al.*, 2000) as well as thermal conductivities of polymers (Le Bras and Bourbigot 1998). The thermal conductive network present in these materials may have accelerated the decompostion process.

**Table 6.3.** The effect of different CNT grades on peak heat release rate (PHRR), total heat release (THR) and heat release capacity (HRC) of PP nanocomposite. Compounding time 15 min, (1 wt.% MWNTs).

Comple	PHRR	THR	HRC
Sample	(W/g)	(kJ/g)	$(J/g^{-k})$
PP	1051	40.3	1034
+Nanocyl 9000	1070	39.2	1050
+Nanocyl 7000	1066	37.7	1046
+Nanocyl 3100	1061	36.2	1040
+Thin MWNT-COOH	1058	36.9	1035
+Short thin MWNT-NH <sub>2</sub>	1061	37.7	1039

 Table 6.4. The effect of CNT loading on peak heat release rate (PHRR), total heat

 release (THR) and heat release capacity (HRC) of PP/CNT (Nanocyl 3100).

Sampla	PHRR	THR	HRC
Sample	(W/g)	(kJ/g)	$(J/g^{-k})$
РР	1051	40.3	1034
+ 0.5 wt.% CNT	1055	39.8	1036
+ 1 wt.% CNT	1059	38.7	1039
+ 2 wt.% CNT	1080	37.9	1060

*Table 6.5.* The effect of sepiolite loading on peak heat release rate (PHRR), total heat release (THR) and heat release capacity (HRC) of PP.

Sample		PHRR	THR	HRC
		(W/g)	(kJ/g)	( <b>J</b> / <b>g</b> <sup>-k</sup> )
РР		1051	40.3	1034
+ 1 wt.%	Sep	1072	38.6	1046
+ 2.5 wt.%	Sep	1102	37.9	1078
+ 5 wt.%	Sep	1111	38.8	1090
+ 10 wt.%	Sep	1121	36.1	1102

*Table 6.6.* The effect of mixed nanofiller (MWNT plus sepiolite) loading on peak heat release rate (PHRR), total heat release (THR) and heat release capacity (HRC) of PP.

Sample	Peak HRR (W/g)	Total HR (kJ/g)	HR Capacity (J/g <sup>-k</sup> )
+ 10 wt.% Sep + 0.5 wt.% CNT	1064	36.9	1045
+ 10 wt.% Sep + 2 wt.% CNT	1051	35.9	1032

If heat is conducted through these small samples the mass loss rate will also accelerate and emits more volitile gases which increase the HRC. Therefore, two conventional flame retardant additives were compounded into the PP and tested for comparison. Both these fillers did give a reduction in HRC (Table 6.7). The commonly used ammonium polyphosphate (APP) decomposes into polymeric phosphoric acid and ammonia, which assists in char formation (Rimez *et al.*, 2008).

Aluminium trihydroxide (ATH) is known to release water vapour together with being converted into a stable form of aluminia, which protects the underlying polymer (Hapuarachchi *et al.*, 2007). However, the filler content in these materials was so high that fuel dilution was thought to prevale (Hapuarachchi and Peijs 2009). After these inconsistencies in HRC values, the effect of testing technique was studied. As shown in the schematic of the microcalorimeter (see Figure 6.2), nitrogen gas is introduced to the sample from the bottom inlet during standard operating procedures. The volatile gas stream is then carried to the combustor area where is reacts with oxygen. For one of the test runs, oxygen was introduced to the sample from the bottom gas inlet. Immediately here the HRC was also significantly reduced for the ternary nanocompostie system (Table 6.8).

**Table 6.7.** The effect of convential flame retardant fillers in the microcalorimeter test on peak heat release rate (PHRR), total heat release (THR) and heat release capacity (HRC) of PP.

Sample	PHRR (W/g)	THR (kJ/g)	HRC (J/g <sup>-k</sup> )
PP	1051	40.3	1034
+ 15 wt.% APP	910	35.1	880
+ 50 wt.% ATH	705	26.9	702

Introducing nitrogen (upper burn) and oxygen (lower burn) through the bottom inlet resulted in a reduction of HRC from 1039 to 798 J/g<sup>-k</sup>, respectively for the very same ternary formuation (10wt.%Sep+2wt.%CNT). The reasoning behind this maybe due to the flame retarding mechanism of the ternary system being abled to initiate and form a protective char in an oxidative environment.

It has been well documented that the charring effect of polymeric materials is significantly enhanced when subjected to an aerobic environment (Rimez *et al.*, 2008). This can also be observed while testing in the TGA (Table 6.2). If one wishes to prevent the polymer from charing then nitrogen should be used as the purge gas to protect the sample from oxidizing. However, the microcalorimeter uses an anaerobic pyroloysis method to simulate surface gasification, and caution must be taken when results are to be analysed. Schartel *et al* (2005) assessed the suitablity of the microcalorimeter as a screening tool and commented that this method does not account for important physical effects occurring on larger scales, barrier formation, insulation and flame inhibition. Hence, neither the pyrolysis combustion flow calorimeter (PCFC) nor any other test based on mg-scale samples is suitable to completely replace flame and fire tests.

Sample	Burn Type	PHRR	THR	HRC
		(W/g)	(kJ/g)	( <b>J</b> / <b>g</b> <sup>-k</sup> )
+ 10 wt.% Sep + 2 wt.% CNT	Upper	1064	28	1039
+ 10 wt.% Sep + 2 wt.% CNT	Lower	810	38	798

*Table 6.8.* The effect of the burn type in the PCFC on peak heat release rate (PHRR), total heat release (THR) and heat release capacity (HRC).

The performance in fire tests can be estimated from the PCFC, but identifying precisely whether a material will pass or fail a specific test from the investigated set of materials with similar performance is clearly limited. Several effects that determine fire behaviour such as wicking, dripping, intumesence etc are not covered by milligram based methods such as the microcalorimetry

### 6.3.3 Cone Calorimetry

Heat release rate measurements were conducted on unfilled PP as well as the optimised ternary PP nanocomposite (Table 6.9; Figure 6.7). Due to its wholly aliphatic hydrocarbon structure, PP by itself burns very rapidly without leaving a char residue. The reaction to fire properties of the composite materials were evaluated using cone calorimeter. The most important parameters from cone calorimetry are: the heat release rate (Babrauskas and Peacock 1992), and especially its peak heat release (PHRR); the mass loss rate (MLR), which usually tracks very well with the PHRR; the total smoke release (TSR), which is a measure of the amount of smoke produced; and the total heat released (THR).

Sample	PHRR	THR	TSR	Mean	Mean	Residual
	$(kW/m^2)$	$(MJ/m^2)$	$(m^2/m^2)$	CO <sub>2</sub>	CO	Mass
				(kg/kg)	(kg/kg)	(%)
РР	1933	176	1964	2.08	0.04	2
+ 10 wt.% Sep + 2 wt.% CNT	355	241	2090	1.07	0.03	10

*Table 6.9.* Cone calorimeter data of PP and its ternary nanocomposite.



*Figure 6.7. Heat release rate vs. time for unfilled PP and ternary PP nanocomposite (10 wt.% sepiolite + 2 wt.% MWNT).* 

Heat release rates of the two specimens, unfilled PP and the PP ternary nanocomposite system, were measured and the results are shown in Figure 6.7 and Table 6.9. The time to ignition for the ternary system was slightly shortened. This was believed to be due to the increased thermal conductivity of the nanocomposite caused by the introduction of the nanotubes. The CNTs act as thermal conductors, which assist the thermal decomposition process (also seen in the TGA scans, see Figure 6.4). The behaviour of the specimens was visually observed during testing. As expected, the PP sample melted and behaved like a liquid accompanied by numerous bubbles and their bursting on the surface. Polypropylene has a high self-ignition temperature, a rapid decomposition rate and hence high flammability. As a consequence the unfilled PP had a PHRR of 1933 kW/m<sup>2</sup> which was reduced to 355 kW/m<sup>2</sup> for the 10 wt.% sepiolite plus 2 wt.% MWNT ternary nanocomposites system.

The lower flammability is not due to retention of a large fraction of fuel (see Table 6.9) in the form of carbonaceous char in the condensed phase. The new nanostructure present in the resulting combustion residue appears to enhance the performance of the residue through reinforcement of the carbonaceous char layer. This multilayered carbonaceous silicate structure can act as an excellent insulator and mass transport barrier, slowing down the escape of volatile products generated during decomposition by creating a tortuous path for the combustible gas to escape and for the oxygen rich air to enter. The clay network increases the melt viscosity and results in restrained mobility of the polymer chains during combustion, which leads to significant improvements in flame retardancy for the nanocomposite. There is no significant difference in the total smoke release (TSR), namely CO and CO<sub>2</sub> which suggests that the source of the improved flammability properties of this formulation is due to differences in the condensed phase decomposition and not a gas phase effect.

The low carbon monoxide measured indicated that complete combustion had taken place whereas smouldering is typical of incomplete combustion which would result in a much higher CO measurement. The primary parameter that is thought to be responsible for the lower HRR of the nanocomposites is the mass loss rate (MLR). During combustion the average MLR was 0.2 and 0.03 g/sec for PP and ternary nanocomposites, respectively. It is believed, that this effect is caused by the ability to initiate the formation of char barrier on the surface of the burning polymeric nanocomposite that drastically limits the heat and mass transfer to the burning zone.

### **6.4 Conclusions**

The objective of this work was to test and develop a flame retardant polypropylene nanocomposite. The use of sepiolite nanoclay in combination with multiwalled carbon nanotubes showed that the heat release rate (HRR) was significantly reduced by 82 % compared to the neat polymer in the cone calorimeter. Initial screening tests involved thermogravimetric analysis (TGA) and microcalorimetry or PCFC but caution must be adopted when interpreting results gained from the tests. Specimen sizes of a few milligrams can cause issues due to unrealistic behaviour when compared to identical materials tested on a larger scale in a cone calorimeter. Testing in the microcalorimeter can limit the behaviour of the material due to its small size and arbitrary shape, whereas specimen dimensions are standardised when testing in the cone calorimeter. In the cone calorimeter a much larger surface area is available for the flame retarding mechanisms to take full effect compared to the microcalorimeter. Another possible concern is the testing environment in the microcalorimeter as these tests are conducted in an enclosed system with controlled gas flows. Anaerobic environments have shown to hinder the flame retarding effect of materials, especially the char formation as part of the flame retarding mechanism. The cone calorimeter on the other hand is an open apparatus which resembles more real life scenarios.

### 6.5 References

Babrauskas. V and Peacock. R.D: *Heat release rate-the single most important variable in fire hazard*. Fire Safety Journal. 1992. **18**: p. 255-272.

Berber. S, Kwon. Y.K and Tománek. D: Unusually High Thermal Conductivity of Carbon Nanotubes. Physical Review Letters. 2000. 84: p. 4613-4616.

Bilotti. E, Fischer. H.R and Peijs. T: *Polymer nanocomposites based on needle-like sepiolite clays: Effect of functionalized polymers on the dispersion of nanofiller, crystallinity, and mechanical properties.* Journal of Applied Polymer Science. 15<sup>th</sup> January 2008. **107**(2): p. 1116-1123.

Bilotti. E, Zhang. R, Deng. H, Quero. F, Fischer. H. R, Peijs. T: *Sepiolite needle-like clays for PA6 nanocomposites: an alternative to layered silicates*? Composites Science and Technology. 2009. **69**. No 15-16: p. 2587-2595.

Bilotti. E, Deng. H, Zhang. R, Lu. D, Bras. W, Fischer. H.R, Peijs. T: *Synergistic reinforcement of highly oriented polypropylene tapes by sepiolite nanoclay.* Macromolecular Materials and Engineering (2009) In Press: <u>DOI:</u> 10.1002/mame.200900156

Blumstein. A: *Polymerization of adsorbed monolayers: II. Thermal degradation of the inserted polymers.* Journal Polymer Science Part A. 1965. **3**: p. 2665-2673.

Ciselli. P, Wang. Z and Peijs. T: *Reinforcing potential of carbon nanotubes in oriented polymer fibres*. Materials Technology. March 2007. **22**(1): p. 10-21.

Deng. H, Skipa. T, Zhang. R, Lellinger. D, Bilotti. E, Alig. I and Peijs. T: *Effect of melting and crystallization on the conductive network in conductive polymer composites.* Polymer. 17<sup>th</sup> July 2009. **50**(15): p. 3747-3754.

Deng. H, Zhang. R, Reynolds. C.T, Bilotti. E and Peijs. T: A Novel Concept for Highly Oriented Carbon Nanotube Composite Tapes or Fibres with High Strength and Electrical Conductivity. Macromolecular Materials and Engineering. 12<sup>th</sup> November 2009. **294**(11): p. 749-755.

Deng. H, Zhang. R, Bilotti. E and Peijs. T: *Effective reinforcement of carbon nanotubes in polypropylene matrices*. Journal of Applied Polymer Science. 2009. **113**. No 2: p. 742-751.

Dubois. P, Peeterbroeck. S, Alexandre. M, Nagy. J.B, Pirlot. C, A. Fonseca, N. Moreau,
G. Philippin, J. Delhalle, Z. Mekhalif, R. Sporken, G. Beyer and Dubois. P: *Polymer-layered silicate-carbon nanotube nanocomposites: unique nanofiller synergistic effet.*Composites Science and Technology. November 2004. 64(15): p. 2317-2323.

Dubois. P and Alexandre. M: *Performant Clay/Carbon Nanotube Polymer Nanocomposites, Advanced Engineering Materials.* 2006. **8**. No 3: p. 147-154.

Ebbesen. T.W, Lezec. H.J and Hiura. H: *Electrical conductivity of individual carbon Nanotubes*. 1996. Nature. **382**: p. 54-56.

Einsele. U, Koch. W and Herlinger. H: *Investigations into the development of heat when textiles burn in air*. Melliand Textilberichte. 1984. **65**(3): p. 200-206.

Gilman J. W, Kashiwagi T, Lichtenhan J. D: *Nanocomposites: A Revolutionary New Flame Retardant Approach.* SAMPE Journal. August 1997. **33**. No. 4: p. 40-46.

Gorrasi. G, Sarno. M, Di Bartolomeo. A, Sannino. D, Ciambelli. P and Vittoria. P: *Incorporation of carbon nanotubes into polyethylene by high energy ball milling: morphology and physical properties.* Journal of Polymer Science, Part B: Polymer Physics. 2007. **45**: p. 597-606.

Hapuarachchi. T.D, Ren. G, Fan. M, Hogg. P.J and Peijs. T: *Fire Retardancy of Natural Fibre Reinforced Sheet Moulding Compound*. Applied Composite Materials. 2007. **14**: p. 251-264.

Hapuarachchi. T.D and Peijs. T: Aluminium trihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin. Express Polymer Letters. 2009. **3**. No 11. p. 743-751.

Hapuarachchi. T.D, Bilotti. E, Reynolds. C.T and Peijs. T: *Multiwalled Carbon Nanotubes and Sepiolite Nanoclay as Flame Retardants for Unsaturated Polyester*. In press Fire and Materials. Kashiwagi. T, Grulke. E, Hilding. J, Groth. K.M, Harris. R.H, Butler. K.M, Shields. J.R, Kharchenko. S and Douglas. J.F: *Thermal and Flammability Properties of Polypropylene/Carbon Nanotube Nanocomposites*. Polymer. May 2004. **45**. No 12: p. 4227-4239.

Kashiwagi. T, Du. F, Winey. K.I, Groth. K.M, Shields. J.R, Bellayer. SP, Kim. H, Douglas. J.F: *Flammability Properties of Polymer Nanocomposites with Single-Walled Carbon Nanotubes: Effects of Nanotube Dispersion and Concentration*. Polymer. January 2005. **46**. No 2: p. 471-481.

Kim. H.S, Park. B.H, Yoon. J.S and Jin. H.J: *Thermal and electrical properties of poly(l-lactide)-graft-multiwalled carbon nanotube composites*. European Polymer Journal. 2007. **43**: p. 1729-1735.

Lánská. B, Doskočilová. D, Matisová-Rychlá. L, Puffr. R and Rychlý. J. *Thermooxidation of lactam-based polyamides with amino end-groups. Thermooxidation of hexano-6-lactam and decomposition of 6-hydroperoxy hexano-6-lactam in the presence of primary amines.* Polymer Degradation and Stability. 1999. **63**: p. 469-479.

Le Bras. M and Bourbigot. S In: Le Bras M, Camino G, Bourbigot S and Delobel R, Editors. Fire *retarded intumescent thermoplastics formulations, synergy and synergistic agent-a review*. The Royal Society of Chemistry, Cambridge (1998). p. 64-75.

Leszczyńska. A, Njuguna. J, Pielichowski. K and Banerjee. J.R: Polymer/montmorillonite nanocomposites with improved thermal properties: part I. Factors influencing thermal stability and mechanisms of thermal stability improvement. Journal of Thermoanalytical and calorimetric methods. 2007. **453**. p. 75-96.

Leszczyńska. A, Njuguna. J, Pielichowski. K and Banerjee. J.R Polymer/montmorillonite nanocomposites with improved thermal properties: part II. Thermal stability of montmorillonite nanocomposites based on different polymeric matrixes. Journal of Thermoanalytical and calorimetric methods. 2007. **454**: p. 1-22. Levchik. S.V, Weil. E.D and Lewin. M: *Thermal decomposition of aliphatic nylons*. Polymer International. 1999. **48**: p. 532-557.

Liu W, Chen. D.Q, Wang. Y.Z, Wang. D.Y and Qu. M.H: *Char-forming mechanism of a novel polymeric flame retardant with char agent*. Polymer Degradation and Stability. 2007. **92**(6): p. 1046-1052.

Lyon. R.E and Walters. R.N: *Pyrolysis combustion flow calorimetry*. Journal of Analytical and Applied Pyrolysis. 2004. **71**(1): p. 27-46.

Ma. J, Bilotti. E, Peijs. T and Darr. J.A: *Preparation of polypropylene/sepiolite nanocomposites using supercritical CO*<sub>2</sub> *assisted mixing*. European Polymer Journal. December 2007. **43.** No 12: p. 4931-4939.

Ma. H, Tong. L, Xu. Z and Fang. Z: Synergistic effect of carbon nanotube and clay for improving the flame retardancy of ABS resin. Nanotechnology. 2007. **18**: p. 375602 (8pp).

Marosfoi. B.B, Szabo. A, Marosi. G, Tabuani. D, Camino. G and Pagliari. S: *Thermal and spectroscopic characterization of polypropylene-carbon nanotube composite*. Journal of Thermoanalytical and calorimetric methods. 2006. **86**: p. 669-673.

NIST IR6242. Flammability Studies of Polymer Layered Silicate (Clay) Nanocomposites. October 1998. National Institute of Standards and Technology. Annual Conference on Fire Research: Book of Abstracts. November 2-5, 1998, Gaithersburg, MD, Beall, K. A., Editor(s), 37-38 pp, 1998.

Park. C, Ounaies. Z, Watson. K.A, Crooks. R.E, Smith. J, Lowther. S.E, Conell. J.W, Siochi. E.J, Harrison. J.S, St Clair. T.L: *Dispersion of single-wall carbon nanotubes by in situ polymerization under sonication*. Chemical Physics Letters. 2002. **364**: p. 303-308.

Pasquini. N: *Polypropylene Handbook*. Hanser Gardner Publications; 2<sup>nd</sup> Revised edition (31<sup>st</sup> July 2005).

Peeterbroeck. S, Laoutid. F, Taulemesse. J.M, Monteverde. F, Lopez-Cuesta. J.M, Nagy. J.B, Alexander. M and Dubois. P: *Mechanical Properties and Flame-Retardant Behavior of Ethylene Vinyl Acetate/High-Density Polyethylene Coated Carbon Nanotube*. Advanced Functional Materials. 2007. **17**: p. 2787-2791.

Rimez. B, Rahier. H, Van Assche. G, Artoos. T, Biesemans. M, Van Mele. B: *The thermal degradation of poly(vinyl acetate) and poly(ethylene-co-vinyl acetate), Part I: Experimental study of the degradation mechanism.* Polymer Degradation and Stability. April 2008. **93**(4): p. 800-810.

Schartel. B, Potschke. P, Knoll. U and Abdel-Goad. M: *Fire behaviour of polyamide* 6/multiwall carbon nanotube nanocomposites. European Polymer Journal. 2005. **41**: p. 1061-1070.

Schartel B, Pawlowski. K.H and Lyon. R.E: *Pyrolysis combustion flow calorimeter: A tool to assess flame retarded PC/ABS materials*? Journal of Thermoanalytical and calorimetric methods. 15 October 2007. **462**(1-2): p. 1-14.

Wang. L.S, H.B. S.B. Kang, Wang Y, Wang Liu and R: Solubilities, thermostabilities and flame retardance behaviour of phosphorus-containing flame retardants and copolymers. Fluid Phase Equilibria. 2007. **258**(2): p. 99-107.

Wang. Z, Ciselli. P, Peijs. T: *The extraordinary reinforcing efficiency of single-walled carbon nanotubes in oriented poly(vinyl alcohol) tapes.* 14<sup>th</sup> November 2007. Nanotechnology. **18**(45). Article number 455709.

Wei C, Srivastava. D, Cho. K: *Thermal expansion and diffusion coefficient of carbon nanotubes-polymer composite*. Nano Letters. 2002. **2**: p. 647-650.

Zhang. J, Hereid. J, Hagen. M, Bakirtzis. D, Delichatsios. M.A, Fina. A, Castrovinci. A, Camino. G, Samyn. F and Bourbigot. F: *Effects of nanoclay and fire retardants on fire retardancy of a polymer blend of EVA and LDPE*. Fire Safety Journal. May 2009. **44**(4): p. 504-513.

Zhang. R, Baxendale. M and Peijs. T: Universal resistivity-strain dependence of carbon nanotube/polymer composites. Physical Review B. November 2007. **76**(19): Article number 19543.

Zhang. R, Dowden. A, Deng. H, Baxendale. M and Peijs. T: *Conductive network formation in the melt of carbon nanotube/thermoplastic polyurethane composite*. Composites Science and Technology. August 2009. **69**. No 10: p. 1499-1504.

Zhang. S, Horrocks. A.R, Hull. R and Kandola. B.K: *Flammability, degradation and structural characterization of fiber-forming polypropylene containing nanoclays flame retardant combinations.* Polymer Degradation and Stability. 2006. **91**: p. 719-725.

# 7

# Multiwall Carbon Nanotubes and Nanoclays as Flame Retardants for Polylactic Acid and its Natural Fibre Reinforced Composites

# 7.1 Introduction

In previous chapters, the materials selection spectrum has been across the scale from thermoset resin to thermoplastic to finally a fully bio-based and biodegradable polymer system. The main purpose was to move away from a thermoset to a fully bio-based and biodegradable system with enhanced flame retardant properties. In order to meet the recyclability criteria, a polylactic acid (PLA) nanocomposite system was selected. As observed in Chapters 5 and 6, using carbon nanotubes in conjunction with nanoclays can dramatically reduce the peak heat release rate (PHRR) of the base polymer. Therefore, the objective is to formulate and test an optimised nanocomposite system based on a PLA resin. This resin system will be used to manufacture a natural fibre reinforced composite as an end product.

Oil depletion as well as ecological aspects of both production and disposal of standard petroleum-based plastics is of worldwide concern. These factors have motivated many researchers to develop products derived from biomass (Peijs et al., 1998, 2000; Oksman et al., 2003). Cellulose is both the most common biopolymer and the most common organic compound on Earth. About 33 % of all plant matter is cellulose; i.e. the cellulose content of cotton is 90 % and that of wood is 50 % (Nishino et al., 2003). Some biopolymers such as polylactic acid (PLA), poly-3hydroxybutyrate (PHB) and thermoplastic starch can be used as plastics, replacing petroleum-based commodity plastics such as polypropylene, polystyrene or polyethylene. Among these biobased polymers, polylactic acid (PLA) has currently the greatest commercial potential because of its relatively high melting point, crystallinity and stiffness compared to other biopolymers (Plackett et al., 2003; Barkoula et al., 2009). Moreover, PLA is a versatile polymer made from renewable agricultural materials such as corn or potatoes that are fermented into lactic acid. PLA is a linear aliphatic thermoplastic polyester, produced by polymerization of lactide, a cyclic dimer derived from lactic acid, which in turn is obtained by the fermentation of corn or sugar beet. By replacing traditional polymer materials which are derived from crude oil with biopolymers, issues to do with dwindling fossil fuel stocks and disposal problems can be tackled. Biodegradable polymers such as PLA are especially of interest for applications where mechanical recycling is problematic, since the material is 100 % biodegradable and compostable.

However, to achieve the mechanical performance needed for many engineering applications these polymers need to be reinforced to create engineering polymer composites. By using natural fibres such as hemp, flax or kenaf, fully "bio-based composites" can be manufactured (Barkoula *et al.*, 2009). One of the main advantages of natural fibres (NF) is their "lightweight potential". Natural fibres have a 40 % lower density than glass fibres (GF), which allows the construction of lighter parts, compared to plastic parts reinforced with GF or minerals fillers (Shen and Patel, 2008; Corbiere *et al.*, 2001).

This not only makes these materials competitive with traditional composites such glass fibre reinforced plastics (GRP) but is also essential to give them additional ecoadvantages through being lightweight which is essential for transport applications as a result of improved fuel efficiency and reduced emissions (John and Thomas, 2008). Mohanty et al (2000) compiled an extensive overview into biofibres, biodegradable polymers and biocomposites to take a closer look into the feasibility of implementing these types of materials within the industrial and domestic sectors. However just like with other plastics, the poor flame retardancy of PLA restricts its application and development in important fields such as construction and transportation. Several works have been published in the field of fire testing of natural fibre composites (Gilman and Kashiwagi, 1997; Beyer, 2009; Nazare et al., 2006; Bourbigot et al., 2008). A note worthy study was completed by Schartel et al (2008), who looked into improving the fire retardancy of flax fibre reinforced polypropylene (PP) composites. This group studied the effects of adding ammonium polyphosphate (APP) and expandable graphite (EG) into the polymer composite, as a flame retardant (FR) additive. The heat release rate (HRR) was reduced from 167 to 35 kW/m<sup>2</sup> for a composite based on 30 wt.% flax fibre and the addition of 25 wt.% of expandable graphite (EG) additive.

To date only a few studies have been devoted to the flame retardancy of PLA. Réti *et al* (2008) studied the efficiency of different intumescent formulations to develop flame retardant PLA, and the quantity of these additives have been optimised to decrease the quantity of ammonium polyphosphate in the formulation. In the most recent work, Zhan *et al* (2008) studied the use of spirocyclic pentaerythritol bisphosphorate disphosphoryl melamine (SPDPM) as an intumescent flame retardant for PLA. The SPDPM generated char which significantly improved the flame retardancy and anti-dripping performance of PLA with 25 wt.% additive. Imparting flame retardancy into these materials is possible but only with relatively high loadings of inorganic filler (Hapuarachchi *et al.*, 2007). This causes detrimental effects to the mechanical properties of the composite and embrittlement.

The initial discovery by Kojima *et al* (1993) within the Toyota group demonstrated that a polyamide-6/clay nanocomposite, containing only 5 wt.% nanoclay could lead to an increase of 40 % in tensile strength, while at the same time increasing the heat distortion temperature (HDT) and also maintaining a high impact strength. Due to the silicates fundamental unit thickness of 1 nm and high aspect ratio in combination with their high intrinsic stiffness, these nanofillers, when well dispersed, will reinforce polymers far more efficiently than conventional fillers like calcium carbonate or glass fibres. This good level of reinforcement at low loadings has beneficial effects on the processability of the polymer due to a lower viscosity and density of the final nanocomposite material and more importantly less embrittlement than microcomposites with equivalent mechanical properties. Since the early work on polyamide-6 and nanoclay various reviews have been reported on the subject of polymer layered silicate nanocomposites (Morgan *et al.*, 2005, 2006).

Schartel *et al* (2006) studied the thermal and flame retarding effects of phosphonium modified silicates in epoxy resins. The mechanism is thought to be due to the clay acting as a barrier to the flame trying to penetrate the unconsumed polymer underneath the protective char layer. Layered clays have performed well in retarding the flame due to their excellent barrier properties. A recent addition to the nanoclay group is sepiolite which is a natural hydrous magnesium silicate. As a clay mineral, structurally it consists of two sheets of SiO<sub>4</sub> tetrahedra bonded via oxygen atoms to a central sheet of octahedrally arranged magnesium atoms. It has a needle-like profile which helps the flowability of the polymer when melt produced. Bilotti and others (Bilotti *et al.*, 2008; Franchini *et al.*, 2009; Marosfoi *et al.*, 2008) have looked at the dispersion of sepiolite within thermoplastic polymers as well as studying the effect on mechanical and thermal properties of the resulting nanocomposite.

Since the inadvertent discovery of carbon nanotubes (CNTs) by Iijima (1991) there has been a great deal of research into possible applications (Jia *et al.*, 2000; Xia *et al.*, 2003; Zhang *et al.*, 2004; Erik *et al.*, 2005; Wang *et al.*, 2007, 2008). Kashiwagi *et al* (2004) was one of the first to introduce CNTs into polypropylene (PP) with the sole purpose of reducing its flammability behaviour.

Their team reported that a possible mechanism for the reduction in peak heat release rate (PHRR) may have been due to the formation of a structured network layer. Beyer *et al* (2002) has also looked into using crude and purified MWNTs to decrease the flammability of ethylene vinyl acetate (EVA) copolymer. Dubois *et al* (2004) took the concept further and explored the idea of using both CNTs and nanoclay fillers together in an EVA matrix. A synergic improvement was recorded for this ternary system when compared with the binary base systems.

Ma *et al* (2007) also investigated a ternary CNT/nanoclay system with acrylonitrile butadiene styrene (ABS). Both studies recorded a reduction in the PHRR, and suggested that the CNTs acted as a sealing agent to create a network with the clay layers, forming a much tighter char than clay alone. The concept of synergism is often used in the enhancement of flame retardant polymers. By definition, synergism means the enhanced performance of a mixture of two or more components compared to that of a single component at the same concentration. In the field of fire science, this concept helps to limit the amount of volatile gases escaping from the degrading polymer and impedes the oxygen ingress.

This research will consist of combining the flame retarding potential of carbon nanotubes and nanoclay to develop a ternary PLA nanocomposite with enhanced flame retardancy. These formulations will be screened for their contribution to possible fire hazards using the microcalorimeter. The pyrolysis combustion flow calorimeter (PCFC) also known as the microcalorimeter measures the heat release capacity (HRC) of milligram samples which is advantageous when testing different nanocomposite batches. PCFC data has been shown to correlate well with other established fire test data (Cone Calorimeter), flammability results (LOI, UL-94) and combustion tests (Bomb Calorimeter) and as such is seen as a powerful, low cost tool to assess and predict flammability properties (Lyon and Walters 2004). Finally an optimised polymer nanocomposite formulation will be selected to scale up and produce a natural fibre reinforced composite based on a non-woven hemp mat and PLA. This polymer composite will be investigated with respects to its reaction to fire performance using the cone calorimeter.

# 7.2. Experimental Procedure

### 7.2.1 Materials

The base polymer was a polylactic acid (Biopearls M110) resin in granular form with melt flow index (MFI) of 20 g/10 min, from Jongboom Holding B.V (Netherlands). Before being processed, the PLA was first dried in a vacuum oven at 40 °C for 24 hours to remove water and other volatile components. The sepiolite nanoclay (Sep) was supplied by Tolsa S.A. (Spain). The bulk density of the clay is  $60 \pm 30$  g/L, and the BET surface area is  $320 \text{ m}^2/\text{g}$ . The characteristic average dimensions of the individual sepiolite nano fibres are approximately 1-2 mm in length and 20-30 nm in diameter. So the aspect ratio is within the range of 100-300, high enough to lead to good mechanical reinforcement (Bilotti *et al.*, 2008). The carbon nanotubes were Nanocyl 3100 thin multiwalled carbon nanotubes (CNT) with 95+% purity and supplied by Nanocyl S.A (Belgium). The reinforcing natural fibre mat was a non-woven needle punched hemp mat (800 g/m<sup>2</sup>) from Hemcore Ltd (UK).

### 7.2.2 Processing

The compounding of the nanocomposite was carried out on a DSM Xplore micro 15 co-rotating twin-screw extruder. This mini extruder is equipped with conical co-rotating screws having a length of 150 mm, an L/D ratio of 18 and a net capacity of 12 g. The processing scheme was to compound the polymer at 200 °C for 20 minutes at a mixing speed of 200 rpm. After carrying out the bench scale thermal analysis tests (using the microcalorimeter and thermal gravimetric analysis), the chosen formulation was up-scaled using a Collin ZK25 co-rotating twin-screw extruder with K-Tron gravimetric feeders. Master batches of sepiolite and CNTs (20 wt.% each) were compounded separately, then diluted with polymer to the filler content required (10wt.%Sep+2wt.%CNT). The final batches were pelletized using the Collin CSG/171/1 attachment. Films were produced using a Collin Tech-line CR72T film line. Composites were made by a conventional film stacking technique; a layered structure was formed by laying alternating layers of hemp mat and PLA film.

The final PLA hemp nanocomposites were hot-pressed into  $220 \times 200 \text{ mm}^2$  plates weighing approximately 240 g each and comprising of 30 vol.% of hemp. A Collin P300E hydraulic hot press was used at a pressure of 5 bar for 10 minutes at 190 °C for consolidation. A manufacturing scheme is presented in Figure 7.1.



*Figure 7.1.* Flow diagram of manufacturing and testing procedure involved in developing flame retardant natural fibre composite.

### 7.2.3 Characterisation

Thermal gravimetric analysis (TGA) and derivative thermal analysis (DTA) was carried out on a TA Instruments Q500, with specimen size of 5 mg. The temperature range was from 30 °C to 1000 °C at a ramp rate of 10 °C/min in air and nitrogen atmosphere. The specimens for the microcalometer were approximately 5 mg and the tests were carried out in triplicate and the results averaged. The gas mixture was an 80:20 N<sub>2</sub>:O<sub>2</sub> mix. For each run, the pyrolzer was set to a 60 °C/min heating rate to reach 750 °C from room temperature. The combustor temperature was pre-set to 900 °C. Cone calorimetry was carried out on samples of  $100 \times 100 \times 5$  mm<sup>2</sup>. All of these materials were conditioned at 23  $\pm$  3 °C at a relative humidity of 50%  $\pm$  5% for 24 hours prior to testing. The samples were wrapped with aluminium foil around the back and edges before placing the specimen onto the holder and then into the cone calorimeter. A retainer frame was used to reduce edge burning effects. All the tests were carried out in accordance with ISO 5660 unless stated otherwise. All the cone tests were conducted on the cone calorimeter assembled by Fire Testing Technology Ltd, (East Grinstead, UK) in accordance to ASTM E-1354 specifications which is located at the Interscience Communications Laboratories, Watford. The specimens were positioned horizontally and exposed to an irradiance of 50 kW/m<sup>2</sup>. The specimens were pilot ignited and run in triplicate. A Carbite HTF18000 oven was used to prepare the SEM samples for morphology characterisation. The samples were put into an alumina pan (7.5 cm  $\emptyset$  and 3 cm deep). The heating program was from room temperature to 325 °C at a rate of 10 °C/min and a ramp down rate of 50 °C/min back down to room temperature.

# 7.3. Results and Discussion

### 7.3.1 Screening using TGA

### 7.3.1.1 PLA/MWNTs

The addition of inorganic fillers can improve the thermal stability of filled polymer systems to some extent. Many studies have reported that polymer/CNT composites exhibit higher thermal stability than that of the polymer matrix alone (Marosfoi *et al.*, 2006; Gorrasi *et al.*, 2007; Kim *et al.*, 2007). Figure 7.2 show the TGA traces of PLA in air and nitrogen. Figure 7.3 illustrates the thermogravimetric scan obtained from the TGA of PLA with CNTs.



*Figure 7.2. Thermal gravimetric analysis scans of PLA in air and nitrogen, showing the onset decomposition temperature.* 



**Figure 7.3.** Thermal gravimetric analysis scans of PLA with CNTs in (a) air and (b) nitrogen showing the effect of an aerobic and anaerobic environment to the decomposition behaviour of the PLA nanocomposites.

The mass loss signal did not change significantly in width or height with CNT content, indicating little or no contribution of the CNTs to the thermal resistance of the resin. The residues after 400 °C corresponded well with the char yield of PLA plus the different amounts of CNTs. The addition of CNTs resulted in a negative effect to the onset decomposition temperature for the PLA when tested in air (Figure 7.3a). The CNTs are believed to behave in a catalyzing way in an oxidising atmosphere. Interestingly, when the formulations were tested in a nitrogen rich atmosphere the decomposition temperature was reduced when the CNTs content was above 2 wt.%. Hence, loading PLA with 10 wt.% CNTs showed the largest detrimental effect on thermal stability (Figure 7.3b). A reason for this might be due to the percolation threshold which for this system is thought to be 2 wt.% of CNT, causing a percolating network of nanotubes which can act as a conducting path way causing an early onset temperature.

The CNTs showed no effective barrier behaviour at the initial stages of decomposition and merely acted as an inert filler with respect to thermal decomposition of the PLA matrix. Similar thermal behaviour was also observed for PA6/CNT nanocomposites by Schartel et al (2005). In later work they observed a decrease in thermal stability for polycarbonate with the addition of CNTs (Schartel et al., 2008). Two possible mechanisms were postulated: (i) the presence of CNTs may have led to a reduction in cross-linking of the polymer; (ii) additional components or impurities, such as compatibilizers or remaining iron oxides from nanotube synthesis may have acted as catalyst during the oxidative decomposition of nanocomposite (Kashiwagi et al., 2004). It is well known that the thermal decomposition of PLA is lead by random chain scission or specific chain scission because its repeated aliphatic ester structure is relatively easy to hydrolyze and break down (Li et al., 2001; Fan et al., 2004). Recently it was also reported that radical or radical promoting species located on crushed CNT surfaces influence the decomposition of the polymeric matrix (Peeterbroeck et al., 2007). The presence of acidic or basic impurities may enhance depolymerisation of aliphatic ester in PLA thus resulting in premature decomposition. However, with respect to pyrolysis under fire, the highly effective char yield for PLA with the addition CNTs was the main result noticed in this area of testing.

### 7.3.1.2 PLA/Sepiolite

Figure 7.4a and 7.4b shows, TGA traces of PLA with sepiolite nanoclay tested in air and nitrogen. The addition of sepiolite brings about a slight early onset decomposition temperature in air when compared to unfilled PLA. Similar thermal behaviour has already been reported for EVA based nanocomposites (Lim *et al.*, 2002), for which optimal thermal stabilisation was obtained at a filler content around 3 wt.%. Such behaviour was explained by the relative extent of exfoliation in which the polymer chains have enough clay platelet galleries to enter for protection. Indeed, at low filler content, exfoliation dominates but the amount of exfoliated silicate layers is not sufficient to promote any significant improvement to the thermal stability.



*Figure 7.4.* Thermal gravimetric analysis scans of PLA with sepiolite clay in (a) air and (b) nitrogen.

The superimposed image in Figure 7.4a shows that the onset decomposition temperature is slightly decreased with sepiolite loading. The interpretation of this phenomenon is commonly a catalytic effect of the nanoclay on the pyrolysis of PLA (Manos et al., 2001; Tartaglione et al., 2008). The clay acts as a heat barrier, which enhances the formation of char after thermal decomposition. This heat barrier effect may result in a reverse thermal stability. Put differently, the stacked needle structure could hold accumulated heat that could be used as a heat source to accelerate the decomposition process, in conjunction with the heat flow supplied by the outside heat source (Ray and Yamad, 2003). When unmodified sodium montmorillonite is introduced into a non-polar polymer matrix a microcomposite is obtained with large filler particles and no intercalation or exfoliation with polymer is usually observed which means that these materials are sometimes referred to as microcomposites or immiscible nanocomposites. When clay layers are only partly intercalated/exfoliated and non-homogeneously dispersed, the performance of the polymeric material can be similar to other composites with higher loadings of particles of microscopic dimensions.

It is usually well accepted that improved thermal stability of polymer clay nanocomposites is mainly the result of the formation of char which hinders the diffusion of volatile decomposition products by creating a labyrinth effect or tortuous path. The direct result of the decrease in permeability has been observed in exfoliated nanocomposites (Zhu et al., 2001; Gilman et al., 1999; Gilman, 1999; Alexandre and Dubois et al., 2000; Kotsilkova et al., 2001). Figure 7.5 shows the TGA thermogram for the nanocomposite formulation selected on the basis of their performances in TGA and microcalorimetry (which is discussed later). The formulations with above 2 wt.% CNT (Figure 7.3) and 10 wt.% sepiolite (Figure 7.4) show the best performance in terms of residual char content towards the later part of the heating scan. A material possessing a high char yield is very important with respect to creating a protective barrier for volatile gases escaping and oxygen ingress during a fire. The combination of sepiolite nanoclay and carbon nanotubes is thought to cause a tight char. The CNTs act to bridge the clay and in doing so reduced the pore density caused by thermal decomposition. This was verified by morphological studies carried out by scanning electron microscopy (SEM) in Figures 7.9a-c.



*Figure 7.5. Thermal gravimetric analysis scans of PLA ternary nanocomposite systems in air, showing the increased residual char.*
Loading	Nanofiller	Onset	Peak	Residual
		Decomposition	Decomposition	Mass
		Temperature	Temperature	(wt. %)
		(°C)	(°C)	
PLA		337	364	1
1 wt.%	CNT	331	357	3
1 wt.%	Sep	326	359	2
2 wt.%	CNT	333	360	3
10 wt.%	Sep	334	364	7
10 wt.%	CNT	322	348	3
1  wt.% + 2  wt.%	Sep+CNT	331	366	3
10 wt.% + 2 wt.%	Sep+CNT	334	364	11
10 wt.% + 10 wt.%	Sep+CNT	336	362	13

Table 7.1. Parameters obtained	for the PLA	nanocomposites	from the	TGA
--------------------------------	-------------	----------------	----------	-----

#### 7.3.2 Microcalorimetry

Tables 7.2-7.4 shows the nanocomposite results acquired from the microcalorimeter. The heat release capacity (HRC) defined as the maximum heat release rate divided by the constant heating rate in the test. This has been proposed as the single best measure of the fire hazard of a material (Lyon and Walters, 2004; Lyon et al., 2006). The largest reduction in HRC is from 2-5 wt.% CNTs. The authors believe that a percolating network is created above 2 wt.% (Deng et al., 2009). This might assist in conducting the heat throughout the whole material rather than causing localised decomposition. The effect of the 10 wt.% sepiolite clay did not have the same reduction in HRC as did the CNTs. This could be due to the morphology of the sepiolite clay. Previous studies (Zhang and Horrocks, 2003; Lau et al., 2006; Alexandre and Dubois, 2006; Zhang et al., 2009) have shown that the mechanism of nanoclays in reducing the flammability of polymers is to create a barrier on the surface of the polymer which protects the underlying material from being consumed by the gas phase combustion. Such nanoclays as montmorillonite have a plate-like morphology which is thought to cover a larger surface area of the polymer due to its flat shape. However, sepiolite clay has a needle-like shape (Bilotti et al., 2009) so total surface coverage is not as efficient.

Sample		Heat Release Capacity (J/g <sup>-k</sup> )
PLA		525
+ 0.5 wt.%	CNT	490
+ 1 wt.%	CNT	466
+ 2 wt.%	CNT	452
+ 5 wt.%	CNT	303
+ 10 wt.%	CNT	260

Table 7.2. The effect of CNT on the heat release capacity of PLA.

Table 7.3. The effect of sepiolite clay on the heat release capacity of PLA.

Sample		Heat Release Capacity (J/g <sup>-k</sup> )
+ 1 wt.%	Sep	451
+ 2.5 wt.%	Sep	433
+ 5 wt.%	Sep	427
+ 10 wt.%	Sep	370

**Table 7.4.** The effect of ternary nanocomposite formulations on the heat release capacity of PLA.

Sample			Heat Release Capacity (J/g <sup>-k</sup> )
1 wt.%	Sep + 0.5 wt.%	CNT	447
1 wt.%	Sep + 2 wt.%	CNT	401
10 wt.%	Sep + 0.5 wt.%	CNT	330
10 wt.%	Sep + $2 \text{ wt.\%}$	CNT	262
10 wt.%	Sep + 10 wt.%	CNT	211

Table 7.4 shows the HRC results from the microcalorimeter after combining sepiolite and CNTs into a ternary nanocomposite system. All the ternary formulations show synergistic behaviour over their individual component loadings (see Tables 7.2 and 7.3). The largest drop in HRC occurred with a sepiolite loading of 10 wt.%.

A further reduction came about with a 2 wt.% loading of CNT. Again, the reasoning behind this is thought to be due to the nanotubes bridging the sepiolite clay and forming a tighter char during decomposition. This has been indicated by SEM micrographs of specimens comprising of (i) PLA+CNT; (ii) PLA+Sep and (iii) PLA+Sep+CNT (see Figures 7.9a, b and c, respectively). Therefore, using the results attained from the TGA and microcalorimeter, a 10wt.%Sep+2wt.%CNT formulation was selected as an optimal formulation for larger composite production. The justification for this composition is that 10 wt.% sepiolite is an adequate amount needed to create a protective barrier layer while 2 wt. % CNTs is sufficient to create a network within the system. This is a satisfactory trade-off between performance and costs of CNTs.

#### 7.3.3 Cone Calorimetery

Cone calorimetery was conducted on the optimised samples. The heat release rate (HRR) was measured as this parameter is one of the most important parameters to characterise fire hazard (Babrauskas and Peacock, 1992).



*Figure 7.6. Heat release rate profile of the specimens tested on the cone calorimeter.* 

The heat release rate (HRR) plots from the cone calorimeter are presented in Figure 7.6. The results show a large difference in behaviour between PLA and PLA ternary nanocomposite. Upon heating, the unfilled PLA specimen began to melt and bubble (Figure 7.7a). For the nanocomposite, the nanofillers increased the melt viscosity of the ternary system which eliminated bubbling and caused the specimen to maintain its shape (Figure 7.7b). Another interesting observation is that contrary to general belief, is that the introduction of natural fibres into the polymer did reduce the heat release rate. The hemp fibres are thought to have charred and protected the underlying polymer (Hapuarachchi *et al.*, 2007).

Sample	Peak HRR (kW/m <sup>2</sup> )	Total Heat Release (MJ/m <sup>2</sup> )	Total Smoke Release (m <sup>2</sup> /m <sup>2</sup> )	Mean CO <sub>2</sub> (kg/kg)	Mean CO (kg/kg)	Residual Mass (wt. %)
PLA	485	104	5	150	4.6	1.6
PLA/hemp	361	116	26	1.58	0.02	3.5
PLA ternary nanocomposite	265	118	112	0.82	0.03	3.5
PLA ternary nanocomposite /hemp	340	116	57	1.57	0.02	10

*Table 7.5.* Parameters obtained from the cone calorimeter for the PLA composites.

The total heat release, the integral of the heat release rate curve over the duration of the experiment is practically unchanged throughout the samples (Table 7.3); this suggests that the reason for the improved flammability properties of these materials is due to differences in the condensed phase decomposition processes and not due to a gas-phase effect. A silicate rich barrier being formed at the start of pyrolysis may explain the reduction in the peak heat release rate (PHRR). Changing the decomposition pathways, resulting in charring and influencing the chemical reactions in the gas phase which can result in flame inhibition, are not the only mechanisms to improve fire retardancy behaviour. Physical mechanisms such as cooling, barrier formation, and changing the heat capacity, thermal conductivity, or viscosity also have an influence on fire behaviour. A silicate char surface layer acting as a barrier for heat and mass transportation is probably the main flame retardant mechanism. From the cone calorimeter test results, the nanocomposite shows a lower initial peak heat release and a plateau-like behaviour. The HRR curve changes into a shape that is typical for char or residue forming material. However, the introduction of the hemp fibre mats lead to a detrimental effect on the HRR. Figure 7.6 shows that there is an initial sharp rise in HRR for the hemp reinforced specimens. This is believed to be due to the thinner layer of resin on the surface, which is consumed by the flame at a faster rate. The ternary nanocomposite resin system has the lowest PHRR because it has a lower surface to volume ratio which creates a protective char coating during flaming. The HRR profile plateaus and decays as the char protection decreases the amount of polymer material (fuel) available for combustion and also reduces the ingress of oxygen. The hemp reinforced specimens displays another issue towards the later stages of the test. At around 400 seconds the HRR rises again, even for the hemp ternary nanocomposite system. Figure 7.8 shows the HRR profile for the specimens excluding the unfilled PLA specimen.



*Figure 7.7. Photographs taken during cone calorimetery testing (a) unfilled PLA and (b) PLA ternary nanocomposite system, showing the resistance to melting.* 



*Figure. 7.8. HRR profile and photographs of* (*a*) *PLA/hemp composite during testing* (*b*) *PLA ternary nanocomposite post testing* (*c*) *PLA ternary hemp composite post testing*.

The hemp fibre composites show severe lofting and delamination during flaming combustion (Figure 7.8a and 7.8b). This causes a rise in HRR as more material is exposed and presented as fuel to the flame.

The hemp reinforced ternary nanocomposite specimen however shows a much lower second PHRR compared to the unfilled PLA/hemp composite. Delamination may be cause for concern with respect to mechanical failure during combustion. To get more insight into the behaviour of the nanocomposites during combustion and its flame retarding mechanisms, a heat treatment experiment was carried out to study the surface morphology after exposure. Three specimens comprising of (i) PLA+2wt.%CNT; (ii) PLA+10wt.%Sep and (iii) a ternary nanocomposite system based on 10 + 2 wt.% (Sep+CNT). These 30 mg specimens were place into an air circulating oven which was heated to 325 °C at 10 °C/min; corresponding to the onset decomposition temperature observed by TGA. The SEM images show the different surface morphologies (Figure 7.9a-c). The CNT filled specimen shows some porosity (Figure 7.9a) but the addition of sepiolite clays seemed to have created a tighter network during heating (Figure 7.9c). This may assist in explaining the improved flame retarding mechanism of the ternary polymer nanocomposites.



(a)





(c)

**Figure. 7.9.** SEM micrographs of PLA nanocomposite specimens after being exposure to 325 °C (a) PLA+CNT (b) PLA+Sep (c) PLA ternary system.

#### 7.4. Conclusions

The objective of this research was to develop a fully biobased natural fibre composite with improved flame retardancy. Achieving this target was accomplished by using a PLA polymer derived from crops together with two different nanofillers to create synergy with respects to flame retardancy. A microcalorimeter was utilised to screen nanocomposite formulations for their suitability for further development. This technique had the advantage of quick test turnaround times as well as only consuming small amounts of materials which is ideal with nanocomposites. Carrying across the data from the microcalorimeter and TGA to full composite production indicated promising results. A feature which was not expected was the reduction of PHRR in the cone calorimeter after the introduction of hemp fibre mat into the PLA resin, which acted in its self as a flame retardant. The ternary nanocomposite based on sepiolite and CNTs showed the best performance with 58 % drop in PHRR. However this was reduced by the introduction of the non-woven hemp fibre mats by only a 45 % drop. Due to the thick layered structure the composites delaminated during the cone calorimeter testing thus exposing the underlying material. Short fibre compounds may be a more suitable type of composite as this avoids the layered structure of mat-based composites, which may help alleviate lofting and delamination during burning.

#### 7.5 References

Alexandre. M and Dubois. P: *Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials.* Material Science and Engineering Research. 2006. **28**: p. 1-63.

Babrauskas. V and Peacock. R.D: *Heat Release Rate: The Single Most Important Variable in Fire Hazard.* Fire Safety Journal. 1992. **18**: p. 255-272.

Barkoula. N.M, Garkhail. S.K and Peijs. T: *Biodegradable composites based on flax/polyhydroxybutyrate and its copolymer with hydroxyvalerate*. Industrial Crops and Products, In Press, corrected proof available online 17<sup>th</sup> September 2009. doi:10.1016/j.indcrop.2009.08.005.

Beyer. G: Short Communication: Carbon Nanotubes as Flame Retardants for Polymers. Fire and Materials. 2002. 26: p. 291-293.

Beyer. G: *Nanocomposites - A new class of flame retardants*. Plastics, Additives and Compounding. March 2009/April 2009. **11**(2): p 16-17/19-21.

Bilotti. E, Fischer. H.R and Peijs. T: *Polymer nanocomposites based on needle-like sepiolite clays: Effect of functionalized polymers on the dispersion of nanofiller, crystallinity, and mechanical properties.* Journal of Applied Polymer Science. 15<sup>th</sup> January 2008. **107**(2): p. 1116-1123.

Bilotti. E, Zhang. R, Deng. H, Quero. F, Fischer. H.R and Peijs. T: *Sepiolite needle-like clay for PA6 nanocomposites: An alternative to layered silicates*? Composites Science and Technology. 2009. In Press. <u>doi:10.1016/j.compscitech.2009.07.016</u>.

Bourbigot. S, Fontaine. G, Duquesne. S and Delobel. R: *PLA nanocomposites: quantification of clay nanodispersion and reaction to fire*. International Journal of Nanotechnology. 2008. **5** (6-8): p. 683-692.

Corbiere. N.T, Gfeller. L.B, Lundquist. L, Leterriery. Y, Manson. J.A.E and Jolliet. O: Life cycle assessment of biofibres replacing glass fibre as reinforcement in plastics. Resources conservation and recycling. November 2001. **33**(4): p.267-287.

Deng. H, Zhang. R, Bilotti. E and Peijs. T: *Effective reinforcement of carbon nanotubes in polypropylene matrices*. Journal of Applied Polymer Science. 2009. In Press. <u>doi 10.1002/app.30783</u>

Erik. T, Chunyu. L and Tsu. W. C: *Nanocomposites in context*. Composites Science and Technology. 2005. **65**: p. 491-516.

Fan. YJ, Nishida. N, Shirai. Y, Tokiwa. Y and Endo. T: *Thermal decompositon behavior of poly(lactic acid) stereocomplex*. Polymer Degradation and Stability. 2004. **86**: p. 197-208.

Franchini. E, Jocelyne. G and Jean. F.G: *Sepiolite-based epoxy nanocomposites: Relation between processing, rheology and morphology.* Journal of Colloid and Interface Science. 1<sup>st</sup> January 2009. **329**(1): p. 38-47.

Gilman. J.W, Kashiwagi. T, Brown. J, Lomakin. S and Giannelis. E: *Flammability Studies of Polymer Layered Silicate Nanocomposites*. (Ed): CAe, Kliger H.S. Rasmussen. Chemistry and Technology of Polymer Additives. Chapter 14. 1999, Blackwell Science Inc, Malden MA, Ak-Malaika S; Golovoy A; Wilkie CA, Editor(s): p. 249-265. 1999.

Gilman. J.W and Kashiwagi. T: *Nanocomposites: A Revolutionary New Flame Retardant Approach.* SAMPE Journal. 1997. **33**: p. 40-46.

Gilman. J.W: Flammability and Thermal Stability Studies of Polymer Layered-Silicate (Clay) Nanocomposites. Applied Clay Science. 1999. **15**: p. 31-49.

Gorrasi. G.M, Sarno. A, Bartolomeo. Di, Sannino. D, Ciambelli. P and Vittoria. V: *Incorporation of carbon nanotubes into polyethylene by high energy ball milling: morphology and physical properties.* Journal of Polymer Science Part B: Polymer Physics. 2007. **45**: p. 597-606. Hakkarainen. M, Karlsson. S and Albertsson. A.C: *Rapid (bio)decompositon of polylactide by mixed culture of compost microorganisms: low molecular weight products and matrix changes.* Polymer. 2000. **41**: p. 2331-2338.

Hapuarachchi. T.D, Ren. G, Fan. M, Hogg. P.J and Peijs. T: *Fire Retardancy of Natural Fibre Reinforced Sheet Moulding Compound*. Applied Composite Materials. 2007.14: p. 251-264.

Jia. Z, Wang. Z, Xu. C, Liang. J, Wei. B, Wu. D and Zhang. Z: *Fabrication of carbon nanotubes/nylon-6 composites by in situ process* J Tsinghua Univ (SCI and Tech) 2000. **40**: p. 14-16.

Iijima. S: Helical microtubules of graphitic carbon. Nature. 1991. 354: p 56-58.

John. M.J and Thomas. S: *Biofibres and biocomposites-Review*. Carbohydrate Polymers. 8<sup>th</sup> February 2008. **71**(3): p 343-364.

Kashiwagi. T, Du. F, Douglas. J.F, Winey. K.I, Harris. R.H and Shields J.R: *Nanoparticle networks reduce the flammability of polymer nanocomposites*. Nature Materials. 2005. **4**: p. 928-933.

Kashiwagi. T, Grulke. E, Hilding. J, Groth. K. M, Jr Harris. R.H, Butler. K.M, Shields. J.R, Kharchenko. S and Douglas. J. F: *Thermal and Flammability Properties of Polypropylene/Carbon Nanotube Nanocomposites*. Polymer. May 2004. **45**(12): p.4227-4239.

Kim. H.S, Park. B.H, Yoon. J.S and Jin. H.J: *Thermal and electrical properties of poly*(*l*-*lactide*)-*graft-multiwalled carbon nanotube composites*. European Polymer Journal. 2007. **43**: p. 1729-1735.

Kojima. A, Usuki. A, Kawasumi. M, Okada. A, Fukushima. Y, Kurauchi. T and Kamigaito. O: *Mechanical Properties of Nylon-6 clay hybrid*. Journal Materials Research. 1993. **8**: p. 1185-9.

Kotsilkova. R, Petkova. V and Pelovski. Y: *Thermal analysis of polymer-silicate nanocomposites*. Journal of Thermoanalytical and calorimetric methods. 2001. **64**(2): p. 591- 598.

Lau. K.T, Gu. C and Hui. D: *A critical review on nanotube and nanotube/nanoclay related polymer composite materials.* Composites Part B. 2006. **37**(6): p. 425-436.

Lim. S.T, Hyun. YH, Choi. H.J and Jhon. M.S: *Synthetic biodegradable aliphatic polyester/montmorillonite nanocomposites*. Chemistry of Materials. 2002. **14**: p. 1839-1844.

Li. S.M, Girard. A.A, Garreau. H and Vert. M: *Enzymatic decompositon of polylactide stereocopolymers with predominant D-lactyl contents*. Polymer Degradation and Stability. 2001.**71**: p. 61-67.

Liu. T.X, Phang. I.Y, Shen. L, Chow. S.Y and Zhang. W.D: Morphology and Mechanical Properties of Multiwalled Carbon Nanotubes Reinforced Nylon-6 Composites. Macromolecules. 2004. **37**(19): p. 7214-7222.

Lyon. R.E and Walters. R.N: *Pyrolysis combustion flow calorimetry*. Journal of Analytical and Applied Pyrolysis. 2004. **71**(1): p. 27-46.

Lyon. R.E, Walters. R.N and Stoliarov. S.I: *Thermal analysis method for measuring polymer flammability*. Journal of ASTM International. 2006. **3**(4): p. 1-18.

Ma. H, Tong. L, Xu. Z and Fang. Z: *Synergistic effect of carbon nanotube and clay for improving the flame retardancy of ABS resin.* Nanotechnology. 2007. **18**(37): Article number 375602 (8pp).

Marosfoi. B.B, Szabo. A, Marosi. G, Tabuani. D, Camino. G and Pagliari. S: *Thermal and spectroscopic characterization of polypropylene-carbon nanotube composite*. Journal of Thermoanalytical and calorimetric methods. 2006. **86**: p. 669-673.

Marosfoi. B.B, Garas. S, Bodzay. B, Zubonyai. F and Marosi. G: *Flame retardancy study on magnesium hydroxide associated with clays of different morphology in polypropylene matrix*. Polymer for Advance Technologies. 2008. **19**: p. 693-700.

Manos. T, Yusof. I.Y, Papayannakos. N and Gangas. N.H: *Catalytic Cracking of Polyethylene over Clay Catalysts*. Comparison with an Ultrastable Y Zeolite. Industrial and Engineering Chemistry Research. 2001. **40**: p. 2220-2225.

Mohanty. A.K, Misra. M and Hinrichsen. G: *Biofibres, biodegradable polymers and biocomposites: an overview*. Macromolecular Materials and Engineering. 2000. **276/277**: p. 1-24.

Morgan. A.B, Chu. L.L and Harris. J.D: *Flammability performance comparison between synthetic and natural clays in polystyrene nanocomposites*. Fire and Materials. July/August 2005. **29**(4): p. 213-229.

Morgan. A.B: Flame retarded polymer layered silicate nanocomposites: a review of commercial and open literature systems. Polymers for Advanced Technologies. 2006. **17**(4): p. 206 - 217.

Nazare. S, Kandola. B.K and Horrocks A.R: *Flame-retardant unsaturated polyester resin incorporating nanoclays*. Polymers for Advanced Technologies. 2006. **17**: p. 294-303.

Nishino. T, Hirao. K, Kotera. M, Nakamae. K and Inagaki. H: *Kenaf reinforced biodegradable composite*. 1<sup>st</sup> International EcoComp Conference, September 2001 Queen Mary University of London, London, England. Composites Science and Technology. July 2003. **63**(9): p. 1281-1286.

Oksman. K, Skrifvars. M and Selin. J.F: *Natural fibres as reinforcement in polylactic acid (PLA) composites*. 1<sup>st</sup> International EcoComp Conference, September 2001, Queen Mary University of London, London, England. Composites Science and Technology, July 2003. **63**(9): p. 1317-1324.

Peeterbroeck. S, Alexandre. M, Nag. J.B, Pirlot. C, Fonseca. A, Moreau. N, Philippin. G, Delhalle. J, Mekhalif. Z, Sporken. R, Beyer. G and Dubois. P: *Polymer-layered silicate-carbon nanotube nanocomposites: unique nanofiller synergistic effect*. Composites Science and Technology. November 2004. **641**(5): p. 2317-2323.

Peeterbroeck. S, Laoutid. F, Swoboda. B, Lopez. C.J.M, Moreau. N, Nagy. J.B, Alexandre. M and Dubois. P: *How Carbon Nanotube Crushing can Improve Flame Retardant Behaviour in Polymer Nanocomposites*? Rapid Communications. 2007. **28**(3): p. 260-264.

Peijs. T, Garkhail. S, Heijenrath. R, Van den Oever. M and Bos. H: *Thermoplastic composites based on flax fibres and polypropylene: Influence of fibre length and fibre volume fraction on mechanical properties*. Conference Information: 10<sup>th</sup> Rolduc Polymer Meeting on Petro Polymers vs. Green Polymers, May 05-07, 1997 Kerkrade, Netherlands, Macromolecular Symposia, Feb 1998, **127**: p. 193-203.

Peijs. T: *Natural fiber based composites*. Materials Technology. December 2000. **15**(4): p. 281-285.

Plackett. D, Andersen. T.L, Pedersen. W.B and Nielsen L: *Biodegradable composites based on L-polylactide and jute fibres*. 1<sup>st</sup> International EcoComp Conference, September 2001 Queen Mary University of London, London, England. Composites Science and Technology. July 2003. **63**(9): p. 1288-1296.

Ray. S.S and Yamad. K: *Polymer/layered silicate nanocomposites: a review from preparation to processing.* Progress in Polymer Science. 2003. **28**: p. 1539-1641.

Réti. C, Casetta. M, Duquesne. S, Bourbigot. S and Delobel. R: *Flammability properties of intumescent PLA including starch and lignin*. Polymers for Advanced Technologies. 2008. **19**(6): p. 628-635.

Schartel. B, Braun. U, Knoll. U, Bartholmai. M, Goering. H and Neubert. D: *Mechanical thermal and fire behavior of bisphenol A polycarbonate/multiwall carbon nanotube nanocomposites*. Polymer Engineering and Science. 2008. **48**. p. 149-58.

Schartel. B, Potschke. P, Knoll. U & Abdel G. M: *Fire behaviour of polyamide* 6/multiwall carbon nanotube nanocomposites. European Polymer Journal. 2005. **41**: p.1061-1070.

Schartel. B, Braun. U, Knoll. U, Bartholmai. M, Goering. H & Neubert. D: *Mechanical thermal and fire behavior of bisphenol A polycarbonate/multiwall carbon nanotube nanocomposites.* Polymer Engineering and Science. 2008. **48**. p. 149-58.

Schartel. B, Knoll. U, Hartwig. A and Pütz. D: *Phosphonium-modified layered* silicate epoxy resins nanocomposites and their combinations with ATH and organo phosphorus fire retardants. Polymers for Advanced Technologies. 2006. **17**(4): p. 281-293.

Shen. L and Patel M.K: *Life Cycle Assessment of Polysaccharide Materials*: A Review. Journal of Polymers and the Environment. April 2008. **16**(2): p. 154-167.

Tartaglione. G, Tabuani. D, Camino. G and Moisio. M: *PP and PBT composites filled with sepiolite: Morphology and thermal behaviour*. Composite Science and Technology. 2008. **68**. p. 451-460.

Wang. Z, Ciselli. P and Peijs. T: *The extraordinary reinforcing efficiency of singlewalled carbon nanotubes in oriented poly(vinyl alcohol) tapes.* Nanotechnology. 14<sup>th</sup> November 2007. **18**(45): p 455709 (9pp).

Wang. W, Ciselli. P, Kuznetsov. E, Peijs. T and Barber. A.H: *Effective reinforcement in carbon nanotube-polymer composites*. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences. 13<sup>th</sup> May 2008. **366**(1870): p. 1613-1626.

Xia. H.S, Wang. Q and Qiu. G.H: *Polymer-Encapsulated Carbon Nanotubes Prepared through Ultrasonically Initiated In Situ Emulsion Polymerization*. Chemistry of Materials. 2003. **15**(20): p. 3879-3886. Zhan. J, Song. L, Nie. S and Hu. Y: *Combustion properties and thermal degradation behavior of polylactide with an effective intumescent flame retardant*. Polymer Degradation and Stability. March 2009. **94**(3): p. 291-296.

Zhu. J, Morgan. A.B, Lamelas. F.J and Wilkie. C. A: *Fire Properties of Polystyrene-Clay Nanocomposites*. Chemistry of Materials. 2001. **13**(10): p. 3774-3780.

Zhang. J, Hereid. J, Hagen. M, Bakirtzis. D, Delichatsios. M.A, Fina. A, Castrovinci. A, Camino. G, Samyn. F and Bourbigot. S: *Effects of nanoclay and fire retardants on fire retardancy of a polymer blend of EVA and LDPE*. Fire Safety Journal. May 2009. **44**(4): p. 504-513.

Zhang. S and Horrocks. A.R: *A review of flame retardant polypropylene fibres*. Progress in Polymer Science. 2003. **28**: p. 1517-1538.

Zhang. W, Shen. L, Phang. I and Liu. T: *Carbon Nanotubes Reinforced Nylon-6 Composite Prepared by Simple Melt-Compounding*. Macromolecules. 2004. **37**: p. 256-259.

# 8

# Predicting the Performance of an Optimised Bio-based Composite in the Single Burning Item Test

#### 8.1 Introduction

The purpose of this chapter is to demonstrate the commercial potential of the natural fibre composites which have been developed throughout this thesis. The optimised PLA composite will be simulated in a large scale test setup. As mentioned before, untamed fire can be an unwanted type of combustion. Therefore a prerequisite of early commercialising of a product is to carry out full-scale fire testing. However, this is a costly and time consuming technique. Especially in the field of nanomaterials, manufacturing and testing a several meter panel can be impracticable especially for academic institutions. For this reason, computer modelling can be very helpful to demonstrate a materials performance when placed in a real life scenario where a fire can be a threat. There are many fire models available on the market. All of them have their own special features, such as: predicting flame spread, smoke progression and calculating egress time. The objective of this chapter is to give a brief overview into the field of fire modelling and use a specific software package to predict a materials performance during the single burning item test (SBI).

## 8.2 The Construction Product Directive and Euroclass Classification

The choice of material for walls and ceilings can significantly affect the spread of fire and its rate of growth, even though they are not likely to be the materials first ignited. The specification of linings is particularly important in circulation spaces where surfaces may offer the main means by which fire spreads and where rapid spread is most likely to prevent occupants from escaping. Two properties of lining materials that influence fire spread are the ignitability (the energy needed for ignition) and the energy production when burning. The European construction products directive, CPD, is aiming at removing barriers of trade for construction products between member states of the European Union and those countries outside of the EU having an agreement with EU to use the CPD, for example Norway (CPD 89/106/EEC 1988).

The European Classification Systems (Euroclass), devised for the classification of reaction to fire, is part of the ongoing harmonisation of European standards. Similarly to the adoption of European fire resistance test standards, the schedule for use of the Euroclass system as a basis for assessing the suitability of a product for a particular end use is dependent on the national building regulations. The background of the harmonisation process lies on the Commission Decision 94/611/EC implementing Article 20 of Directive 89/106/EEC on construction products in the field of fire safety which was amended in 2003. The Euroclass decision includes a classification system for building products based on their reaction to fire performance. It additionally defines the test methods according to which construction products shall be categorised. In the Euroclass system, floor coverings and other surface linings are considered separately. Reaction to fire has traditionally been assessed using at least 30 different national standards across Europe. This system also includes new tests designed to better evaluate the reaction of building products to fire.

These methods are the cone calorimeter test (ISO 5660-1:1993, ISO/DIS 5660-2:1999), the Single Burning Item test - or SBI for short (EN 13823:2002), and the room corner test (ISO 9705:1993). All methods are based on the same principles for measurement of rate of heat release and rate of smoke production. These three methods represent three levels of scale. The cone calorimeter method is a small-scale fire test where the test sample has an area of  $0.01 \text{ m}^2$ , the SBI test is an intermediatescale test with an exposed area of  $2.25 \text{ m}^2$ , while the room corner test is in large scale, where  $32 \text{ m}^2$  of the product is tested.

#### **8.3 Fire Modelling**

Nowadays, when one speaks of a fire model, it is usually understood that one is referring to a computer fire model. By now, fire modelling has been in use for more than two decades. The computer program COMPF was released by Babrauskas in 1975 and was the first computer program for predicting room fires to be developed in the U.S. Since the last three decades, tremendous progress has been made in the field. Today, many who have only a limited knowledge of fire science have already had a slight exposure to fire modelling.

#### 8.3.1 Mathematical Models

A model fire model can be accomplished through the use of experimental or mathematical techniques. Experimental methods include such methods as reduced and full-scale replicas of the situation or phenomenon being studied. These models come from various countries. Some deal with a single vented compartment (Kerrison *et al.*, 1998), the others treat multiple interconnected compartments (Shigunov, 2005). Two models emphasize post flashover; the others generally present the history of the fire both before and after flashover (Cadorin and Franssen, 2003). In all cases, the user must be able to input a good deal of information about the heat release rate of the fire.

#### 8.3.2 Zone Models and Field Models

Mathematical methods are commonly divided into two groups: stochastic and deterministic models.

#### 8.3.2.1 Stochastic Model

Stochastic models, also referred to as probabilistic models, treat fire growth as a sequence of events or steps. These events have a given probability of occurring, hence the term probabilistic model. The events, coupled with their probabilities, are used to predict the progress of a fire within a compartment or building. Since these models are based on a probabilistic approach to the fire problem, they typically fail to make use of known physical and chemical equations that can mathematically describe the progress of fire development. One example of a stochastic or probabilistic model is the Building Fire Model developed by Fizgerald (1982); another is the Building Fire Simulation Model (BFSM) maintained by the National Fire Association.

#### 8.3.2.2 Deterministic Models

Deterministic models predict fire development based on the solution of mathematical equations that describe the physical and chemical behaviour of fire. The probability of an event occurring is not an integral part of the approach. Most of the compartment fire models available today are deterministic. There are two types of deterministic compartment fire models: field and zone models.

#### 8.3.2.3 Field Model

Field models, as applied to compartment fire modelling, are those models that are based on an approach that divides an enclosure into a large number of elemental volumes. The model then solves the fundamental equations governing the transfer of mass, momentum and energy between these small volumes to predict the progress of a fire within the enclosure. Field models are also referred to as computational fluid dynamics (CFD) models, because they are extensions of computer codes that were originally developed to solve complex fluid flow problems. This type of modelling can be considered as a micro approach to the fire modelling problem. Field models are currently not considered for widespread use. This is primary due to the extensive computer requirements that are not generally available. Also, a more detailed understanding of the fundamental physical phenomena, such as turbulence, combustion kinetics and chemistry, etc are needed. As affordable personnel computing processing power continues to increase, it is expected that field modelling will gradually become the preferred approach to simulate compartment fires. However, this will take some time, and zone models will remain popular in the fire science and fire protection engineering community for the time being.

#### 8.3.2.4 Zone Model

Zone models predict fire development within an enclosure by solving the conservation of mass, momentum and energy equations for a small number of zones (control volumes). Typically, the enclosure is divided into two distinct zones: an upper hot gas layer and a lower uncontaminated cold gas layer (Figure 8.1). This technique can be considered as a macro approach to the fire-modelling problem. Zone models have been widely accepted and applied due to their relatively simplified approach to the modelling problem, especially when compared to the overwhelming requirements of field models. When properly applied, zone models have proven to be a source of good engineering approximations of fire development within enclosures.

Emmons (1983) stated, "The zone model provides all the accuracy required for engineering decision making". The Harvard Code, FIRST, CFAST and ASET as well as most of the other compartmental fire models available today are zone models.



*Figure 8.1.* Schematic diagram for typical two-zone model. Image from Cadorin and Franssen, 2003.

#### **8.4 Scale of Reaction to Fire Tests**

Experimental techniques used to measure the fire properties of composites range in size from bench top scale apparatus for testing small specimens weighing only a few grams up to full scale tests for large structures. Regardless of scale, it is important that fire reaction tests are performed in conditions that closely replicate the type of fire to which the composite will be exposed to.

The most popular methods for measuring reaction to fire properties are bench scale tests, because these are quick, inexpensive and usually provide consistent, reproducible data. Bench scale tests are often used to screen materials for their flammability and toxic smoke production. A further use of such test is to generate data that can be used to validate models for predicting the behaviour of materials in large scale fires (Babrauskas, 1995). A limitation of many bench scale tests (especially for heat release and smoke density) is that they ignore the effects due to fire growth.

Instead, they are said to relate only to a snapshot of part of the overall fire behaviour of the tested material (Babrauskas and Wickstörm, 1989). Another disadvantage is that it is difficult, if not impossible, to simulate actual fires using bench scale techniques. For example, heat release rate, air movements and the oxygen/fuel ratio that exit in actual fires are often different to those in bench scale fire tests and this can affect substantially the measured reaction to fire properties (Babrauskas, 1991). Another drawback is that the entire sample is often completely consumed whereas in real fires, this may not happen due to the reduced oxygen levels encountered within enclosed and unventilated spaces (Babrauskas, 2000). There are a small number of intermediate scale fire tests that can overcome some of the limitations of bench scale tests. Intermediate scale tests often involve a scale model or part section of a full sized structure, although generally the surface area of the specimen is less than 1-2  $m^2$ .

Such tests are often used to bridge the gap between bench scale and full scale testing, which is expensive. The commonly used intermediate scale tests are single burning item (SBI) test, the furnace test, the U.S Navy quarter scale room fire test and the intermediate scale cone calorimeter.

#### 8.4.1 The Single Burning Item Test (SBI)

The SBI test simulates a practical hazard: a burning waste receptacle (the burning item) in a room corner. It is a relatively new procedure for determining fire reaction and arose as a result of the European Construction Product Directive (CPD), which sought to harmonise test procedures across the European Union. It is envisaged that most construction products, including composite items, will be tested and classed according to the SBI protocol specified in EN 13823 (2002). The SBI procedure was chosen because several fire reaction and resistive properties can be measured in a single test, including the time to ignition, heat release rate, smoke production, flame spread rate and fire growth, under realistic fire conditions. In addition, the generation of flaming droplets and particles during thermal decomposition of the test structure can be evaluated. The SBI apparatus is illustrated in Figure 8.2.

It is an intermediate scale corner fire test consisting of two wall panels made of the test material. One wall is 1.5 m high  $\times$  1 m wide while a second narrower wall is 1.5 m high  $\times$  0.5 m wide. A 0.25 m sided triangular propane gas burner located in the corner generates a heat flux of  $\sim$  50 kW/m<sup>2</sup>, and this is intended to simulate a fire in a waste paper bin. An auxiliary burner is placed 750 mm above the floor in the corner furthest away from the test specimen. The auxiliary burner does not influence the test specimen; it is only used to create a baseline for HRR and smoke production measurements before the start of the actual test. The SBI test is performed inside a fire room that has a fume extraction system in the ceiling.



*Figure 8.2.* (a) Schematic of the single burning item test (b) Photograph of SBI in progress. Images from EN 13823:2002 standards and Exova Warringtonfire, respectively.

The time to ignition and flame spread rate are determined by observing the response of the wall panels to the fire. The heat, smoke and gases released by the burning wall materials are extracted from the room through the exhaust hood in a manner similar to the cone calorimeter. The temperature, air-flow rate, smoke density,  $O_2$  and  $CO_2$ concentrations are measured continuously using sensors inside the exhaust duct. The heat release rate is calculated from the oxygen consumed during burning of the wall materials using the oxygen consumption principle. It is also possible to measure changes to the structural capacity of the wall panels when exposed to fire.

While the SBI procedure offers a credible European alternative to a wide range of nationally based test protocols, a number of drawbacks have been noted; the most significance being the scale of the test, which results in significantly higher costs than many other fire reaction tests such as the cone calorimeter. The other problem arises from the requirement that the specimens be provided in the form of flat sheets. This is appropriate for cladding or panels, but the majority of composite products, including mouldings, pultruded sections and pipes are not available in this form. Interim solutions have involved the making up of flat sections from strips of products but it is probable that an alternative procedure may eventually be needed. Some success has been achieved in predicting product performance in the SBI test from the result of the cone calorimeter.

### 8.5 Prediction of Bio-based Composite Performance in Single Burning Item Performance Using Cone Calorimeter Data

#### 8.5.1 Introduction

The ConeTools program allows the user to predict the SBI test results by means of small scale cone calorimeters test results at one heat flux level. Therefore this model is an excellent tool for product development and quality control.

The ConeTools model by Wickström and Göransson (1992) has been the focus of this chapter, because it has been used for many years in the Nordic countries, and has proven to be both stable and efficient. To extend the applicability of this model would therefore be of great practical interest, both regarding product development and product control. The theory behind the model has later been used to develop a model for predicting heat release rate in the Single Burning Item test (Messerschmidt *et al.*, 1999). Myllymäki and Baroudi (1999) have investigated if the same approach could be used to predict smoke production in large-scale tests, and their conclusions were promising. The materials that were put through the ConeTools software were the optimised polylactide composite that was developed in the previous chapter. Table 8.1 presents the list of materials that were studied.

**Table 8.1.** Cone calorimeter data from the specimens below were put into theConeTools software.

Reference	Material	Thickness (mm)
P1	PLA	5
P2	PLA/Hemp	5
P3	PLA ternary nanocomposite	5
P4	PLA ternary nanocomposite/Hemp	5

#### 8.5.2 The FIGRA Classification

The FIGRA (FIre Growth RAte) parameter, defined as the maximum of heat release rate divided by time, is shown to predict well the tendency to fire growth for a number of different products in different scenarios. The calculation of the FIGRA is described in detail by Van Hees, Sundstörm and Thureson (1999). FIGRA is defined as the growth rate of the burning intensity, HRR, during a test, in this case the SBI. FIGRA is calculated as the maximum value of the function (heat release rate over the elapsed test time with units of W/s as shown in equation 1.

$$FIGRA = 1000 \times \max\left(\frac{RHR_{av}(t)}{t - 300}\right)$$
(1)

In addition, certain threshold values of HRR and the total heat release rate must first be reached before FIGRA is calculated. Threshold values are needed to avoid that very small and early values of HRR are included as this leads to unrealistic FIGRA values. As an example, the green line represents the points at which the FIGRA value is always equal to 250 W/s. If we therefore position a real combustion curve on this graph, we have an immediate graphical display of the class to which the material belongs.



**Figure 8.3.** Graphical representation of lines with a constant FIGRA value of 120,250,750 W/s. Image from Federation of European Rigid Polyurethane Foam Associations report "Figra Report".

As can be seen for the example test in Figure 8.3, this material has a relatively high RHR(t)/t ratio at the start of combustion and the curve is taken to a position in the class E area, therefore determining in which sector the material belongs. The European system for testing and classification of reaction-to-fire properties, also called the system of Euroclasses, has been developed through thorough correlation analyses of data from the room corner test and the SBI test.

Results from the SBI test are used as a base for the classes A, B, C and D, with additional classes  $S_1$ ,  $S_2$  and  $S_3$  for smoke production (EN 13501-1:2002). The FIGRA is seen to be the primary classification parameter for the SBI test. Lateral flame spread and total heat release will be safety net parameters which mean they will only determine the classification for products showing either extreme flame spread or a high heat release rate after the first peak value. The classifications for the products studied in this chapter are shown in Table 8.4.

*Table 8.2.* Classes of reaction to fire performance for construction products excluding floorings. Source Council Directive 89/106/EEC 2000.

Classification	FIGRA [W/s]	THR <sub>600s</sub> [MJ]
A1	$\leq 20^{*}$	4.0
A2/B	$\leq 120^{*}$	7.5
С	$\leq 250^{**}$	15
D	$\leq 750^{**}$	-
E/F	No criterion	No criterion

<sup>\*</sup> For classification A1, A2 and B, FIGRA = FIGRA

\*\* For classification C and D, FIGRA = FIGRA

*Table 8.3.* Some typical classification for some construction products. Source Council Directive 89/106/EEC 2000.

Classification	Products	Performance description
A1	Stone, Concrete	No contribution to fire
A2	Gypsum boards (thin paper),	No contribution to fire
В	Gypsum boards (thick paper), flame retardant wood	Very limited contribution to fire
С	Coverings of gypsum boards	Limited contribution to fire
D	Wood, wood based panels	Acceptable contribution to fire
Е	Some synthetic polymers	Acceptable contribution to fire
F	No performance determined	No performance requirements

#### 8.5.3 The Model

In the ConeTools model, the ignition time as well as the complete heat release curve from the cone calorimeter are used. There are products for which it is not possible to predict their behaviour in large scale based on small scale tests. Examples are products with a protective surface, joints or products that melt. These need to be tested in large scale to get results that can be used for evaluating their potential fire hazards. The calculation model is described below. It solves two equations in order to predict the behaviour in the SBI. These are; the area of fire growth (flame spread) and heat release rate.

Three major assumptions have been made in the prediction model for HRR in the SBI:

- 1. The burning area growth rate and HRR are decoupled.
- 2. The burning area growth rate is proportional to the ease of ignition, i.e. the inverse of the time to ignition in small scale.
- 3. The history of the HRR per unit area at each location in the SBI test is the same as in small scale.



*Figure 8.4.* Suggestion of three different routes for development of the effective heat releasing area in the SBI test. Image from Hansen 2002.

The fire spread can follow two different routes. All products start to spread along route II. A product is assumed to spread along route III if the calculated sustained flame height is at least 1.5 m, which is equal to the height of the test sample. Otherwise the product is assumed to spread route II. Within the different flame spread regimes, the burning area growth rate of a product depends on ignitability, i.e. time to ignition in the cone calorimeter. This ignition time is assumed to be a time equal to half of the ignition time found in the cone calorimeter. The area growth rate is described by the following;

$$A(t) = A_{\max}\left[1 - \left(1 + \frac{t - \frac{t_{ign}}{2}}{t_{ign}}\right) \exp\left(-\frac{t - \frac{t_{ign}}{2}}{t_{ign}}\right)\right]$$
(2)

where  $A_{max}$  is the maximum area involved and  $t_{ign}$  is time to ignition in the cone calorimeter. One the flame spread rate is determined; the HRR is calculated assuming that products always give the same HRR per unit area as a function of time in small scale as in the SBI. All parts of the tested product are assumed to burn in the same way in the SBI as in the cone. However, this is an over simplification. The HRR depends more or less on the actual heat flux level received by the product as a function of time.

The heat release from the SBI test is obtained by summing up the contributions from each of the total burning area and the burner

$$\dot{Q}_{total} = \dot{Q}_{product} + \dot{Q}_{burner}$$
(3)

where  $\dot{Q}_{burner}$  is constant at 30 kW while  $\dot{Q}_{product}$  varies with time as the fire spreads, the involved area A(t) increases as described above and the burning intensity at each position is time dependant.  $\dot{Q}_{product}$  is obtained by adding the contributions from burning parts which have started to burn at various times. The HRR of the specimen at each location is then assumed to go through the same history as was measured in the cone calorimeter.  $\dot{Q}_{product}$  is calculated using the Duhamel's integral

$$\dot{Q}_{product} = \int_0^t \dot{A}(\tau) \dot{q}''_{bs} (t-\tau) d\tau \qquad (4)$$

where  $\dot{A}$  is the time derivation of the burning area, t is the time,  $\dot{q''}_{bs}$  is the heat release per unit area as recorded in the cone calorimeter and  $\tau$  is a dummy variable. The following very simple numerical solution to the Duhamel's integral is the approach used in this model

$$\dot{Q}_{product} = \sum \Delta A_i \, \dot{q}^{\prime \prime}_{bs}^{N-i} \tag{5}$$

Where  $\Delta A_i$  is the incremental burning area growth at the time increment *i*, and  $q''_{bs}$  is the HRR per unit area after (*N*-*i*) time increments as recorded in the cone calorimeter. The model has been developed to be used with the cone calorimeter at a heat flux level of 50 kW/m<sup>2</sup>. To be able to use the model with the cone calorimeter, a correction was introduced for both ignition time and the HRR level. The correction is based mainly on fine tuning the results

$$t_{ignCorr} = t_{ignCone}(ConeFlux/SBIFlux)$$
  
HRR<sub>Corr</sub>=HRR<sub>Cone</sub>(SBIFlux/ConeFlux)<sup>0.5</sup>

Where  $t_{ignCorr}$  is the corrected ignition time used in the model,  $t_{ignCone}$  the ignition time in the cone calorimeter test, HRR<sub>Corr</sub> the corrected HRR, HRR<sub>Cone</sub> the HRR in the cone calorimeter test and SBIFlux the corresponding reference flux for the cone SBI model being 40 kW/m<sup>2</sup>.

#### 8.6 Results from the ConeTools Software Package

The main input parameters to the model are the ignition time and the complete heat release rate curve both from the cone calorimeter test. The HRR curve is automatically registered by the computer attached to the cone calorimeter but the ignition time is visually observed during the experiment. A screen capture is presented in Figure 8.5. The classification for the bio-based composite is presented in Table 8.6. All of the products gained a class D performance. Which states that the product did not exceed a FIGRA value of 750 W/s. This classification is indicative of wood base products with a thickness  $\geq 5$  mm tested in Euroclasses. This is reasonable due to the cellulose content being present in the form of hemp fibre.



*Figure 8.5. Screen shot of ConeTools input and data generation screen. Image courtesy of Interscience Communications.* 

Reference	FIGRA [W/s]	Euroclass
P1	539	D
P2	579	D
Р3	429	D
P4	504	D

Table 8.4. Simulated FIGRA and SBI classification results from ConeTools software.

(P1-PLA) (P2-PLA/Hemp) (P3-PLA ternary nano) (P4- PLA ternary nano/hemp).

As mentioned before, the main parameter used for the SBI classification is the FIGRA parameter. This is the main classification parameter which is summarised as the maximum value of 30 second averaged heat release rate dived by time. The calculation for the FIGRA index is described in detail in the SBI standard EN 13823. In Table 8.6, results are given for the FIGRA value and Euroclass, which was generated from the ConeTools software. The advantage of this predictive software is the use of only one heat flux level (50 kW/m<sup>2</sup>). All of the PLA specimens achieved a Euroclass D classification. This is common for wood/cellulose based products. Table 8.6 shows that P2 has the highest FIGRA value. These coinsides well with the cone calorimeter data. P3 has the lowest, which is thought to be due to the CNT and sepiolite nanoclays protecting the specimen thus reducing the HRR. It can be also seen that the addition of the hemp fibre mat plies results in detrimental fire behaviour which shows similar behaviour in the cone calorimeter. P1 has the third highest FIGRA value but was expected to have the largest due to being a pure polymer. However, the PLA (P1) melts and creates a pool before igniting and releasing its maximum heat release. This will affect the FIGRA as ignition times are used for calculation. However, there are two important differences between the cone calorimeter and the SBI test that affects all modelling attempts. Firstly, the heat exposure in the cone calorimeter is radiative and well defined whereas the SBI includes flame impingement producing a non-constant exposure on the specimen surface, leading to different behaviour.

Secondly, physical effects in the SBI test (edges, joints, bending, collapsing etc) are not observed in the cone calorimeter. Therefore, a model based on the cone calorimeter test results cannot simulate all the features of the SBI test. The essential feature of both models is that only a single cone calorimeter test at a single heat exposure level is required as an input without any additional data or material parameters. Thus the model provides a practical and economical tool for product development and quality control.

#### 8.7 Conclusions

The main objective of this chapter was to evaluate the optimised bio-based composite for real life applications. To achieve this, the product must pass strict fire testing procedures and guidelines in order to be granted permission to allow the manufacturer of the product to release it into the public domain. The main issue with this is the scale at which testing must be conducted. This is especially problematic for academic intuitions. A possible solution for this is to use fire modelling to predict the behaviour of the product in a real life scenario. This chapter also served as a brief introduction into fire modelling. A number of applications ranging from very complex models such as CFD to screening models are available for prediction of test methods such as the SBI method used for the Euroclasses. In the past many of these models for prediction of test methods were only useful for those who had developed the method but the recently developed ConeTools software can also be used by industry and researchers. Limitations such as the fact that cone calorimeter uses small samples need to be considered but the cost reduction factor and the wide availability of the cone calorimeter should be taken into account. No other screening tests need to be developed at the moment since they will have at least the same limitations if not more. The products here gained a Class D performance, however, the performance on these materials in the SBI are all speculative. For e.g. P1 which is the unfilled PLA had a FIGRA value of 539 W/s.

Therefore, one would imagine that if a specimen of  $1.5 \times 1$  m was heated, then it would then rapidly melt and thus affect the FIGRA value. So to fully assess the behaviour of these materials in the SBI, the material of interest would have to be tested in the practical sense.

#### 8.8 References

Babrauskas. V: Fire *test methods for evaluation of fire retardant efficacy in polymeric materials*. In: Fire Retardancy of Polymeric Materials, ed. A.F. Grand and C.A. Wilkie, New York: Marcel Dekker, Inc, 2000, p. 81-113.

Babrauskas. V: *COMPF: A Program for Calculating Post-flashover Fire Temperatures* (UCB FRG 75-2). Fire Research Group, University of California, Berkeley (1975).

Babrauskas. V. Designing products for fire performance: the state of the art of test methods and fire models. Fire Safety Journal. 1995, **24**: p. 299-312.

Babrauskas. V and Wickstörm. U: *The rational development of bench scale fire test for full scale fire predictions*. In: Proceedings of the 2<sup>nd</sup> International Fire Safety Science Symposium. 1989, p. 813-822.

Babrauskas. V: *Effective measurement techniques for heat, smoke and toxic fire gases*. Fire Safety Journal. 1991. **17**: p. 13-26.

Cadorin. J.F and Franssen. J.M: A tool to design steel elements submitted to compartment fires-Ozone V2. Part 1: pre and post flashover compartment fire model. Fire Safety Journal. 2003. **38** n 5, p. 395-427.

Emmons. H.W: *The Calculation of a Fire in a Large Building*. Journal of Heat Transfer. 1981. **105**: p. 151-158.

FIGRA project: Fire grow evaluation, FIGRA. February 2005. http://www.pu-europe.eu. Fizgerald. R.W: *The Anatomy of Building Fire safety*. Worcester Polytechnic Institute, Worcester, MA, 1982.

Hansen. A.S: *Prediction of Heat Release in the Single Burning Item Test*. Fire and Materials. 2002. **26**: p. 87-97

Kerrison. L, Galea. E. R, Patel. M. K: A two-dimensional numerical investigation of the oscillatory flow behaviour in rectangular fire compartments with a single horizontal ceiling vent. Fire Safety Journal. 15<sup>th</sup> June 1998. **30**(4): p. 357-382.

Messerschmidt. B, Van Hees. P and Wickström U: *Prediction of SBI (Single Burning Item) test results by means of Cone Calorimeter test results.* Conference Proceedings, Volume 1, Interflam 99, 8<sup>th</sup> International Fire Science & Engineering Conference, Edinburgh, Scotland, 29<sup>th</sup> June - 1<sup>st</sup> July 1999. p. 11-22.

Myllymäki. J and Baroudi. D: *Prediction of smoke production and heat release by convolution model*. NORDTEST Technical report 389. Espoo, Finland (1999).

SBI: European Standard - Reaction to fire tests for building products - Building products excluding floorings exposed to the thermal attack by a single burning item. EN 13823:2002.CEN Central Secretariat, Brussels 2002.

Shigunov. V: A zone model for fire development in multiple connected compartments. Fire Safety Journal. September 2005. **40**(6): p. 555-578.

Van Hees. P, Sundström. B and Thureson. P: *Testing and classification of wall and ceiling linings in a harmonised European system*. Fire and Materials Conference proceedings, San Antonio, USA, February 1999.

Wickström. U and Göransson. U: *Full-scale/Bench-scale Correlations of Wall and Ceiling Linings*. Fire and Materials. 1992. **16**: p. 15-22.
## 9

## **Summary and Future Work**

## 9.1 Summary

Because of their eco-friendly character natural fibre reinforced plastics have caught the attention of many. However, similar to the performance of their synthetic counterparts, natural fibre composites are susceptible to fire thus limiting their usage. Over the last few decades, carbon nanotubes and nanoclays have generated enormous interest by academia as well as industry. Owing to their unique intrinsic properties, these materials have potential applications in numerous fields. The work carried out in this thesis focuses on the use of nanofillers in combination with natural fibre composites. The objective of this thesis is to systematically develop and characterise flame retardant bio-based polymer composites, using nanofillers as flame retardants. The advantage of using these fillers over traditional micron sized ones is that much smaller filler loading levels are required for similar flame retardancy effects, resulting in reduced overall polymer density while simultaneously solving the issue of embrittlement. Recycling of the final composite will also be easier due to the filler not being a major constituent of the composite in addition to the polymer matrix and reinforcing fibre having the ability to decompose after their service life. In this thesis, the aspects mentioned above have been undertaken. The work carried out in **Chapter 3** describes a feasibility study to assess the potential application of natural fibre reinforced sheet moulding compound materials (NF-SMC) for the use in building applications, with particular emphases to their reaction to fire. The reinforcing fibres in this study were industrial hemp fibre mats. The cone calorimeter which asses the fire hazard of materials by heat release rate (HRR) was used, radiant heat fluxes of 25 and 50 kW/m<sup>2</sup> were utilised to simulate an ignition source and developing room fire conditions, respectively. The results acquired here demonstrate that the NF-SMC can compete with current building materials in terms of their fire behaviour. The peak heat release rate for the fire retardant (FR) NF-SMC was 176 kW/m<sup>2</sup> compared to a non-FR NF-SMC of 361 kW/m<sup>2</sup>. This work was important with respect to setting a good foundation for the continuing development of natural fibre composite.

The purpose of **Chapter 4** was to observe any further possible flame retardant improvements to the unsaturated polyester (UP) resin from the previous Chapter using "greener" non-toxic flame retardants. The use of aluminum trihydroxide (ATH) in combination with ammonium polyphosphate (APP) was expected to impart an improved flame retardant effect in the UP system. Thermal gravimetric analysis showed an improved thermal stability between 200-600 °C with the addition of ATH and APP formulation. A combination of both FR's showed an improved ignition delay time as well as a decrease in the peak heat release rate and carbon monoxide yield. However, synergistic behaviour was not witnessed but instead a mere fuel replacement effect on the role of the micron sized fillers is more plausible. In general, synergism can be defined as two or more components working together to produce a result not obtainable by any of the components independently. The polymer used plays an important part in the effectiveness of these two FR fillers and their combination does not work with all polymers as shown in the literature.

The additional reduction in the PHRR with the addition of APP does not justify its use due to the resultant difficulties with increased viscosity, which will result in major processing difficulties in adopting these materials in potential fibre reinforced composites.

In Chapter 5, conventional flame retardant fillers were replaced with multiwalled carbon nanotubes (MWNTs) and sepiolite nanoclays (Sep). The synergistic effect on thermal decomposition and HRR in particular the PHRR of unsaturated polyester resin were investigated using; thermal gravimetric analysis (TGA), pyrolysis combustion flow calorimetery (PCFC) also known as microcalorimetry and also the cone calorimetery. Initial microcalorimeter findings confirmed a synergistic effect for a ternary system comprising of a 10:0.5 wt.% mixture of sepiolite:MWNT respectively, which resulted in a 40 % reduction in PHRR. This result was also confirmed within the better established cone calorimeter by a 50 % reduction in PHRR in contrast to unfilled UP. The most important benefit of the ternary system is that it reduces the PHRR, which is the most critical fire hazard, by a synergistic reaction involving the formation of a stable residual char. The mechanism behind this reduction is thought to be due to the bridging of the MWNTs between the sepiolite clay needles, creating a tight protective surface layer. This char formation reduces the amount of small volatile polymer pyrolysis fragments - or fuel - available for flame. This in turn reduces the amount of heat released and feed back into the polymer surface. The char also insulates the underlying polymer, due to its low thermal conductivity, and reradiates externally impinging energy away from the polymer. The char also functions as a mass transport barrier by physically delaying the volatilisation of decomposition products and or trapping decomposition products through chemical reaction. TGA also confirmed the advantage of such a ternary system through a 36 °C shift in the onset decomposition temperature and an 11 % increase in residual char.

However, even though achieving a flame retardancy is one of the objectives of this thesis, another is it to develop a system with better recyclability. For this a move away from a thermoset to a thermoplastic system is essential. Chapter 6 reports on the testing and development of a polypropylene (PP) nanocomposite. The work utilises the unique properties of sepiolite in combination with MWNTs to develop an optimised ternary nanocomposite system were the HRR was significantly reduced by 82 % compared to the neat polymer in the cone calorimeter. Initial screening tests involved TGA and microcalorimetry but caution must be adopted when interpreting results gained from these tests. Specimen sizes of a few milligrams can cause issues due to unrealistic behaviour when compared to identical materials tested on a larger scale in a cone calorimeter. Testing in the microcalorimeter can limit the behaviour of the material due to its small size and arbitrary shape, whereas specimen dimensions are standardised when testing in the cone calorimeter. In the cone calorimeter a much larger surface area is available for the flame retarding mechanisms to take full effect compared to the microcalorimeter. Another possible concern is the testing environment in the microcalorimeter as these tests are conducted in an enclosed system with controlled gas flows. Anaerobic environments have shown to hinder the flame retarding effect of materials, especially the char formation as part of the flame retarding mechanism. The cone calorimeter on the other hand is an open apparatus which resembles more real life scenarios.

Finally, with respects to materials development, the objective of **Chapter 7** was to develop a fully bio-based polylactic acid (PLA) composite using the technology gained from the previous chapters. Achieving this target was accomplished by using a PLA polymer derived from crops together with two nanofillers to create synergy with respects to flame retardancy. The microcalorimeter was utilised to screen nanocomposite formulations for their suitability for further development. Carrying across the data from the microcalorimeter and TGA to full composite production indicated promising results. A feature which was not expected was the reduction of PHRR in the cone calorimeter after the introduction of hemp fibre mats into the PLA resin, which acted in its self as a flame retardant.

The ternary nanocomposite based on sepiolite and MWNTs showed the best performance with a 58 % drop in PHRR. However this was reduced by the introduction of the non-woven hemp fibre mats to only a 45 % drop. Due to the thick layered structure the composites delaminated during the cone calorimeter testing thus exposing the underlying material.

The main objective of the final Chapter was to evaluate the optimised bio-based PLA composite for commercialisation and real life applications. To achieve this, the product must pass strict fire testing procedures and guidelines in order to be granted permission to allow the manufacturer of the product to release it into the public domain. The main issue with this is the scale at which testing must be conducted. This is especially problematic for academic intuitions. A possible solution for this is to use fire modelling to predict the behaviour of the product in a real life scenario. The ConeTools software package was used to predict the behaviour of the material in a single burning item test (SBI), which is a standardised test for assessing a products contribution to flame spread, which is to be used by the construction industry. The products here gained a Class D performance, which is common for cellulose based products, however, the performance on these materials in the SBI are all speculative. For e.g. P1 which is the unfilled PLA had a FIGRA value of 539 W/s. Therefore, one would imagine that if an unfilled thermoplastic specimen of  $1.5 \times 1$  m was heated, then it would rapidly melt and thus affect the FIGRA value. So to fully assess the behaviour of these materials in the SBI, the material of interest would have to be tested in the practical sense.

## 9.2 Future Work

The development of a fully bio-based natural fibre composite was accomplished by using polylactic acid (PLA) as the matrix and hemp mats as the reinforcement. Nanofillers helped to achieve the required flame retardancy. However, as seen in Chapter 7, the hemp mats cause a lofting issue in which the specimen delaminates during cone calorimetry testing. This causes the heat release rate to rise due to more

unburnt material being presented as fuel. Therefore, to further develop this composite, chopped hemp fibre should be used in a compound which would alleviate this issue. Although, the developed composites have improved flame retardancy in comparison to its pure polymer, the mechanical properties are unknown. Therefore a range of mechanical tests would be required before possible commercialisation can take place.