Formulation and Burning Behaviour of Fire Retardant Polyisoprene Rubbers

by

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Student Declaration

I declare that while registered as a candidate for the research degree, I have not been a registered candidate or enrolled student for another award of the University or other academic or professional institution.

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Name of School Centre of Fire and Hazards Science in the School of Forensic and Investigative Sciences.

Abstract

This research aimed to develop new fire retardant rubber formulations, by surveying the existing knowledge base for fire retardant approaches for polyisoprene rubber, characterising unmodified compounds, formulating and studying fire retarded compounds for use within suspension and anti-vibration mounting systems. Materials have been prepared on a bench scale and evaluated for physical properties. Thermal decomposition has been studied using Thermogravimetric Analysis (TGA) in both air and nitrogen. Burning behaviour has been studied using a horizontal burning rate method, Limiting Oxygen Index (LOI) and the cone calorimeter.

Basic rubber mixtures were prepared to investigate the interactions between the polymer and additives, under TGA conditions. Zinc oxide was found to have little effect on the polymer decomposition, while silica reduced thermal stability. When decomposed in air, increasing levels of carbon black reduce the rate of mass loss in the polymer. Comparing formulations with different cross-linking types, sulphur without cross-linking increases the heat release in a cone calorimeter; but when low levels of sulphur form efficient cross-links, heat release is suppressed, as also occurs with organic peroxide cross-linking.

The effect of carbon black on burning behaviour was compared with inorganic fillers. Within the cone calorimeter, material containing carbon black formed a char-like residue which provides some reduction in the rate heat release, and did not contribute to the fuel load. The use of inorganic fillers yielded more rapid burning behaviour. Any level of carbon black addition gives a reduction in the rates of heat, smoke, CO, and CO_2 release, confirming that carbon black had a stabilising effect.

Intumescent formulations were prepared using ammonium polyphosphate (APP), pentaerythritol and melamine, and separately using expandable graphite (EG). Within the cone calorimeter both systems yielded a significant reduction in the first peak of heat release rate, but a much higher second peak than for the unmodified compound. This second peak value is associated with the significant levels of intumescence observed. The use of EG gave a greater level of fire retardance compared to the APP formulation.

Hydrated fillers, and blends thereof, were investigated; an equal blend of aluminium hydroxide (ATH) and magnesium hydroxide (MH) was found to yield the lowest peak release rate on the cone calorimeter. Hydrated fillers were investigated with synergists proposed in the literature. Little benefit was noted for these additives when used as partial replacements for the filler.

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List of abbreviations

ACN	polyacrylonitrile
AEM (EAM)	ethylene-acrylic rubber
AVS	anti-vibration system(s)
APP	ammonium polyphosphate
ATH	aluminium hydroxide, aluminium trihydrate
BIIR	brominated isobutene-isoprene rubber
BR	polybutadiene
CIIR	chlorinated isobutene-isoprene rubber
CO	carbon monoxide
CO	polyepichlorohydrin
CO2	carbon dioxide
CR	polychloroprene
CSM	chlorosulphonated polyethylene
DBDPO	decabromodiphenyl oxide
DCP	dicyclopentadiene
DPNR	de-proteinised natural rubber
ECO	polyepichlorohydrin ethylene oxide copolymer
EG / EXG	expandable graphite
ENB	ethylene norbornene
ENR	epoxidised natural rubber
EPDM	ethylene propylene diene modified rubber
EPM	ethylene propylene rubber
EV	Efficient Vulcanisation cross-linking
EVA	ethyl vinyl acetate
FAA	Federal Aviation Administration
FKM	fluorocarbon rubber
FR	Flame/fire Retardant
FTIR	Fourier Transform Infra-red Spectroscopy
FTP	Fire Test Procedures
HB	Horizontal Burn
HNBR	hydrogenated acrylonitrile-butadiene rubber
HRR	Heat Release Rate
IIR	isobutene-isoprene (butyl) rubber
IMO	International Maritime Organisation
IR	synthetic polyisoprene rubber
IRHD	International Rubber Hardness Degree
KTN	Knowledge Transfer Network
LOI	Limiting Oxygen Index
MARHE	Maximum average rate of heat emission
MC	Melamine Cyanurate
MWNT	multi-wall carbon nanotubes
NBR	acrylonitrile-butadiene (nitrile) rubber
NBS	National Bureau of Standards (Now NIST, National Institute of Standards & Technology)
NMR	Nuclear Magnetic Resonance
NR	Natural Polyisoprene Rubber

NR	natural rubber
OH	Oxygen / Hydrogen functional group
PIN	Polymer Innovation Network
PMDI	Polymeric diisocyanate diphenylmethane
PNR (NOR)	polynorbornene
PPHR	parts per hundred rubber
PU	polyurethane
PVC	poly vinyl chloride
Q - MQ, VMQ, PMQ	silicone rubber
RHR	Rate of Heat Release
RTV	Room Temperature Vulcanisate
SBR	styrene butadiene rubber
SWNT	single-wall carbon nanotubes
VMQ	silicone rubber
ZB	zinc borate

CHAPTER 1. INTRODUCTION

The aim of this research is to develop polyisoprene formulations which impart fire safety to rubber anti-vibration and suspension mounts. This will be achieved by meeting the following objectives:

1 Survey the existing knowledge of the thermal decomposition and fire retardance of rubber based systems.

2 Investigate practically the thermal decomposition and burning behaviour of rubbers, and identify the relationships between them.

3 Study the physical properties, thermal decomposition and fire performance of formulations containing fire retardants.

The project was based at Trelleborg Industrial AVS in conjunction with the University of Central Lancashire. The purpose of the introduction is to familiarise the reader with a range of topics relevant to this research programme.

1.1 Background

Trelleborg is an international manufacturing company founded in 1905. The core business is the manufacture of polymeric products, with sales of approximately £2.6 billion and around 25,000 employees in 40 countries. Trelleborg Industrial Anti-vibration Systems (TIAVS) is a business unit within Trelleborg Engineered Systems, and designs and manufactures rubber-to-metal bonded engineering products, anti-vibration mountings and suspension components for rail, marine, off-highway, industrial, defence and power generation applications. TIAVS was formed in the year 2000, but has existed since 1906 known as the Leicester Rubber Company, the John Bull Rubber Company, Dunlop, Polymer Engineering Division and Metalastik until being acquired by Trelleborg. This results in a unique legacy of many original designs in the area of rubber to metal bonded products, especially in the area of Rail and Marine anti-vibration and suspension applications, examples in Figure 1. TIAVS manufacture anti-vibration products predominantly in polyisoprene rubber compounds, chosen because they result in a product with high elasticity and low damping to give a high level of vibration isolation and ride comfort. Around 20% on the products manufactured by TIAVS are for rail vehicles, many of which are applied in metro and underground systems (Figure 2), where the demand for products with enhanced fire retardance has risen in recent years.

Primary suspension & traction control

Engine mounting

Secondary suspension

Figure 1 Typical rubber to metal bonded rail mountings

Figure 2 Jubilee line bogie using TIAVS rubber suspension

The fire load (combustible matter) associated with 5-20 kg rubber per spring is a concern to rolling stock manufacturers and train operators. As a result Trelleborg Industrial AVS made a strategic decision to start material development with the following objectives: To better understand customers needs and the wide range of fire standards in use; to test present materials; and to develop materials with an improved level of fire resistance with low toxic emissions and low smoke density, but with no loss of physical properties. Following a successful KTN SPARK award in conjunction with the University of Bolton to evaluate a fire retardant flexible coating for rubber systems [1], a decision was made to commence a combined programme of industrial and academic research into fire retardant rubber. This PhD, with the Centre for Fire and Hazard Science at the University of Central Lancashire, was undertaken to meet these objectives.

1.2 Polymers

Organic polymers comprise a significant part of our normal environment, and fuel the majority of unwanted fires.

1.2.1 Types of Polymer

A polymer may be defined as “a large molecule built up by repetition of small, simple chemical units” [2]. They may be classified in a number of different ways. Polymerisation processes can be divided into two techniques; [3] condensation polymerisation is a reaction between two bi-functional molecules resulting in a larger molecule, often with the elimination of a small molecule such as water; and addition polymerisation, often initiated and propagated by a free radical, regenerated during the process.

In practical terms, polymers in commercial usage in areas related to this project are often placed into one of four categories: thermoplastics, thermosetting resins, vulcanised elastomers and thermoplastic elastomers [4]. Thermoplastics, consisting of reversibly entangled macromolecules, may be highly branched or linear, and may be highly amorphous, as in the case of polystyrene (PS); or achieve a high level of crystallisation, as with high density polyethylene (HDPE). They are often supplied as granules, which melt upon heating so they can be formed in articles by moulding or extrusion, and solidify on cooling. This process can be repeated which allows re-processing and recycling of post-consumer waste.

Thermosetting resins, such as phenolic formaldehyde, undergo irreversible chemical change upon heating to form highly cross-linked products, and do not melt or soften upon further heating. They tend to have a higher resistance to temperature and burning. Polyesters and polyurethanes are groups which include both thermoplastic and thermosetting polymers, but the latter are often processed starting with liquid pre-polymers and may be cast or moulded into products.

Rubbers are divided into thermoplastic and thermosetting types. Traditional thermosetting rubbers still account for the majority of rubber used world-wide, since they still have superior physical properties at a low cost, produced from elastomers and various functional additives, which are lightly cross-linked by heating.

Thermoplastic elastomers (TPE) are typically block copolymers that possess elastic properties, but within a narrower temperature range than vulcanised rubbers. The original TPEs were developed using a block copolymer consisting of styrene (S) and butadiene (B), with the structure S-B-S. This created a material with predominantly elastic behaviour at room temperature (due to the butadiene), and thermoplastic behaviour when heated (due to the styrene content) [5].

1.2.2 Elastomers and additives

1.2.3 Polymer classification and nomenclature

This section reviews some commonly used and speciality elastomers which have a commonality of being linear, predominantly amorphous, polymers which require cross-linking. Other materials which can exhibit rubbery behaviour such as ethylene vinyl acetate (EVA), plasticised polyvinyl chloride (PVC), polyurethanes and thermoplastic elastomers are less commonly used in ‘conventional’ rubber technology and are therefore not covered in this review. To clarify the terminology for these materials, an elastomer is an elastic polymer (raw and unmodified), and rubber generally refers to a cross-linked compound comprising elastomer and additives.

A common set of categories and abbreviations for elastomers are given in ISO 1629 [6] and ASTM D1418 [7], based on the same principles with some minor differences in nomenclature. The latter standard is used for this work. The chemical structures, common chemical names, abbreviations, key properties and main application areas of some elastomers are summarised in Table 1 .Within these standards the abbreviations are categorised based on common chemical features denoted by a letter, the more commonly used groups R, M, O and Q discussed below.

‘R’ group elastomers

The ‘R’ group defines rubbers having an unsaturated carbon chain based on conjugated dienes, encompassing the traditional elastomers which are still the highest volumes used. Polyisoprene was the world’s first commercially produced elastomer, normally derived from the latex of the rubber tree Hevea Brasilienis, and a synthetic version was developed on an industrial scale during the Second World War. Polyisoprene compounds, whether natural (NR) or synthetic (IR), are economical and have a combination of suitable physical properties, which includes a low dynamic response, low hysteresis and high levels of durability, and are often used within transportation applications [8]. In addition NR latex is used in prophylactic products such as condoms and surgical gloves, but has some residual protein which has been associated with allergic reactions, so de-proteinised natural rubber (DPNR) may be preferred. Natural rubber can also be chemically modified, an example being epoxidized natural rubber (ENR), produced in grades at 25% (ENR25) and 50% epoxidization (ENR50), with higher damping and a moderately improved oil resistance compared to NR. ENR is less flammable than polyisoprene and its decomposition has a higher activation energy, which is suggested to be due to greater thermal stability of the combined C-C-O bonds than the C=C bonds [9].

Polybutadiene (BR) is a high resilience elastomer with very low damping and the lowest glass transition temperature of the hydrocarbon rubbers. It is often blended with styrene butadiene rubber (SBR) in the use of tyre tread, and confers improved wear resistance and wet grip. SBR, with around 25% styrene, is most commonly used in car tyres due to a combination of wear resistance, economy and grip. When used in conveyor belting and carpet backing applications, fire retardant SBR formulations are often required.

Acrylonitrile butadiene rubber (‘nitrile’, NBR) is a copolymer produced by emulsion polymerisation, with polyacrylonitrile (ACN) typically present at levels of 18-50%. Higher levels of ACN give increasing levels of oil resistance but decreasing low-temperature flexibility [10]. Variations of NBR are available – blends of PVC with NBR give improved ozone resistance and reduced flammability, whilst hydrogenated nitrile (HNBR) with a fully saturated backbone chain imparts improved heat resistance.

Isobutylene isoprene (IIR) rubber has high damping, low gas permeability, excellent oxidative stability and ozone resistance, making it suitable for outdoor applications such as flexible roofing. Co-vulcanisation in contact with other diene rubbers is problematic because of low unsaturation within the polymer structure [11], so halogenated grades using a substituted chlorine atom (CIIR) or bromine atom (BIIR) in the IR repeat unit are widely used.

Polychloroprene (CR) has moderate resistance to mineral oils and heat, and with 40% chlorine has lower flammability with self extinguishing behaviour, and will yield a high char level.

Polynorbornene (PNR) is a speciality polymer which is often used in high damping applications and where high friction is required. It will accept large quantities of oil, so can be formulated to hardness levels of 20 IRHD, but with acceptable physical strength [12].

'M' group elastomers

The 'M' group defines rubbers based on a saturated polymer based on polymethylene $(-CH_2-)_n$, the highest volume of these being ethylene propylene (diene modified) rubber (EPM, EPDM). EPM is a copolymer using ethylene and propylene monomers, typically at a ratio of 60-40% mol; with good resistance to heat ageing, light, ozone and oxygen, and is cross-linked with organic peroxides. For EPDM, a termonomer is employed which has a non-conjugated double bond, with typical termonomers dicyclopentadiene (DCP) and ethylene norbornene (ENB). These allow sulphur vulcanisation systems to be used, enabling good physical properties and easier processability. Compared to diene rubbers EPDM can be significantly extended with fillers and paraffinic oils, making it inexpensive. When used for applications such as within rail vehicles it requires the addition of fire retardants, and the use of hydrated fillers is a common approach to reduce flammability and smoke yield [13].

Ethylene acrylic elastomers (AEM, also known as EAM) are predominantly random copolymers of ethylene and methyl acrylate, with a small addition (1-5% mol) of a monomer based on an alkenoic acid to enable cross-linking. AEM has good resistance to heat ageing and organic fluid resistance and high damping, with a consistent level of dynamic behaviour over a wide temperature range. AEM will accept a high level of filler and retain some elasticity, ideal for the addition of hydrated fillers.

Chlorosulphonated polyethylene (CSM) is manufactured by the chlorination and chlorosulphonation of polyethylene, yielding polymer containing 29-43% chlorine and 1-1.5% sulphur, with compounds having good resistance to ozone, heat, mineral oil, acids and bases.

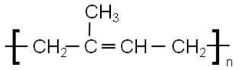
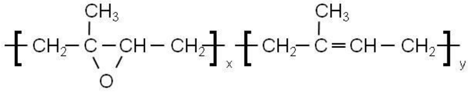
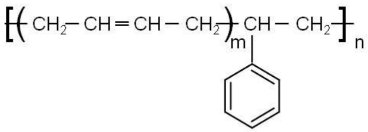
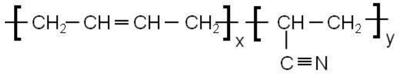
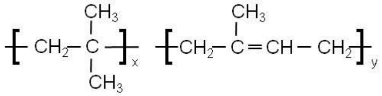
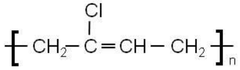
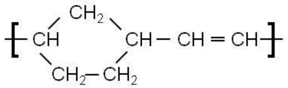
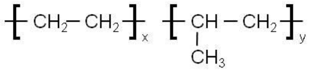
Fluorocarbon elastomers (FKM) rubbers were originally developed as a copolymer of vinyldiene fluoride and hexafluoropropylene. This FKM dipolymer is manufactured as Viton A^{TM} by DuPont®, with a fluorine content of 66%. Other fluorine containing monomers are often used in addition, such as tetrafluoroethylene for instance. The cross-linked compounds have extremely good thermal stability and oil resistance due to the high strength of the C-F bonds, making it ideal for applications in aggressive environments such as fuel and oil seals [14].

'O' group elastomers

Polyepichlorohydrin is available as a homopolymer (CO) and as a copolymer with ethylene oxide (ECO) improving the low temperature flexibility. They have low gas permeability, excellent ozone resistance, good heat resistance and low swelling in hydrocarbon fuels.

‘Q’ group elastomers

Rubbers comprising silicon and oxygen in the polymer chain are collectively designated Q rubbers, commonly known as silicones. The silicon-oxygen repeat unit structure has two groups attached to the silicon atom, typically methyl substituents (MQ). The use of a phenyl group (PMQ) improves the low temperature flexibility and resistance to radiation. The use of an additional 0.2-0.5% mol vinyl side group (VMQ) dominates silicone rubbers due to the improved compatibility with cross-linking agents (typically organic peroxides) leading to improved physical properties and processing. Some grades of silicone are polymerised using platinum catalysts which lead to a purer polymer with no peroxide residue, useful for materials for food contact or as medical implants. Q rubbers are often used in applications where resistance to a wide range of temperature is necessary; since the polymer can remain flexible at very low temperatures (around -60°C depending on the side groups), but with thermal stability enabling longer term service up to 200°C [15]. Lower physical strength and high cost compared to hydrocarbon rubbers has limited usage in larger products.

Chemical repeat unit	Chemical name	Abbreviation	Key properties	Main area of use
R group elastomers				
 $\left[CH_2-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_2 \right]_n$	polyisoprene, natural rubber	IR, NR	High resilience, low damping, toughness	Truck tyres, anti-vibration (AV)
 $\left[CH_2-\overset{CH_3}{\overset{\vert}{C}}\underset{\diagdown O \diagup}{-}CH-CH_2 \right]_x \left[CH_2-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_2 \right]_y$	epoxidised natural rubber	ENR	Improved oil resistance and higher damping than NR	AV dampers, tyre lining in 'green' tyre
$\left[CH_2-CH=CH-CH_2 \right]_n$	polybutadiene	BR	Wet grip, high resilience	Blended in tyres
	styrene butadiene rubber	SBR	High abrasion resistance and grip	Passenger tyres, carpet backing, conveyor belt
 $\left[CH_2-CH=CH-CH_2 \right]_x \left[\underset{\underset{C\equiv N}{\vert}}{CH}-CH_2 \right]_y$	acrylonitrile-butadiene rubber	NBR	Oil resistance	Oil seals, conveyor belting
 $\left[CH_2-\underset{\underset{CH_3}{\vert}}{\overset{CH_3}{\overset{\vert}{C}}} \right]_x \left[CH_2-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_2 \right]_y$	isobutene-isoprene rubber	IIR	Low gas permeability	Tyre linings and inner tubes, adhesive, roofing
 $\left[CH_2-\overset{Cl}{\overset{\vert}{C}}=CH-CH_2 \right]_n$	polychloroprene	CR	Outdoor resistance, mild oil and heat resistance	Inflatable boats, AV mounts, belting, adhesives
	polynorbornene	PNR (NOR)	High damping and friction, low hardness possible	Motor racing and winter tyres blended with SBR
M group elastomers				
 $\left[CH_2-CH_2 \right]_x \left[\underset{\underset{CH_3}{\vert}}{CH}-CH_2 \right]_y$	ethylene propylene (diene modified) rubber	EPM, EPDM	Environmental, heat and ozone resistance	Door and windows seals, roofing

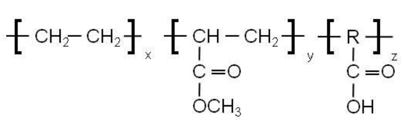
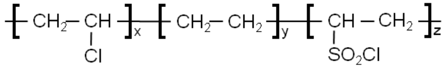
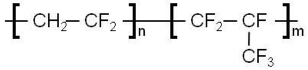
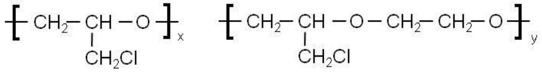
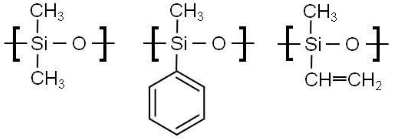
 $\left[CH_2-CH_2\right]_x\left[\underset{\substack{\vert\\C=O\\\vert\\OCH_3}}{CH}-CH_2\right]_y\left[\underset{\substack{\vert\\C=O\\\vert\\OH}}{R}\right]_z$	ethylene-acrylic rubber	AEM (EAM)	Oil resistance, heat resistance, low smoke emission	Railcar flooring, gangway connectors, environmental protection
 $\left[CH_2-\underset{\substack{\vert\\Cl}}{CH}\right]_x\left[CH_2-CH_2\right]_y\left[\underset{\substack{\vert\\SO_2Cl}}{CH}-CH_2\right]_z$	chlorosulphonated polyethylene	CSM	Environmental, ozone, heat, oil resistance	Industrial hose, belting, adhesives, roofing
 $\left[CH_2-CF_2\right]_n\left[CF_2-\underset{\substack{\vert\\CF_3}}{CF}\right]_m$	fluorocarbon rubber	FKM	Oil, fuel and heat resistance	Internal combustion and jet engine seals
O group elastomer				
 $\left[CH_2-\underset{\substack{\vert\\CH_2Cl}}{CH}-O\right]_x\quad\left[CH_2-\underset{\substack{\vert\\CH_2Cl}}{CH}-O-CH_2-CH_2-O\right]_y$	polyepichlorohydrin	CO, ECO	Hydrocarbon fuel resistance	Fuel hose, seals and gaskets
Q group elastomer				
	silicone rubber	(Q) MQ, VMQ, PMQ	Low and high temperatures, low smoke yield	Aerospace and high temperature seals, medical devices

Table 1 Summary of rubber types, abbreviations, benefits and application areas [16]

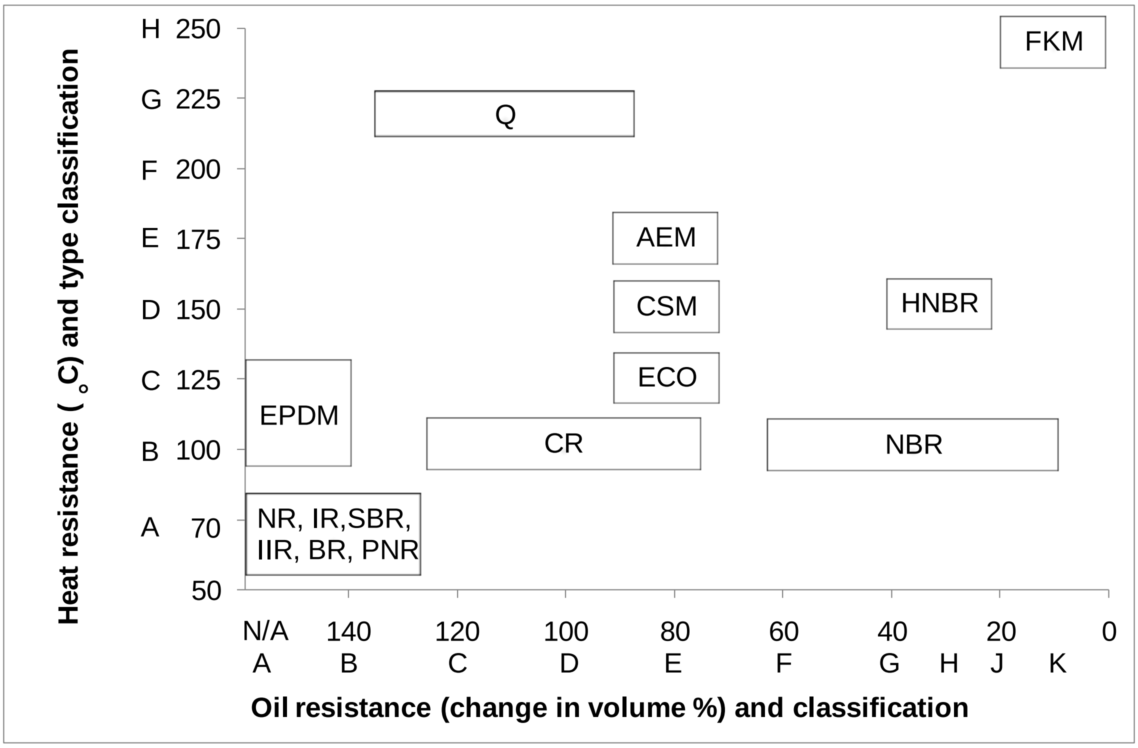


Figure 3 Polymer types within ASTM D2000 classifications

Another method of rubber classification is by physical properties, a common method being ASTM D2000 [17]. Developed for the automotive industry this standard is applied widely, using two main criteria to classify rubbers compounds: heat resistance, and oil swelling, typical classifications in Figure 3.

Shen [18] has summarised some applications requiring fire retardant compounds and identified some suitable elastomers (Table 2).

Applications	Polymer base
Wire and Cable	EPDM, CR, EVA, CSM, Q, PU
Conveyor belting	SBR, CR
Flooring	SBR
Roofing membranes	EPDM, CSM
Foam insulation	EPDM
Tubing	NBR
Coated fabrics	CR, PU

Table 2 Typical applications and elastomers (from Shen)

1.2.4 Compounding of rubber

Elastomers are not useful in the raw state; unmodified natural rubber, for instance, becomes extremely stiff when cooled below 0°C, and soft and sticky above 70°C. Even at room temperature elastomers have poor dimensional stability, so are of little practical use in formed products. To produce useful products, elastomers are converted into rubber compounds, which are complex mixtures of functional ingredients, to permit cross-linking, the modification of physical properties, processability and protection from environmental conditions. It is necessary to consider each of these components in order to discuss the flammability of the complete material.

Component	Function	Typical pphr *
Polymer	Defines the elastomeric properties	100
Filler	Reinforcement, increase modulus, reduce cost by dilution	10-200
Oil	Soften, low temperature flexibility, processing, reduce cost by dilution	2-50
Antidegradants	Antioxidant, antiozonant, UV absorbers, chelates	1-3
Cross-linking agent	Form cross-links between polymer chains	0.5-5
Accelerators	Speed up cross-linking process	0.5-5
Cure activators	Enable efficient cross-linking	2-7
Functional additives	Fire retardants, pigments, process aids, blowing agents	various

Table 3 Generic rubber compound formulation

* parts per hundred rubber

In Table 3 typical formulation ranges are shown; and the main additive groups of filler, oil, antidegradants and cross-linking systems are considered in more detail below.

1.2.5 Fillers

The majority of rubber compounds contain filler, with reinforcing fillers usually added to improve the physical properties, such as tensile strength and abrasion resistance for example. The most common reinforcing agent for rubber is carbon black, which also behaves as an effective black pigment and UV absorber. It is typically manufactured in the ‘furnace method’ by thermally cracking a heavy aromatic hydrocarbon feedstock under controlled conditions. In the primary stage a natural gas / air mixture is fully combusted, and in the secondary stage the feedstock is injected into the hot exhaust gas and quenched in a water mist to obtain carbon black nuclei, which are carbon particles formed from poly-cyclic aromatic (PAH) and benzene particles with a controlled morphology [19,20] . The carbon black is subsequently filtered, pelletised (to reduce dust nuisance and aid incorporation and dispersion) and graded. Carbon blacks are graded primarily by particle size (measured surface area for nitrogen adsorption), and secondarily by structure (measured by oil absorption number) within the classification system ASTM D1765 [21](Figure 4).

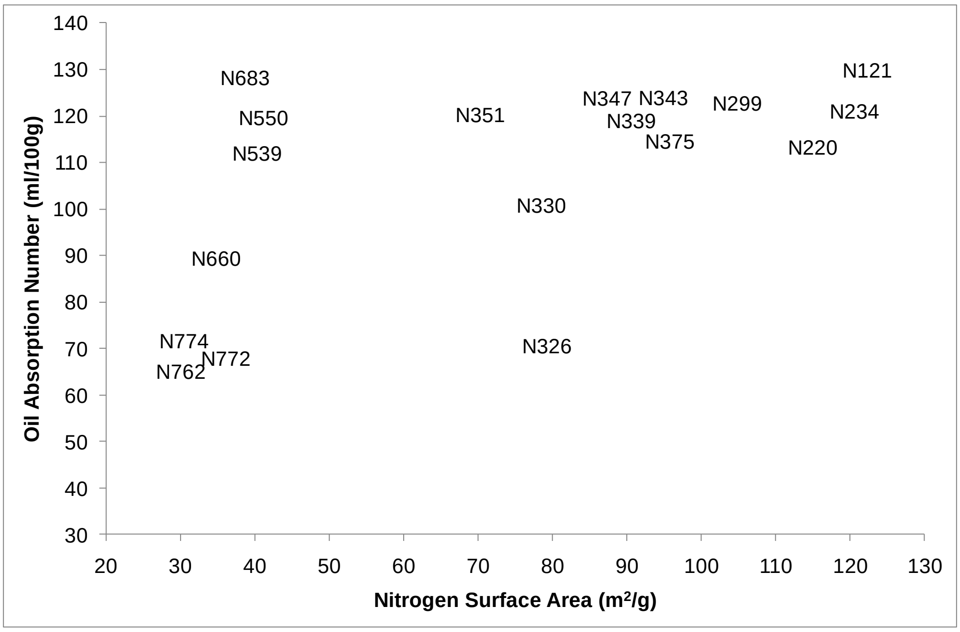


Figure 4 ASTM D1765 classifications for carbon black in rubber

Other reinforcing fillers, including precipitated silica, have developed in recent years to high volumes used within car tyres [22], used to impart low rolling resistance whilst retaining grip. Silane coupling agents are employed to improve the levels of polymer to silica, and silica to silica bonding necessary for good physical properties. Non-reinforcing fillers include calcium carbonate, china clay (hydrated aluminium silicate), talc (hydrated magnesium silicate), magnesium carbonate, magnesium oxide and barytes (barium sulphate). These are typically diluents used to primarily cheapen products, but may also be used as functional additives, such as to increase the modulus, change the electrical properties, pigment, or impart increased fire or fluid resistance [23].

Work has been carried out in elastomers with nano-scale fillers, such as single-wall carbon nanotubes (SWNT)[24] and carbon nanofibrils[25]. Small additions of such materials can impart significant changes on the compound properties far beyond that capable of normal micro-sized reinforcing filler when they are able to be fully dispersed within the polymer matrix.

1.2.6 Oils

Mineral oils are often added to rubber compounds to function as plasticisers and extenders. The type of oil is generally classified according to the predominant chemical structure, namely whether aromatic, naphthenic and paraffinic [26], the choice being determined by polarity of both materials. A dissimilar polarity will tend to lead to reduced compatibility, resulting in increased migration particularly at elevated temperatures. Paraffinic oil is the usual choice for EPDM, a non-polar straight chained polymer, whereas aromatic oils were traditionally used with highly polar elastomers. Naphthenic oils are typically used for NR compounds, showing high compatibility. Low loadings of oil are suitable for improved processing qualities such as reduced viscosity and more efficient incorporation of fillers during mixing, and at high loadings are used with bulk fillers to extend the mixture. They are also used to reduce the hardness of the cured compound, useful where the desired hardness is below the cured, unfilled rubber value. For NBR, AEM and CSM phthalate and sebacate plasticisers are used to improve low temperature flexibility but retain thermal stability. Less flammable plasticisers are available such as phosphate esters and phosphonates which are compatible in the polar elastomers such as CR, and may be added as part of a fire retardant system.

1.2.7 **Antidegradants**

The majority of rubber compounds, particularly those with unsaturation, use antidegradants and waxes to provide improved resistance to environmental conditions. Chemical additives collectively known as antidegradants are regularly added to rubber compounds to protect them from the effects of oxygen, ozone, heat, light and repeated mechanical deformation [27]. Phenolics are a group of non-staining antioxidants based on phenol, regularly used in light-coloured rubber compounds. Amine based antidegradants are highly effective antioxidants, para-phenylene diamines, for instance, give both antioxidant and antiozonant activity, along with some resistance to metal ions and flexural fatigue.

Paraffin waxes are often employed in diene rubbers to provide a physical barrier to ozone, which attacks double bonds, so causing cracking at the rubber surface [28]. The paraffin wax is not fully soluble in the rubber compound, so migrates to the surface creating a barrier over time providing good static protection. However, if the product application is under repeated displacement, use of a wax will not be sufficient due to material movement breaking the surface film. In this case, para-phenylene diamine based antiozonants such as 6PPD are used, which work to scavenge ozone to prevent surface cracking.

1.2.8 Cross-linking systems

Cross-linking increases the thermal stability of elastomers by introducing short links between the long polymer chains, maximising the elasticity of the polymer over a wider range of temperature than for an un-crosslinked elastomer. The most common cross-linking agent is sulphur, used in conjunction with an organic accelerator, zinc oxide and fatty acid activator. Zinc oxide is widely used within both sulphur and peroxide curing rubber compounds, described as an activator or co-agent, with the effect being to increase the cross-linking efficiency of the cure system, combining with a fatty acid such as stearic acid into a zinc stearate complex upon heating. Ground sulphur is typically used, which exists as an eight-membered ring. Along with zinc oxide and stearic acid, organic accelerators are used to efficiently produce cross-links.

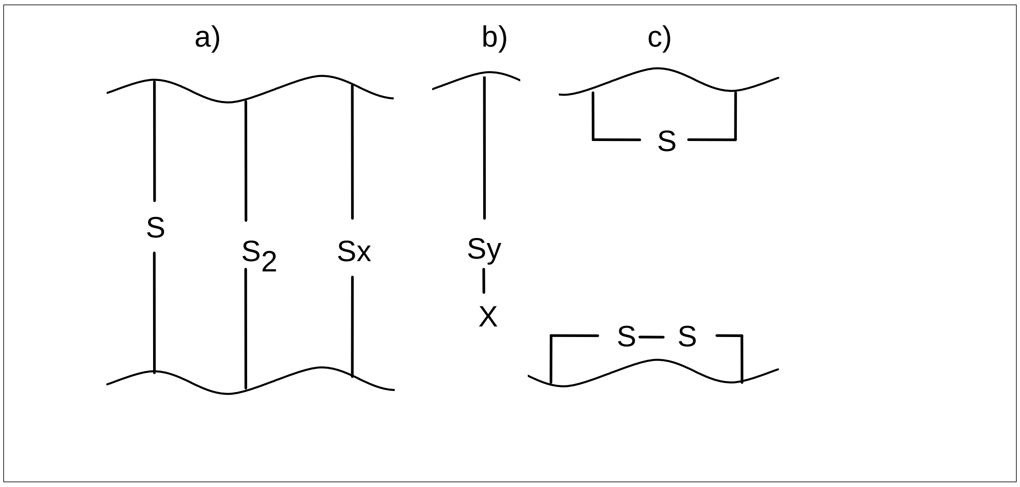


Figure 5 Schematic view of sulphur cross-links across polymer chains

Sulphur combines within the vulcanisate network in a number of ways, (Figure 5) [26].

a) Monosulphidic, disulphidic and polysulphidic cross-links are useful cross-links

b) Pendant sulphides

c) Cyclic monosulphides and disulphides

b) and c) are likely to leave the compound more susceptible to degradation in service due to the weaker sulphur-carbon bond energy.

Cross-linkage	Conventional	Semi-EV	Efficient Vulcanisation	Organic peroxide
Sulphur pphr	2.0-3.5	1.0-1.8	0.3-0.8	N/A
Accelerator pphr	0.4-1.0	1.3-2.0	2.5-6.0	N/A
Majority bond type	poly-sulphidic	mono and poly-sulphidic mixture	mono-sulphidic	carbon-carbon
Bond energy kJ.mol^{-1}	<268	<268 - 284	284	351

Table 4 Comparison of cure systems

Conventional cross-linking systems employ higher levels of sulphur, characterised with higher physical strength and good durability, but higher levels of compression set (permanent deformation) and inferior ageing properties (Table 4) [29]. This is due to the prevalence of poly-sulphidic cross-links, which have lower bond energies with a tendency to break and reform under mechanical stress. In an Efficient Vulcanisation (EV) system, the scarcity of sulphur leads to over 80% mono-sulphidic cross-links, which have greater bond energy resulting in a vulcanisate with improved resistance to thermal decomposition and low compression set, but with reduced strength and elongation. A semi-EV system can give a wide range of cross-link types, and the resultant vulcanisate will have a mix of high elasticity and ageing properties. An alternative to sulphur vulcanisation is in the use of organic peroxides, most commonly used in fully saturated elastomers. The use of peroxide results in a carbon-carbon bond, which has a bond energy significantly higher than for a sulphur cross-link. Other cross-linking systems are available often tailored for specific polymer types. In IIR, for example, phenolic-resin cross-linking is commonly used, and in FKM a hexamethylene diamine carbamate cure system is common.

1.2.9 Physical tests for rubber

Many methods exist to impart fire retardant properties to natural or synthetic rubbers. A key aspect of this project to make fire retarded rubbers whilst maintaining their physical performance. This will be characterised using the industry standard tests outlined in section 2.3.

1.3 Thermal decomposition of polymers

1.3.1 General Schemes

Exposure of an organic polymer to prolonged high temperatures inevitably leads to thermal decomposition, otherwise known as pyrolysis. Prior to this physical changes may take place, such as melting [30]. The mechanisms of pyrolysis can be categorised into the following schemes.

End-chain scission, often known as ‘unzipping’ or chain de-polymerisation, is a process of degradation usually associated with linear polymers. It is akin to a reverse of addition polymerisation, where the polymer decomposes into monomer from the ends of the polymer chains.

Random chain scission, sometimes known as random degradation, is the breaking of bonds within the polymer chain, most likely to initiate at a ‘weak link’ due to a chain defect. This defect may be due to remainders of polymerisation such as initiator, or some head-head repeat units in a copolymer. The product of random chain scission will be a broad distribution of molecular species, from sub-monomer fragments up to larger oligomers.

Chain stripping is a process of decomposition where side groups are detached from the backbone chain, an example being the degradation of polyvinyl chloride (PVC) [31]. Unlike the previous two mechanisms, free radicals are not necessary for the initial reaction. For PVC the chlorine atom is stripped from the chain, forming HCl, and the chain becomes unsaturated. The resultant unsaturated chain is then susceptible to further changes by thermal degradation, such as random chain scission.

In thermal decomposition, cross-linking can take place leading to the formation of a carbonaceous char. This is a term for a larger covalently bonded structure, often comprising an aromatic complex. This matter is of a sufficiently high molecular weight to remain in the condensed phase, although some smaller particles will be likely to form dense smoke particulates. An example of this process is for the secondary degradation of PVC, where the unsaturated chain then readily forms aromatic species through a cyclization mechanism [31]. The subsequent large char structure is chemically similar to graphite and is more thermally stable than the polymer, so providing a barrier to burning in thicker products.

Another degradation mechanism specific to cross-linked rubber is de-crosslinking, otherwise known as reversion; a mechanism where cross-links are degraded upon heating [32], allowing softening and melting of the polymer.

1.3.2 Flaming combustion of methane

Flaming combustion can only take place within the gas phase, so the polymer needs to be degraded to sufficiently small molecules to enable this; an example of this is given in Table 8. These may as small as a methyl radical. The smallest stable hydrocarbon molecule is methane, so this is the classic example given within standard texts [30,31]. The stoichiometric equation for the burning of methane is given in ---- (1).

$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ ---- (1)

Simply put, methane will combine with oxygen to burn with a flame to give water and carbon dioxide. In reality, however, this reaction occurs in a number of steps as follows. The methane molecule is thought to start to breakdown from free radical attack, as shown in (2), (3) and (4). All of these reactions are exothermic with low activation energies.

$CH_4 + OH\cdot \rightarrow CH_3\cdot + H_2O$ ---- (2)

$CH_4 + H\cdot \rightarrow CH_3\cdot + H_2$ ---- (3)

$CH_4 + \cdot O\cdot \rightarrow CH_3\cdot + OH\cdot$ ---- (4)

The methyl radical is then thought to react with oxygen to create formaldehyde (methanal) (5).

$CH_3\cdot + O_2 \rightarrow HCHO + OH\cdot$ ---- (5)

Two rapid steps then follow on to consume the formaldehyde (6) and to generate carbon monoxide (7).

$HCHO + OH\cdot \rightarrow CHO\cdot + H_2O$ ---- (6)

$CHO\cdot + OH\cdot \rightarrow CO + H_2O$ ---- (7)

The carbon monoxide then reacts to form carbon dioxide, probably using an $OH^\bullet$ radical (8).

$CO + OH\cdot \rightarrow CO_2 + H\cdot$ ---- (8)

The production of carbon dioxide has consumed two free radicals, but yields only one, so would not be able to provide a continuing process were it not for the following processes involving the hydrogen radical. This is known as chain branching.

$H\cdot + O_2 \rightarrow HO\cdot + \cdot O\cdot$ ---- (9)

$\cdot O\cdot + H_2 \rightarrow HO\cdot + H\cdot$ ---- (10)

$\cdot O\cdot + H_2O \rightarrow HO\cdot + OH\cdot$ ---- (11)

A direct reaction between the hydrogen radical and water produces most of the $OH^{\bullet}$ radicals.

$$H_2O + H\cdot \rightarrow HO\cdot + H_2 \quad \text{---- (12)}$$

These reactions take place preferentially at different points of the flame, so the whole process is complex and dynamic. At a higher point of the flame where the temperature is highest the carbon monoxide is oxidised to carbon dioxide.

$$CO + OH\cdot \rightarrow CO_2 + H\cdot \quad \text{---- (13)}$$

To place these mechanisms into the context of burning behaviour, this simplified view demonstrates the importance of free radicals within the process. Environmental conditions, including temperature and oxygen levels, will affect the rate of both radical production and elimination, in turn determining whether a fire spreads, remains static or extinguishes. This has a clear implication for fire retardation. One tactic to reduce flammability is to use chemistry to interrupt this free radical process. Another is to attempt to reduce the flame temperature to slow the rate of radical formation by which this whole process hangs.

The production of CO is a product of incomplete combustion, usually in an environment of insufficient oxygen. This reaction yields less energy than the full product CO_2, but is undesirable due to the acute toxicity of CO and the production of larger quantities of smoke and other products of incomplete combustion. Overall, from the example of methane, we see that even a small molecule undergoes a complex multistage process of combustion, made more complex for the volatile fragments from polymer decomposition.

1.4 Methods for Studying Thermal Decomposition

Microscale thermal techniques are commonly employed to attempt to understand the chemical mechanisms involved and the effect of additives on polymers.

1.4.1 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) has been defined “as a technique in which the mass change of a substance is measured as a function of temperature whilst the substance is subjected to a controlled heating programme” [33], and is a useful technique for the analysis of materials where volatiles are lost upon heating, such as polymers.

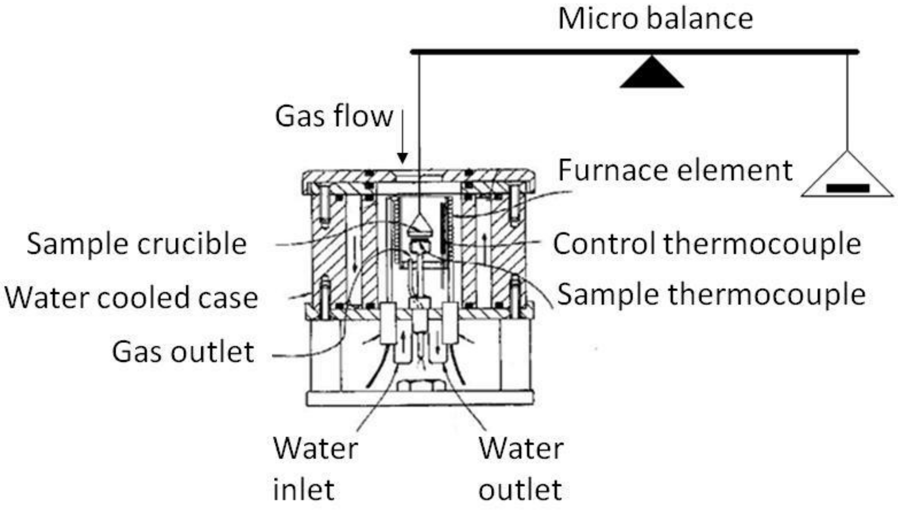


Figure 6 Cut-through view of a Stanton Redcroft TGA

Derivative Thermogravimetry (DTG) presents the TGA data as the rate of mass loss against temperature. The peaks produced may help to pinpoint the temperatures at which mass loss is highest, and can identify overlapping peaks from shoulders in the curves. The TGA unit consists of a microbalance with a suspended inert crucible (Figure 6) which can be placed within a temperature programmable furnace. The sample should be as small as possible to enable as best as possible isothermal conditions, but large enough to enable accurate weight measurement, and representative in the case of a mixture. The sample is pyrolysed in an atmosphere of flowing gas to ensure a steady gas concentration and temperature and to remove volatiles. Nitrogen is often used to create an inert environment without oxidation. The oxygen concentration below a flame is close to 0% [31] so this is often a preferred technique in fire science. To study behaviour before ignition the thermal degradation of a substance in air can be undertaken. Finally to quantify the material which can oxidise, such as char and carbon black, oxygen can be switched into the gas stream when the temperature reaches 600°C. With TGA runs the rate of heating can affect the accuracy and speed of test. A low heating rate improves resolution, but may take an excessive time to test. A high heating rate may be more suitable for quality control checks, but is less discriminating of separate decomposition peaks, although it has been argued that higher heating rates are more representative of those in fires.

1.4.2 Differential Scanning Calorimetry and Differential Thermal Analysis

Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) are related techniques used to study the effects of thermal changes with reference to an inert sample [34]. Whereas TGA measures mass loss, DSC/DTA measures the small changes in heat flow related to chemical or physical changes in a substance. This can be established by either measuring temperature differences or the different power levels required to maintain an even heat. Data collected is usually plotted in the form of heat flow against temperature. Since most physical and chemical reactions involve a change in energy levels, these endothermic or exothermic reactions will be observed by DSC/DTA. Effects such as melting, crystallinity changes, cross-linking, polymerisation and degradation can therefore by studied. In addition quantitative measurements can be determined, including heat capacity and Arrhenius factors such as activation energy.

1.4.3 Simultaneous Thermal Analysis

It is possible to combine TGA and DSC/DTA techniques within one instrument, the advantage of a combined technique being primarily analytical, not economic [35]. The instrument is more complex and may not perform the individual measurements as well as two separate units, but has an advantage of performing both tests under the same conditions, so allowing simultaneous comparative plots to be produced. By being able to compare the mass change with heat flow an improved understanding of the reaction chemistry may be determined.

1.4.4 Evolved Gas Analysis (EGA)

EGA covers a wide range of techniques used to gain understanding of the nature of volatiles evolved during thermal techniques where a purge gas flows from the instrument. Some methods can work in real time (on-line) during a run, such as TG-FTIR (Fourier Transform Infra-Red Spectroscopy). Gas Chromatography (GC) can also be used to separate mixtures of gases into varying molecular weights. Due to the delay in the output of the species separated this becomes an off-line process [35]. The output from the GC column can then be connected to a mass spectrometer (MS) to give a positive identification of the chemical species. This technique has been used to great effect to give a fundamental understanding of many polymer decomposition reactions and is therefore in common use for research. GC–MS can separate, detect, and identify a wide range of chemicals at low levels in mixtures [36]. One approach with polymer analysis is to determine particular reaction temperatures of interest, and to then carry out GC-MS product analysis at that temperature.

1.5 Methods of studying burning behaviour

Burning tests can be categorised in terms of quantitative and qualitative types [37]. The former are designed to accurately reflect the conditions of use, so results can be directly related to levels of hazard. These tests tend to be costly, more complex, and specific to an application. Qualitative tests are not always designed to be a realistic fire scenario, but are easier to perform and may be used to screen materials; as part of a suite of tests they can still indicate an indirect relationship to fire hazard.

1.5.1 Linear Burning Tests

A small scale qualitative flammability method in accordance with ISO 1210 method A [38] can be used for the determination of the linear burning rate of horizontal specimens. Test strips 125 x 13 x 3 mm are evaluated using a gas burner at a 45° angle (with flexible samples such as rubbers, an angled metal strip is withdrawn at a sufficient rate to both maintain the correct angle of the sample without being close to the decomposing material may be used) (Figure 21, page 80). This method is equivalent to the Underwriter Laboratory test UL94HB, but with some differences with respect to the expression of results.

A more severe method is the UL94 vertical burning test, where samples are suspended vertically and exposed to the gas burner as the bottom of the sample for 10 seconds initially, and the flame re-applied for a further 10 seconds, if it initially self-extinguishes.

An advantage of this type of test is the ability to quickly screen materials for burning rate and self-extinguishing ability. Disadvantages can include sensitivity to surrounding air flow affecting repeatability, the lack of discrimination within the broad classifications (HB, V2, V1, V0), and the lack of any measurement of heat and smoke release.

1.5.2 Limiting Oxygen Index (LOI)

Limiting Oxygen Index (LOI) is a qualitative measure of the ability of material to just sustain candle-like burning behaviour at a given percentage of oxygen in nitrogen at room temperature. This is a simple and repeatable measure of an aspect of burning behaviour. However, it can be misinterpreted leading to false conclusions such as inappropriate screening. This method is carried out in accordance with BS EN ISO 4589 part 2 [39]. This single result has subsequently been widely adopted within industry and values are often quoted in literature. This method has the weakness however that it is somewhat unrealistic in comparison to fire scenarios. For a fire retarded polymer it employs an atmosphere of oxygen above atmospheric levels, and at room temperature with a low heat flux. In the best case scenario of vertically downward flame spread this can therefore not be considered adequate alone for the assessment of fire performance, particularly in a developing and established fire.

1.5.3 The Cone Calorimeter

The use of the cone calorimeter is defined within ISO 5660 part 1 [40]. This technique allows the assessment of burning behaviour during radiation imposed from an electrically heated cone assembly. By using oxygen depletion calorimetry, and known test conditions the heat release can be estimated in real time, along with smoke generation, CO and CO_2 evolution and mass loss. Cone calorimetry has become well established as a sophisticated tool for the study of burning behaviour under well-ventilated conditions, from low to moderate (10 – 100 kW m^{-2}) levels of imposed heat flux, so has some credential as a quantitative test in the early stages of a fire. The sample is typically 100 x 100mm square with thickness from 3mm upwards, typically 6mm. The key concept of heat release measurement is the principle of the oxygen depletion principle, where for most combustible materials the amount of heat equivalent to 13.1 kJ +/- 5% is released for every gram of oxygen consumed [41]. The sample is mounted on an insulator, within a stainless steel sample holder. The sample holder sits on a pedestal which has a load cell at the base to record the mass during the test. The sample is exposed to a cone shaped radiant heater, with an electrical spark above the sample until flaming combustion is initiated. Air is drawn past the sample extracting smoke and fumes by an extraction fan. A sampling tube removes gas which is filtered for particulates, dried and fed into gas analysers to determine levels of oxygen, carbon monoxide and carbon dioxide. Across the exhaust duct, a laser and photo-multiplier is used to measure smoke density. All of this information is gathered throughout the test run with time delay compensation, so is considered as being in real time. In addition to the direct data measured as a function of time, a calculation is made within the to determine the heat release rate, effective heat of combustion, oxygen consumed and mass loss per gram of oxygen.

Of particular use with cone calorimetry is that the heat release rate (HRR) can be measured against time, so the rate of fire growth can be observed. The subsequent plot is useful for the comparison of materials, since the pattern of heat release can categorise the behaviour of materials. The cone calorimeter is often chosen for research because it can provide a large stream of data relating to time to ignition, heat release, smoke density and gas emissions from one test. This makes it ideal for screening a large number of samples and providing objective comparative data. However, the small sample size, covered uniformly by the radiant heater, gives little indication of flame spread, while giving valuable information about the rate of flame penetration into the burning fuel.

1.5.4 Smoke Density Chamber (ISO 5659-2)

This method [42] is a bench scale test to both measure the optical density and gather the volatile products of combustion for further analysis. Testing can be carried out in both the flaming and non-flaming modes. The sample (typically 75mm square) is exposed to a cone heater within the unventilated cabinet and smoke density is measured by use of a light source and detector. The test results are only valid for the sample thickness tested, which can affect the rate and overall level of smoke released.

1.5.5 Modelling of burning behaviour

Due to the complex nature of the burning behaviour of polymers, especially when modified with fire retardants, it can be difficult to characterise the cause of changes in heat release. One of the reasons for this is that when introducing additives many changes are imparted to the resultant material. These changes can include physical properties such as density, thermal conductivity and heat capacity, as well as to the more commonly considered properties such as thermal stability and char formation. One way to investigate the effect of each of these changes in isolation, often not possible in experimentation, is to use computer modelling. A thermo-kinetic model, ThermaKin, has been developed[43] within the Federal Aviation Administration Materials Research Laboratory in the USA. This simple one-dimensional model of polymer pyrolysis and gasification can be used to simulate burning in well defined tests such as the cone calorimeter.

1.6 Relationships between polymer structure, degradation and burning behaviour

1.6.1 Heat of combustion

An important quantity in fire science is the Heat of Combustion (ΔH_C), defined as "The amount of heat released when a unit quantity of a fuel is oxidised completely, at baseline conditions of 25°C and atmospheric pressure." [30]. This measures the maximum amount of energy that is released from the efficient combustion of a fuel and oxygen into water and carbon dioxide, typically determined in an oxygen bomb calorimeter [44], a device in which a known mass of fuel is oxidised completely in an oxygen atmosphere. The heat of combustion is calculated based on the rise in temperature and pressure observed, where a negative ΔH_C indicates that heat is released from the reaction, the products being formed having a more stable chemical configuration than the reactants, being an exothermic reaction. In order to achieve a complete reaction (to CO_2 and H_2O) 25 atm of pure oxygen is used. Under these rather extreme conditions most organic materials can be completely oxidised.

Assuming complete combustion to CO_2 and water, simple stoichiometric equations between the starting and final products can be calculated, ignoring the many intermediate stages. This arises from a fundamental principle of thermodynamics originally enunciated in Hess' law of constant heat summation, which states that "the change in enthalpy depends only on the initial and final states of the system, and is independent of the intermediate steps." While the water may be produced as a vapour, the actual energy change refers to the final state of 1 atm pressure at 25°C when it is a liquid. The inappropriateness of the bomb calorimeter conditions to an actual fire scenario, and the need to distinguish between complete combustion (where, for example, all carbon black would be converted to CO_2) has driven the need for an alternative heat release measurement under more realistic conditions. This arises from the fortunate coincidence that for every gram of oxygen consumed on burning most organic materials, 13.1 kJ of heat is released [41]. This is the principle behind oxygen depletion calorimetry used in the cone calorimeter for determination of heat release by measuring oxygen depletion. The heat of combustion, assuming complete combustion, can thus be estimated using the following equation, where:

ΔH_C is in kJ/g, $\Delta(O_2)$ is the molar oxygen demand for complete combustion of the structural unit, and M is molecular weight of a polymer repeat unit.

$$\Delta H_C = \frac{\Delta(O_2) \times 32 \times 13.1}{M}$$

This approach is used to calculate the ranked heats of combustion for some elastomers in Table 5, shows the maximum potential of these polymers to release heat during burning, with the pure hydrocarbon polymers the highest ranked.

Polymer	Stoichiometric equations	Calc ΔH_C kJ/g	Literature ΔH_C kJ/g
EPM	$C_5H_{10} + 7.5\ O_2 \rightarrow 5CO_2 + 5H_2O$	44.8	47.2[45]
IIR	$C_9H_{16} + 13\ O_2 \rightarrow 9CO_2 + 8H_2O$	43.8	45.1[45],44.4[46]
NR/IR	$C_5H_8 + 7\ O_2 \rightarrow 5CO_2 + 4H_2O$	43.1	45.9[47],44.9[48]
BR	$C_4H_6 + 5.5\ O_2 \rightarrow 4CO_2 + 3H_2O$	42.6	43.3[49],45.2[48]
PNR	$C_7H_{10} + 9.5\ O_2 \rightarrow 7CO_2 + 5H_2O$	42.3	
SBR	$0.25(C_8H_8)+0.75(C_4H_6)+6.625\ O_2 \rightarrow 5\ CO_2+3.25\ H_2O$	41.6	43.4[49,49]
ENR50	$C_{10}H_{16}O + 13.5\ O_2 \rightarrow 10\ CO_2 + 8\ H_2O$	37.2	
NBR	$0.3(C_3H_3N)+0.7(C_4H_6)+4.6O_2 \rightarrow 3.4CO_2+2.4H_2O+0.3HCN$	35.8	41.4[45],39.6[49]
AEM	$C_6H_{10}O_2 + 7.5\ O_2 \rightarrow 6CO_2 + 5H_2O$	27.5	
CR	$C_4H_5Cl + 5\ O_2 \rightarrow 4CO_2 + 2H_2O + HCl$	23.7	29.5[45],24.3[48]
MQ	$C_2H_6SiO + 4\ O_2 \rightarrow 2CO_2 + 3H_2O + SiO_2$	22.6	17.4[45],16.3[46]
ECO	$C_5H_9ClO_2 + 6\ O_2 \rightarrow 5CO_2 + 4H_2O + HCl$	18.4	
CO	$C_3H_5ClO + 3.5\ O_2 \rightarrow 3CO_2 + 2H_2O + HCl$	15.9	13.4[46]
CSM	$C_6H_{10}Cl_2SO_2 + 8\ O_2 \rightarrow 6CO_2 + 4H_2O + 2HCl + SO_2$	15.4	
FKM	$C_5H_2F_8 + 5\ O_2 \rightarrow 5CO_2 + 3F_2 + 2HF$	9.8	11.5,15.1[45]

Table 5 Stoichiometric equations and calculated Heat of Combustion

Overall the calculated heats of combustion correspond reasonably to the literature values in Table 5. Exceptions to this rule from the literature are for MQ and one value for FKM. The reason for the MQ deviation is that silicon oxidation does not fit in with the 13.1 kJ per gram O_2 simplification, and in practice carbonyl fluoride (COF_2) results from burning fluoropolymers with small amounts of hydrogen in their structure.

1.6.2 Limiting oxygen index

Previous reviews [50-56] broadly place the burning behaviour of elastomers into two main categories; hydrocarbons with high rates of heat release, and halogenated or inorganic rubbers, with some level of inherent fire retardance. A simple example of the differences encountered between the two rubber categories described can be demonstrated by the small scale ease of extinction test, the limiting oxygen index (LOI). Work by Nakagawa [57] examined a range of rubber conveyor belt materials, and an empirical relationship was suggested between the initial temperatures of mass loss in TGA (Thermogravimetric Analysis) in nitrogen, and LOI and hot plate ignition temperature. This is unlikely to be limited to conveyor belts, and is reasonable, since fuel mass loss in the TGA corresponds with ignition temperature, and although LOI is an ease of ignition test, for non-charring polymers the criteria for extinction are essentially the same as those for ignition. Examples of LOI are shown in Table 6, where values could be found in the literature, for other rubbers, estimations of LOI from two methods in the literature have been used.

Limiting oxygen index estimated using the heat of combustion

From a detailed analysis of LOI and material flammability, Johnson links heat of combustion directly to LOI [50] using the following equation:

$$\mathrm{LOI} = \frac{795}{\Delta H_C}$$

This scheme proposed by Johnson gives fair correlation to measured OI if applied within certain restrictions; atomic C/O ratio must be greater than 6, and not low in hydrogen atoms.

Limiting oxygen index estimated using molecular ratios

Van Krevelen[48] studied the molecular structure and atomic ratios to determine a Combustion Parameter (CP)

$$\mathrm{CP} = \mathrm{H/C} - 0.65\,(\mathrm{F/C})^{1/3} - 1.1\,(\mathrm{Cl/C})^{1/3}$$

Where H/C, F/C, Cl/C are the ratios of the elements in the polymer composition.

(H – hydrogen, C – carbon, F – fluorine, Cl – chlorine)

Where $\mathrm{CP} \geq 1$, $\mathrm{LOI} \approx 17.5$

Where $\mathrm{CP} \leq 1$, $\mathrm{LOI} \approx 60 - 42.6\mathrm{CP}$

This mathematically shows the detrimental effect to LOI performance of hydrogen atoms in the structure and the beneficial effect of halogen atoms to reduced flammability. These concepts are applied with the results in Table 6. The polymers are ranked by LOI using Johnson's calculated LOI method, using the calculated ΔH_C values in Table 5.

Base polymer	Literature values	CP method	Johnson H of C method
	% LOI	% LOI	% LOI
EPM (50% PE)	21[13], 20.5[58], 21.9[59], 20[60]	17.5	17.7
IIR		18.5	18.1
NR, IR	17.5[61], 18.2[62], 18.5[63]	17.5	18.5
BR	18.3[50]	17.5	18.6
PNR		17.5	18.8
SBR (75% BR)	18.5[64], 18.5[64], 19.7[63], 20.6[65]	17.5	19.1
ENR (50% NR)		18.5	21.4
NBR (70% BR)	19.3[58], 19.1[63] 18.0[66]	17.5	22.2
AEM (50% PE)	24[67]	17.5	28.9 *
CR	26-31[52], 26.4[50], 32[60]	36.3	33.6
MQ	25.8-34.0[54], 27.1[68]	17.5	35.2 *
ECO		17.5	43.2 *
CO		21.6	50.1 *
CSM	25.1[54], 27[50], 27[60], 32[60]	24.7	51.5 *
FKM (50% HFP)	31.5[59], 100[52], 55[52]	70.4	81.2

Table 6 Limiting Oxygen Index, Literature and Calculated

*For these polymers the ratio of C/O < 6, so the LOI using a calculated heat of combustion is considered unreliable by Johnson.

Considering LOI values obtained from literature, two problems are encountered: the first is the absence of reported values for some of the polymers, the second is that they refer to compounded and vulcanised rubbers, not pure elastomer. Whilst these values are more useful to the industrial user, they do not allow for a fair evaluation of the methods of prediction reported. Additionally, work by Janowska [49] reported rather high LOI values for BR 25.9[49] , SBR 26.0[49] and NBR 26.5[49], for polymers that were lightly cross-linked with organic peroxide, but otherwise unfilled. For FKM an LOI value of 31% is reported by Hirsch [59], somewhat surprising since fluoroelastomers are promoted as being extremely resistant to burning. The absence of hydrogen and a high percentage of fluorine should provide this low flammability; but there is little reported evidence to support this claim. Fabris [52] reports that FKM materials are extremely sensitive to compounding additives: a lead oxide cured hexafluoropropylene-tetrafluoroethylene FKM compound was quoted with an LOI of 100%, but when cured with magnesium hydroxide was reduced down to 55% LOI. This highlights the difficulty of comparing LOI values for cross-linked compounds which vary considerably in composition.

Considering the calculated LOI values, there is considerable variance for the oxygen containing polymers, as recognised by Johnson. For the hydrocarbon and chlorine containing elastomers the estimates are reasonable ignoring the effects of fillers, etc. LOI is sometimes criticised as a less relevant flammability test since it is not a realistic fire scenario, using an enriched oxygen environment at room temperature. Assuming ignition from an already burning source; a real fire scenario has almost the opposite conditions: high ambient temperature and lower oxygen levels. LOI is still however a widely used measure for materials and within a number of fire specifications, particularly for small products. An example of this is the rolling stock fire code BS6853 [69], with a limit of 28% and 34% for exterior minor use materials, and it is this common acceptance of LOI that still makes it important for the assessment of rubber flammability.

1.7 Fire Safety and Standards for Rail Transportation

1.7.1 Hazards

In the UK during 2000 there were 331 passenger train fires reported. Of these 56% were due to arson [70], with the majority of the remainder technical faults; electrical and mechanical causes accounting for the majority. An additional risk factor for fires is the modern phenomena of deliberate terrorist bombings, witnessed in cities such as London (2005), Madrid (2004), Moscow (2004) and Mumbai (2006) [71].

Rail vehicles present particular difficulties and hazards to passengers and rail operators. Firstly, evacuation of carriages presents difficulties. There will be a delay between the development of a fire and detection, and if the train is moving then there will be a delay for the train to stop, ideally to a place for safe egress. If the train is derailed and turned on its side, then escape will be dramatically slowed, since the configuration of a carriage will create an obstacle course to exit. If the carriage becomes filled with smoke then the time to exit can become much longer. Long egress times are most acute in many older city metro systems, such as the London Underground network, which has a number of deep single tunnels with no possible side access between stations.

In a previous review [72] it is stated that a major cause of fires is related to the high voltage electrical systems involved in mass transit systems, such as arcing or shorting of the third rail, breakdown of insulation around the motor control boxes and grease or dirt collecting underneath the carriage. A number of studies of fire hazards and test methods for rail passenger vehicles were carried out by the NIST (National Institute of Science and Technology). Most fire scenarios evaluated the ignition of litter to test materials such as seat upholstery [72-74]. Kaminski reported tests carried out on the smoke emission of various materials used in Polish rail vehicles [75]. It was concluded that unacceptable smoke levels were produced by some ‘untreated’ rubber products and PVC flooring and covering products.

1.7.2 Fire test standards for the rail Industry

In many of the application areas for rubber, the flammability and burning behaviour is of particular concern. In mass transportation such as rail vehicles, a wide range of fire codes and specifications exist to attempt to minimise the risk of fire, and exposure to smoke and toxic gases to the traveller. There are a large number of fire test standards within the rail industry alone. Some appear almost unique in the detail of application, but many are based on wider industry standard tests used in the construction industry. Most fire requirements have three main aspects that are of interest to rail industry stakeholders, namely burning, smoke and toxicity. Although the standards share these common themes, the actual measures vary greatly, and in most cases results cannot be translated across standards. The greatest variations are apparent with the burning tests, where factors such as ease of ignition, surface flame spread, surface penetration and energy released are quantified. One value is not necessarily a good indicator of the other characteristics. Some typical requirements are noted in Table 7. In addition, some local networks such as London Underground have developed more stringent requirements due to the increased hazard from deep tunnels and limited access, making evacuation difficult.

Territory typically applied	Specification
North America	NFPA 130
European Union (draft)	CEN/TS EN45545-2
UK	BS 6853, GM/RT 2130
France	NF 16-101
Germany	DIN 5510
Italy	UN1501201182

Table 7 Examples of railway fire regulations

Significant rubber articles within rail vehicles may include flooring, door and window seals, gangway connectors, anti-vibration mounts and suspension products. Compliance for rubber products has been difficult to achieve whilst maintaining acceptable physical properties and elasticity, and the stringent requirements of CEN/TS EN45545-2 has led to speculation that rail vehicles designers will exclude larger components made of thermoplastics and rubber to enable compliance [76]. Rail vehicle manufacturers may grant concessions for the use of some non-compliant materials, but this may not be acceptable in the longer term. Most recently Tooley [77] reviewed the current state of railway fire regulations, and cites rubber suspension articles as examples of non-compliant products. The problem of rubber flammability is acknowledged within GM/RT 2130, with rubber suspension elements when externally mounted, and hoses etc., within the area served by the engine fire protection system, are specifically excluded. This presents a significant challenge for rubber compounds to compete with other non-polymeric materials which are not flammable, e.g. steel springs. The approach within CEN TS EN45545-2 to toxicity measurement uses either a static tube furnace NFX-70-100 for small components, or the smoke density chamber ISO 5659-2 for larger components using FTIR for gas analysis. These have been significant problems with reproducibility of this method and the EU TRANSFEU project is attempting to rectify these problems through continuous monitoring using FTIR gas analysis.

1.8 Thermal decomposition of polyisoprene polymer and compounds

1.8.1 Thermal decomposition mechanisms of polyisoprene polymer

Heating polyisoprene polymer leads to mass loss and exothermic behaviour as it decomposes into volatile fragments. The use of thermogravimetric analysis (TGA) to monitor mass loss and differential scanning calorimetry (DSC) to measure the behaviour of elastomers has been used widely to characterise thermal decomposition. These techniques are well established for elastomers and the older published literature has been reviewed by Brazier [78]. Sircar makes extensive use of DSC [79,80] and TGA/DTG [81] to identify the type of polyisoprene, whether synthetic or natural in origin. NR and IR raw polymer have identical DTG curves with a single large mass maximum mass loss peak at 373°C [82] in N_2 with less than 0.5% residue at 500°C. Differences between IR and NR, described later, have been observed in rubber compounds.

Polyisoprene mostly decomposes by random chain scission, the random breaking of bonds within the polymer chain eventually leading to volatile formation. This is likely to initiate at a ‘weak link’ due to a chain defect. This defect may be due to residues from polymerisation such as initiator, or some head to head linkages in the polymer. Whilst the alternative polymer decomposition mechanism, end-chain scission; yields high level of monomer, the products of random chain scission will be a broad distribution of molecular species, from sub-monomer fragments up to larger oligomers. Common chemical species detected from decomposition are regularly identified as isoprene (2-methylbutadiene)(A) and dipentene (1-methyl-4-(1-methylethenyl)-cyclohexene)(B), for which the yield quantities vary considerably, depending on the temperature and conditions of thermal decomposition. Typically, at temperatures below 300°C, the yields of isoprene and dipentene may be in the region of 5 and 15% [83]. At higher temperatures, however, the isoprene yield may be significantly higher. A simplified process of depolymerisation at lower temperatures and by mechanicochemical stress is summarised by Cataldo [84] with the scheme proposed in Figure 7. However, at higher temperatures more species are generated, including 2,4-dimethyl-2-ethenylcyclohexene.

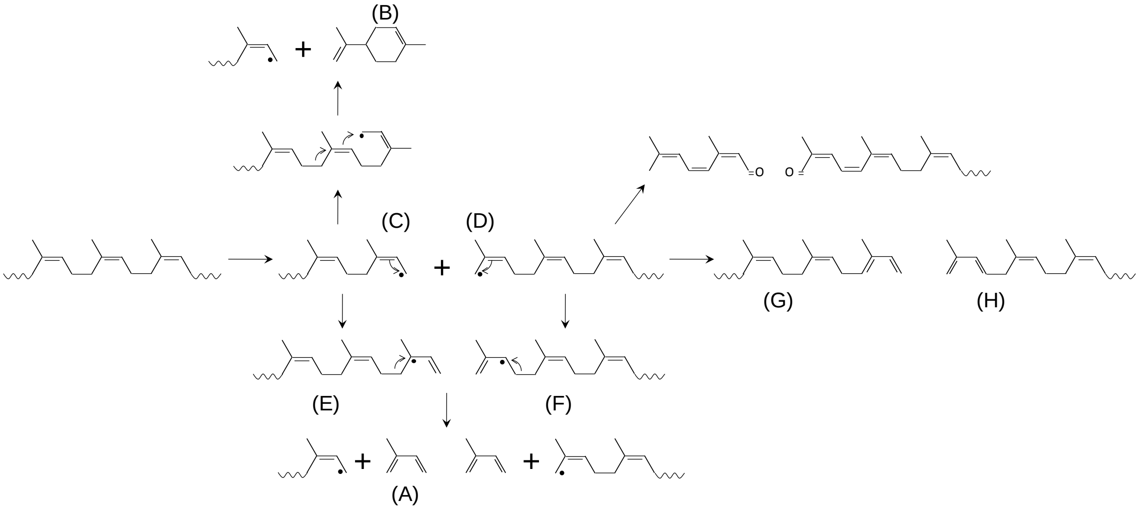


Figure 7 Decomposition scheme for polyisoprene (Cataldo)

Colin [85] studied the thermal oxidation of unvulcanized synthetic polyisoprene; undertaken using FTIR between 40 and 140°C, and rheological changes at 230°C under nitrogen. It is considered in this paper that IR predominantly decomposes by random chain scission at this temperature range. An initial free radical displacing a hydrogen atom then allows available oxygen molecules to be introduced to the main chain, leading to peroxy-radical structures which rapidly reduce the polymer chain length.

Quantitative analysis of the products of thermal degradation was undertaken on polymers including IR by Reshetnikov [86]. Degradation products from 500 to 1000°C are shown in Table 8. At 500°C isoprene evolution predominates, but at 600°C onwards the yield diminishes; a corresponding increase of intermediates such as propylene, isobutylene, ethylene and methylbutene is apparent. From 900 to 1000°C the predominant product is methane, indicating the completion of the decomposition process from polymer to the simplest hydrocarbon.

Substance	Temperature (°C)					
	500	600	700	800	900	1000
methane	0.73	3.47	8.49	38.99	58.24	83.58
ethane	0.31	1.36	3.51	7.58	6.23	4.3
ethylene	1.12	4.72	8.39	10.47	26.36	12.12
propane	0.39	1.11	1.76	1.14	0.51	-
propylene	1.26	4.86	7.11	10.71	3.49	Traces
isobutane	-	Traces	0.26	0.27	-	-
n-butane	-	-	1.17	0.32	-	-
?	-	-	0.24	0.24	-	-
Isobutylene	-	3.76	7.14	12	2.79	-
trans-2-butene	-	Traces	1.03	0.85	Traces	-
cis-2-butene	-	Traces	0.81	0.53	Traces	-
1,3-butadiene	-	0.9	1.68	2.6	1.16	-
3-methyl-1-butene	-	0.84	2.34	Traces	-	-
2-methyl-1-butene	-	6.23	5.3	1.55	-	-
2-methyl-2-butene	Traces	9	14.66	4.2	-	-
isoprene	96.12	63.75	36.14	8.55	1.22	-

Table 8 percentages of polyisoprene degradation products at various temperatures (reproduced from Reshnetikov)

There is some consensus in the literature on the decomposition process to isoprene, but the overall composition of the mixture is more varied. This may result from variations between synthetic polyisoprene and natural rubber, differing techniques and compounding additives. Overall the picture is evident that polyisoprene decomposes dramatically to low molecular weight fragments which vapourise into fuel for combustion, with almost no char to slow down decomposition. This suggests polyisoprene will burn readily with high heat release and with high yields of small aromatic species that will create high levels of smoke.

1.8.2 The effects of additives and cross-linking on the decomposition of polyisoprene

From the literature there is good evidence that cross-linking imparts improved thermal stability to polyisoprene rubber compounds at temperatures below 200°C, but at higher temperatures may have a positive or negative contribution to stability. Colin [87] considered the effect of the influence of sulphur vulcanization, which was measured using mass changes and thickness of oxidised layer (TOL) during oxidation from 60 to 150°C. In comparison to uncured IR, the sulphur cross-linkages impart improved stability, which was observed in the TOL, which increased. This is explained by the ability of sulphur-containing species to destroy hydro-peroxides.

The effects at higher temperatures are considered in a study by Straus of the thermal degradation of natural rubber compounds [83]. Samples were prepared with varying levels of additive typically associated with rubber compounds, and levels of vulcanisation varied. Rates of volatilisation were measured between 300° and 325°C, and the addition of 1 phr stearic acid increased the yield of total volatiles by between 5 and 11%, but showed little effect at pyrolysis temperatures. Volatile yields were also increased in a compound that had experienced a longer and hotter vulcanisation, indicating thermal degradation during the cure process. Additional volatile evolution was also noted after the milling process, indicating degradation during processing. Activation energies for the volatilisation reaction were calculated using the Arrhenius equation, showing a noticeable increase for the compounds containing organic accelerator (typically 274 $kJ.mol^{-1}$) compared to compounds with no accelerator (typically 248 $kJ.mol^{-1}$). Overall, the rate of volatilization was higher for vulcanized than unvulcanized rubber, signifying a destabilising effect of cross-linking at this temperature range.

Pyrolysis studies were performed at approximately 390°C with the capture of condensate and residue at five temperature ranges using liquid nitrogen traps. Analysis was made of the pyrolysate and residue to attempt to understand the effects of additions and vulcanization on products such as char, ash, residual sulphur and notably the presence of small molecules, using a mass spectrometer. The presence of zinc oxide increased the yield of carbonized rubber (char) by a factor of 2. The addition of carbon black also increased overall char yield, but only in proportion to the level of addition, and did not promote char yield in the polymer. The yield of isoprene monomer was examined in detail, and the presence of both carbon black and zinc oxide did not affect yields. The monomer yields were, however, significantly reduced by the process of vulcanization in the presence of sulphur. It was suggested in the paper that a break occurs in the polymer chain at the $CH_2 – CH_2$ bond where the monomer units join, so forming two free radicals, shown in Figure 7 as C and D. This is thought to unzip along the chain to form monomer and dimers (E and F). This process continues until the free radical becomes saturated by abstracting a hydrogen atom or combining back with a free radical (G and H). The presence of sulphur, whether in a cross-link or not, should aid the termination of this process by displacing the double bond which is necessary for the unzipping reaction.

One study by Choi of the pyrolysis of NR vulcanisates using Py-GC/MS has shown that the level of cross-linking can affect the yield ratio of pyrolysis products evolved, which in this study were predominantly isoprene monomer and the cyclic structures 1,4-dimethyl-4-vinylcyclohexene and 1-methyl-4-(1-methylethenyl)-cyclohexene [88]. Jiang [89] also examined the effect of cross-linking on the thermal stability of polyisoprene and polychloroprene. For polyisoprene the onset temperature is slightly reduced, most likely due to the evolution of some smaller chain fragments evolved from cross-linking. The main decomposition step however occurred at a slightly higher temperature, so cross-linking conferred a minor improvement in thermal stability. Overall, compounding additives and vulcanisation has a relatively small influence on the thermal decomposition of polyisoprene, with no influence on the ability of the polymer to yield char. The interaction of cross-linking agents with polymerisation initiators has highlighted differences between natural (NR) and synthetic (IR) polyisoprene. When compounded with carbon black and sulphur into a typical commercial formulation a difference is noted; the NR mix retains a single peak temperature for mass loss, but the IR compound shows a second mass loss peak at around 430°C [82]. In this case the IR grade used was Natsyn 2200 polymer with a high proportion of cis-1,4-polyisoprene units. Sircar [80] refined this observation showing that compounded IR has a significant second peak, at 421°C, and that NR has a very small peak at this temperature which may easily be overlooked. Variation of sulphur levels demonstrates that the sulphur addition caused this effect, with higher levels of sulphur showing the greatest second DTG peak value. Using DSC, Sircar also notes that NR recipes have a generally lower area of exotherm than IR, which varies considerably between commercial grades. It is proposed that IR polymer may behave differently due to cyclisation, catalysed by small quantities of remaining titanium tetrachloride used in Ziegler-Natta polymerisation, since titanium tetrachloride has been reported as a known cyclising agent for NR and IR.

1.9 Burning Behaviour of Rubber

1.9.1 Cone Calorimetry

The Cone Calorimeter (ISO 5660 part 1 [40]) has increasingly become established over the last 30 years as a fire test for a wide range of materials. This technique allows the assessment of burning behaviour while the sample is subjected to infrared radiation from an electrically heated cone assembly, and by using oxygen depletion calorimetry and known test conditions the heat release can be calculated [41] in (close to) real time, along with smoke generation, CO and CO_2 evolution and mass loss. Of particular value is the heat release rate (HRR) as a function of time showing the rate of fire growth, giving a better way to categorise the burning behaviour of materials than a single value. A limited number of reports of cone calorimetry data of rubber were found in the literature, with results below (Table 9).

Material	Source	Imposed heat flux KW/m^2	Time to ignition secs	HRR peak KW/m^2	HRR peak at time secs	HRR average KW/m^2
PNR	Mizuno[90]	50	46	3300	83	
NR	Liu [91]	35	29	1222		630
NR	Wang [92]	35	32	602	~80	365
NR	Wu [63]	50	29	1733	95	
NR	Jincheng [93]	50	25	2080		1600
SBR	Wu [63]	50	18	1984	76	
SBR	Peacock [94]	50	35	300	90	
NBR	Wu [63]	50	46	2355	110	
FR-NBR A	Moon [95]	50	9	142		98
FR-EPM B	Bugajny [96]	50	~50	1650	~170	
FR-EPDM	Zhang [97]	50	81	334		
CR	Cusack [98]	50		314	113	
CR	Lyon [46]	50	46	205		
CR	Peacock [94]	50	45	400	70	
CR	Peacock [94]	50	31	295	50	
CR	Peacock [94]	50	26	190	100	
VMQ	Fang [99]	35	43	361	120	
VMQ	Lyon [46]	50	68	110		

Table 9 Compiled cone calorimeter values for selected rubber compounds

A- Sponge compound fire retarded with 195 pphr ATH

B- Fire retarded with 100 pphr MH

Whilst the cone calorimeter is a useful tool for fire scientists because of the wide range of experimental options and data streams available, this creates difficulties when attempting to compare data from the literature, as Table 9 shows. Different practitioners favour different heat flux rates and report different measures, while other factors which affect heat release are not constant. Indeed, it may well be that reported parameters are selected to show the best improvements in flammability. Sample thickness and the sample holder arrangements [100] can influence measured values, and these variations are not always reported. Considering the data, it is significant that hydrocarbon rubbers have the shortest time to ignition, and the highest peak heat release rates; and that CR and VMQ perform significantly better, with much lower peak heat release rates. Attempts at calculating single measures of burning hazard have been made for the cone calorimeter, such as FIGRA (fire growth rate index)[100] and MARHE (Maximum Average Rate of Heat Emission)[101], but are not universally adopted, so variety in reporting is likely to continue.

1.9.2 Smoke

In an enclosed environment such as a rail vehicle or tunnel, the obscuration effect of smoke can have a significant impact on the ability of people to evacuate [71]. Peacock [94] tested polymeric products for use in trains and found that chloroprene door and window seals exceeded the maximum permissible levels, when tested in the smoke density chamber. Some reported smoke data have been compiled in Table 10.

Material	FR additive	Source	$D_s(1.5)$	$D_s(4)$	time at D16 (secs)	$D_s(max)$
SBR		Peacock [94]	6	147		
CR		Peacock [94]	205	509		
CR		Peacock [94]	202	499		
CR		Peacock [94]	43	347		
CR		Lawson [58]			30	692
AEM		DuPont [67]		60		
FR-AEM	120 ATH	Lawson [64]			103	201
CSM		Lawson [58]				332
FR-EPDM	200 ATH	Lawson [64]			138	354
FR-EPDM	200 ATH	Mouseman [13]		17	168	168
FR-EPDM	200 MH	Mouseman [13]		12	264	66

Table 10 Complied smoke density chamber data for selected rubber compounds

Different measures are taken using the smoke density chamber [102], usually according to the industry requirement. $D_s(1.5)$ and $D_s(4)$ records the smoke density at 1.5 and 4 minutes, time at D16 is the time in seconds to reach a D_s smoke density of 16, and $D_s(max)$ is the maximum smoke value recorded, usually at the end of the test. It is clear however from the literature that CR had the highest levels of smoke density generated, which may be expected under forced combustion. This is due to the action of the chlorine inhibiting flaming combustion, so leading to the formation of the sooty fragments resulting from the coagulation of products of incomplete combustion, such as polycyclic aromatic hydrocarbons and other smoke pre-cursors, which constitute the smoke. This is one reason for avoiding halogenated polymers or fire retardants if smoke is a concern. For a zero-halogen system the use of heavily filled EPDM and AEM is now more commonly used, and Mouseman [13] shows the benefit of magnesium hydroxide in EPDM for low smoke generation.

1.9.3 Toxicity effects from burning rubber

Most fire deaths and most fire injuries result from inhalation of toxic smoke [103]. The main toxicant, carbon monoxide is formed under conditions of under-ventilation, during non-flaming, pyrolysis, and in the presence of halogens [104] [105]. There is limited published data on the toxicity of gases from the burning or pyrolysis of elastomers. One study measured the effects of gaseous emissions from burning polymers on mice [106], where polymer samples were pyrolysed in a tube furnace and the emissions were connected to an animal exposure chamber designed to enable direct observations. Pyrolysis was carried out in two ways; at a linear heating rate from 200°C to 800°C, and at a fixed temperature of 800°C: observations were made of animal behaviour, in stages from the first sign of incapacitation through to death (Table 11); in a related paper [107] CO levels from the toxicity screening programme were determined by gas chromatography of samples of the chamber atmosphere, also collated.

Rubber type	CO ppm 200°C to 800°C	CO ppm 800°C	Mortality time (mins) 200°C to 800°C	Mortality time (mins) 800°C
EPDM	12333	13733	20.7	10.6
SBR	10450		24.1	13.8
IR	10450		22.1	11.7
Silicone	8850			
CR	7317	6400	23.1	12.2
CSM	7000	8100	19.4	9.6
NBR	4550	3900	15.8	4.3

Table 11: Pyrolysis CO yield and mortality rate for selected rubber compounds

NBR has the higher rate of mortality and whilst this work does not detail the species emitted, it could be proposed that the C≡N group on the acrylonitrile may have yielded HCN, a potent toxic gas. The other rubbers had similar mortality times, with no clear distinction between hydrocarbons such as IR, EPDM and SBR, and the halogenated polymers CSM and CR. NBR, whilst the most potent in the toxicity paper, has the lowest CO yield, also suggesting that another toxic gas, such as HCN, was responsible for the higher mortality rate.

More recently, the combined influence of toxic gases has been approached in a more sophisticated, and less contentious manner, with a wider range of gases sampled to study the effects of burning polymers on health. One industry test is NFX 70-100 [108], which burns a sample within a tube furnace and determines the concentration of some known toxic gases. Each measured concentration (t_i) is divided by a nominated ‘critical concentration’ rating, and then each component summed so as to allow an additive toxicity rating, known as the CIT value, calculated in Figure 8.

$$\mathrm{CIT} = 100\,\mathrm{X} \sum \frac{t_i}{cc}$$

Figure 8 Equation for calculation of CIT value for NFX 70-100

Gases measured	Critical concentration “cc”
carbon monoxide	1750
carbon dioxide	90 000
hydrogen chloride	150
hydrogen bromide	170
hydrogen cyanide	55
hydrogen fluoride	17
sulphur dioxide	260

Table 12 Critical Concentrations by gas for NFX 70-100

Relating this to rubber compounds, it is likely that the use of halogenated fire retardants will lead to a high CIT value. It is also likely that NBR will yield a higher HCN yield which has a very low critical concentration, so resulting in a high CIT. The lowest CIT value may be expected to come from silicone rubber, with the lowest generation of CO_2 of all the elastomers (Table 5). This approach is adopted as one method for toxicity assessment within CEN/TS 45545-2 as a mass based method for small articles, the most stringent requirement of a CIT of 0.75 maximum for external cables used in category HL3.

1.9.4 Effect of additives on burning behaviour

The effects of commonly used additives within rubber compounds on flammability provide useful insight. Janowska has investigated the use of fillers in polyisoprene. In one study[109] the effect of surface area of carbon black is considered, showing by thermal analyses that carbon black with a higher surface area improves thermal stability. The flammability of carbon black filled rubber compound was evaluated using limiting oxygen index (LOI), with the highest surface area carbon black yielding the highest value of 27%, and the lowest surface area yielding the slightly lower value of 26%, showing a relatively insensitivity to LOI. For an unfilled formulation an LOI of 19% was obtained, somewhat closer to other literature values (18.2%[62], 18.5%[63]). Mineral filler loadings [110] also improved the LOI value; 10 pphr of precipitated silica improved the LOI to 27% and 60 pphr gave 28%.

It is known that char development in thick articles manufactured in natural rubber compounds reduces burning by generating a surface crust. This char acts as an insulating barrier, which shields the substrate from radiant heat, reduces the conduction of heat through the depth of the substrate, and reduces the rate of fuel gasification. In one study [111] a moulded outer 'collar' was produced in a highly filled natural rubber compound (Figure 9), using material such as asbestos fibres and devolite clay. Whilst the highly filled clay based formulation delivered the highest level of passive fire protection, the addition of a thick collar manufactured in a conventional NR compound was almost as effective.

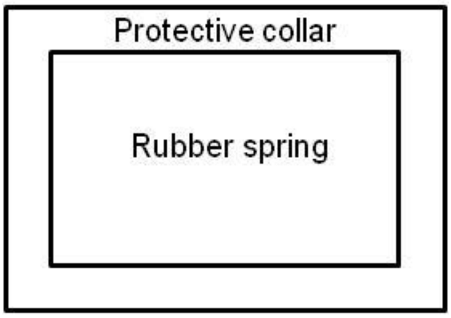


Figure 9 Illustration of protective collar as a passive fire barrier

Carbon black, already present as a reinforcing filler, certainly has some stabilising influence as a protective residue, through its barrier formation. This will be most effective in thicker samples. Whilst it will slowly decompose in air, under a flame where the oxygen concentration is less than 1%, it is not likely to add to the fire load within the time scale of interest. The use carbon black with a large particle size and lower reinforcing behaviour will allow greater loadings of the recipe for a given elastic modulus. Carbon black is a free radical scavenger so may slow decomposition, unlike mineral fillers which show little interaction with the decomposing polymer [109,110]. In contrast to this, the textbook 'Rubber Basics' [112] states that carbon black should be avoided in fire retardant rubber compounds- "…*as carbon black supports combustion, burning readily in the presence of oxygen*". Since carbon black is predominantly elemental carbon, with a sublimation point of over 3915K, within any conceivable fire scenario it can only burn in the solid phase by smouldering combustion in adequate oxygen. This process is somewhat slower than flaming combustion and can make only a small contribution to heat release, but may increase CO yield and afterglow. Thus it is considered that the main reason to reduce the level of carbon black in a fire retardant formulation is to increase the addition levels of an active fire retardant, such as aluminium hydroxide (ATH).

Yao [113] increased the development of char in polyisoprene by creating novel cross-links, made possible by the initial lithiation of the polyisoprene prior to cross-linking. It was suggested that the type of cross-link; not the quantity, has the ability to influence the thermal stability of a polymer. A range of aliphatic and aromatic mono and di-chloro compounds were evaluated for the effect on thermal stability, and the aromatic dihalide cross-links significantly increased char yield, confirming the proposal.

1.10 Fire Retardants

The wide variety of potential fire retardants can be classified in various ways. Three common classifications are mode of action (how they work), means of incorporation, and by chemical type. Each of these classifications is described briefly.

1.10.1 Classification of Fire Retardants by Mode of Action

Many fire retardants operate by more than one mechanism, some of which are described below. It has generally been accepted [114] that fire retardants which work by chemical action are more effective (by level of loading) than fire retardants which work by physical action, though the distinction between the two classifications may not always be clear.

1.10.2 Physical Action

The incorporation of a fire retardant which decomposes endothermically, such as hydrated filler, will remove heat from the material and flame, and gases evolved can dilute the flammable vapours to below the ignition limits (temperature or mass fraction) of the gas mixture. Other additives, such as carbon nanotubes, increase the thermal conductivity of a material, so dissipating heat away from the ignition source. Another approach is the creation of a barrier between the heat source and the underlying material, such as by use of an inert material. Carbon black acts in this way, as does the aluminium residue resulting from the decomposition of ATH. This layer can prevent oxygen reaching the pyrolysis zone, slowing the rate of fuel production or prevent volatile gases reaching the flame, and impede heat transfer by providing a radiation shield and thermal insulation. An enhanced variation of this is the formation of a swollen barrier known as an intumescent fire retardant. Finally the incorporation of non-combustible substances, such as fillers, can inhibit burning by reducing the flammable content.

1.10.3 Chemical Action

The fire retardant may decompose to evolve gases which react within the gas phase to interrupt the radical propagation mechanisms during burning. These gases typically ‘quench’ the flame by producing unreactive radical species which are unable to propagate the free radical reaction necessary for flaming combustion, while increasing smoke, carbon monoxide, and other products of incomplete combustion. Other fire retardants work by promoting char development, so reducing the availability of combustible gases. This is most effective in polymers with a tendency to char, where the fire retardant promotes dehydrogenation of the polymer, leading to unsaturation, cross-linking and cyclization. This deprives the flame of fuel, since the char requires a significantly higher temperature to burn. The char will then also behave as a physical barrier to heat and fuel transfer.

1.10.4 Classification of Fire Retardants by Means of Incorporation

Reactive fire retardants are covalently bonded to the polymer chain. They may become part of the polymer during polymerisation, or grafted on as side chains. As part of the modified polymer, they will not leach or migrate to the surface and remain effective for the life of the product. They are likely to profoundly affect the physical and chemical properties of the new polymer, and will yield different decomposition products. By being integral to the polymer and uniformly distributed within it, they have greater efficacy as fire retardants than when used as an equivalent additive [115].

Additive fire retardants are typically added to the polymer after polymerisation, must be compatible with the polymer, and can migrate to the surface and volatilise or leach out. A third method of protection is the use of a fire retardant coating, typically showing intumescent behaviour [116]. Intumescent coatings, which swell or foam on heating, are used to protect the underlying materials by providing a insulating barrier to heat and gas flow to the substrate. They have also been used extensively to protect structural steelwork from excessive heat during a building fire to prevent buckling and collapse, and for the protection of flammable areas, e.g. in oil installations.

1.10.5 Use of Additive Fire Retardants in Polyisoprene

For most users, the service application dictates the elastomer chosen. On this basis the rubber formulator may typically make use of additives to modify the burning behaviour of the chosen polymer. Such approaches to fire retarding polyisoprene, predominantly natural rubber, are reviewed in this section.

1.10.6 Halogenated additives

Chlorinated waxes have been used in conjunction with antimony trioxide for a range of common elastomers [117]. A wide range of rubber compounds were tested, both unmodified and formulated to become non-burning against a military horizontal strip burning test, similar to UL94 HB test. Natural rubber was rendered non-burning with the addition of 25 phr antimony oxide and 50 phr chlorinated paraffin wax (70% Cl) and synthetic polyisoprene with the addition of 20 phr antimony trioxide and 40 phr chlorinated paraffin wax. Whilst both compounds suffered a significant drop in tensile strength, the IR recipe was affected less, probably due to the lower loading levels.

The use of brominated additives is common and known to be effective in producing reduced flammability and self-extinguishing behaviour. Ismawi [62] determined that the addition of 7.5 phr antimony trioxide and decabromodiphenyl oxide (DBBO) in natural rubber yielded a UL-94 rating of V1 and an LOI of 22.6%. 40 pphr chlorinated paraffin (CP) wax was fairly ineffective, but with 20 pphr antimony trioxide achieved UL94 V2, and with 20 pphr zinc hydroxystannate (ZHS) achieved V0. CP was considered to be relatively inefficient because it promoted dripping in the samples, possibly due to a significant reduction in the compound viscosity.

1.10.7 Phosphorus based additives

Fire retardants containing phosphorus are a large family of materials which may be incorporated into a polymer by additive or reactive techniques [118]. They are considered to work mainly in the condensed phase, by promoting char formation, depriving the gas phase of further volatile decomposition products. It is suggested that depending upon the chemistry of the additive and polymer they also work in the gas phase either as flame inhibitors, interrupting the cycle of free radical generation. Some organic phosphorous compounds are thought to be sufficiently stable under flaming conditions to work by a physical gas-phase action, in which they act as a blanket to exclude oxygen from the flame. Phosphate esters are cited as an example of this action, evidence for this being gained from analyses of the gas emitted and the solid polymer residue [119].

Phosphorus based additives are particularly effective in oxygen containing polymers, such as cellulose, polyurethane and polyester resins [120]. Upon heating in the presence of oxygen the phosphorous decomposes into phosphoric and phosphonic acids, which accelerate chain stripping processes and removal of side groups which may react with the phosphorous to become less flammable species than in a phosphorus-free material.

Red phosphorous is sometimes used for polymers as a fire retardant, but has to be employed with care since it is itself flammable in the pure form. This approach can be highly effective at lower loadings since it is in the most concentrated form, but can in certain conditions revert to the more dangerous allotrope white phosphorus, which is highly toxic and will spontaneously combust in air. To reduce the hazards of red phosphorus powder, masterbatches and dispersions are available for processors [121]. Red phosphorus is often used in conjunction with nitrogen compounds with a high degree of synergism possible. In one study red phosphorus was combined with a novalac resin as a charring agent and melamine as an amino-triazine compound [119,122] in poly(oxymethylene) (POM). POM is a highly flammable polymer, with the low LOI value of 15-16%, with around 53% oxygen within the polymer chain. When the polymer decomposes the flammable gas formaldehyde is evolved as a ready source of fuel for combustion. The phosphorus decomposes to form phosphine which as able to combine with the formaldehyde within the condensed phase to create a cross-linked network, so reducing the level of availability of fuel.

Ammonium polyphosphate (APP) is a commonly used phosphorous based fire retardant, usually most successfully in oxygen containing polymers. It is often used in intumescent paint formulations and coatings, in conjunction with a blowing agent, such as melamine, and a source of carbon, such as pentaerythritol (PER) [121], although many degraded polymers can themselves provide the source of carbon [123]. In one study [124] APP was studied within a polyurethane coating, with consideration being given to the rheological behaviour of the mixture during thermal decomposition. This highlights the importance of the visco-elastic properties on the ability of the fire retardant to act as a blowing agent, so creating an intumescent barrier to heat and mass flow; if the melt viscosity of the degraded polymer is not sufficiently low at the temperature of the gas evolution then volumetric expansion will be hindered. A study of the use of ammonium polyphosphate in SBR, and an interaction with aluminium trihydroxide, was made by Castrovinci [125]. APP gave significant reductions in levels of peak heat release, CO, CO_2 and smoke when incorporated at 12%, by the formation of an inorganic continuous shield known as ultraphosphate. During this degradation of APP the evolution of ammonia and water act as blowing agents, forming intumescent foam below the ultraphosphate glass at the burning surface. At much lower and higher levels however, the effect was less effective. From thermal decomposition and evolved gas analysis it was advanced that at the higher loadings the APP promoted degradation of the SBR polymer, reducing the effectiveness of ultraphosphate at the surface. The interaction of APP with $Al(OH)_3$ was also considered, and interestingly a strong antagonism was reported. At an optimum APP loading of 12%, as little as 1% $Al(OH)_3$ reduced the effectiveness of the fire retardants. APP generates acidic gases, whilst $Al(OH)_3$ is basic which promotes a reaction between the two materials. The $Al(OH)_3$ reduces the production of ammonia and acidic OH from APP than from APP when heated alone, observed by a significantly reduced mass loss from TGA. Aluminium phosphate is generated as a result, which disrupts the generation of the glassy form of ultraphosphate, so reducing the effectiveness of the surface barrier.

One family of phosphorus based fire retardants are liquid phosphate esters, which have been used within both reactive and additive systems [126] [118]. In a reactive system they will become an integral part of the copolymer, but as an additive they can serve an additional function, as a plasticiser. In this way they can be considered as replacements for mineral oils in elastomers. Even if the burning behaviour of the elastomer does not benefit greatly from the presence of the phosphate ester, the replacement of a flammable mineral oil will slightly reduce the fuel content of the formulation. The effect of 2-ethyl hexyl diphenyl phosphate was studied in natural rubber, added at levels of 10, 15 and 20 pphr [127]. The effect on flammability as measured by LOI was minimal, with an increase from 17.0% for an unmodified recipe, to 17.5% at the 15 and 20 phr addition levels. There were adverse effects on the physical properties of the rubber compound, with a reduction in the retained tensile strength and elongation at break after hot air ageing, and a noticeable surface bloom, indicating a lack of compatibility between the polymer and the phosphate ester. The lack of any charring tendency in polyisoprene’s structure would indicate that phosphate esters are unlikely to act as a fire retardant in the condensed phase, possibly explaining the poor performance. The mild improvement reported may be due to flame quenching action of phosphorus in the gas phase. In an earlier study, a natural rubber compound was tested with the addition of 7 phr of a phosphorylated cashew nut shell liquid (PCNSL) and 10 phr of a brominated version of PCNSL [128]. Even with the presence of a halogenated additive, the burning behaviour was poor. The LOI was measured at 17%, very close to that of the unmodified material. With 100 pphr of ATH as well, the LOI increased to 22%. The effect of the ATH without PCNSL was not reported however, so any synergy between the two additives cannot be ascertained. Overall it is considered that the addition of phosphate esters alone would not be sufficient to have a significant impact on the burning behaviour of polyisoprene.

1.10.8 Nitrogen containing fire retardants

Upon thermal decomposition, melamine produces ammonia gas, which dilutes the fuel content in the gas phase. In addition, it also acts as a blowing agent in intumescent systems. In terms of efficiency they are classed as being in between halogenated materials and hydrated fillers such as aluminium and magnesium hydroxide, which require the highest loading levels [129]. Melamine cyanurate (MC) [56] has been used at 17% in a polyisoprene compound, along with 5% chlorinated wax and 1% antimony trioxide. This yielded an increase in LOI from 19 to 28%. MC functions by endothermic decomposition when heated, leading to the production of ammonia, and various decomposition products such as melem, melam and melom. These condensation products can form a superficial char layer, which can slow down further thermal decomposition by acting as a stabilising barrier to heat flow.

1.10.9 Phosphorus / Nitrogen Synergism

Jincheng [93] synthesised an intumescent fire retardant (IFR) using phosphorus and nitrogen based chemistry (Figure 10).This was added to natural rubber in steps up to 60 pphr, at which point UL94 V0 was achieved along with an LOI of 27.5%. Heat release rate was also reduced to around a third of the unmodified NR compound. Some drop in physical strength was also measured, but remained at acceptable levels.

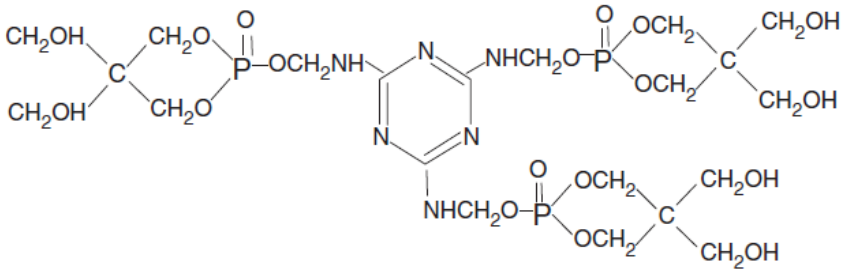


Figure 10 Structure of a phosphorus / nitrogen IFR structure (Jincheng)

1.10.10 Zeolites

Zeolites are naturally occurring or manufactured aluminosilicate minerals that are porous, with a regular pore structure of molecular dimensions, and often known as molecular sieves. Whilst they are predominantly used in detergents and the construction industry, they are finding use in various other fields, and are of increasing interest as fire retardants. It is considered that the zeolite acts by promoting char formation and stabilising the residue. An approach was taken to fire retard natural rubber by Jincheng [130], using a system of a proprietary APP/PER/melamine additives compared to a microencapsulated version with 4A zeolite. Use of the zeolite system resulted in improved FR properties when added at levels of over 50 pphr, for APP, PER, ME, and 4A zeolite mixture with a mass ratio of 3: 1: 1: 0.15. This works out at an addition of zeolite of 3% within the FR mixture, or 1.5 pphr for the rubber compound.

1.10.11 Inorganic Fire Retardants and Synergists

Fillers which decompose endothermically to release water and inert gases appear very attractive as fire retardants, with low toxicity and low smoke. The drawback of these materials, such as aluminium and magnesium hydroxide, is that they need to be added at high quantities to be effective. Table 13 contains a compilation of some decomposition properties of mineral fillers by Hollingbery [131] and the relative contribution of fire retardant effects calculated by Hull [132]. These data indicate that the largest fire retardant effect is the removal of heat by endothermic decomposition, whether by the loss of water or carbon dioxide. The most important property for fire retardance is most likely the temperature for the onset of decomposition, which would ideally coincide with the onset of polymer decomposition, so maximising the cooling benefit when it is of most value. An important feature of a mineral filler not quantified, however, is the role of the residue following decomposition. An ideal material would fuse into a single mass; providing an insulating barrier, and absorbing and re-radiating heat, so acting as en effective heat-sink.

Name	aluminium hydroxide	magnesium hydroxide	hydro-magnesite	huntite	UltraCarb®
Chemical formula	$Al(OH)_3$	$Mg(OH)_2$	$Mg_5(CO_3)_4(OH)_2.4H_2O$	$Mg_3Ca(CO_3)_4$	approx.60:40 hydromagnesite: huntite
Onset of decomposition (°C)	180-200	300-320	220-240	~400	220-240
Enthalpy of decomposition (Jg^{-1})	1300	1450	1300	980	990
volatile content by mass (%)					
water	35	31	19	0	11
carbon dioxide	0	0	38	50	43
Total	35	31	57	50	54
volatile content by volume (% at 373K, 1atm)					
water	59.4	52.7	32.3	0	14.2
carbon dioxide	0	0	26.4	21.6 & 8.7	21.8
Total	59.4	52.7	58.7	30.3	36
Residue content (%)					
Al_2O_3	65	-	-	-	-
MgO	-	69	43	34	40
CaO	-	-	-	16	6
Relative Contribution Fire Retardant Effects (%)					
Filler	9	19	10	20	14
Endotherm	55	56	56	58	57
Residue	13	9	14	9	12
Gas	23	15	21	13	18

Table 13 Comparison of decomposition and products for some hydrated fillers

Aluminium Hydroxide (ATH)

$$2\ Al(OH)_3\,(s) \xrightarrow{180\text{-}200°C} Al_2O_3\,(s) + 3\ H_2O(g)$$

Aluminium hydroxide, also known as alumina trihydrate and abbreviated to ATH, is the highest tonnage fire retardant in use. This inexpensive material has to be used at high loadings to be effective. In a review article by Horn on inorganic hydroxides [133] which mentions the use ATH in NR, 40-70% by weight is considered necessary, dependant on the thickness of the product and the flammability requirement. At around 180^oC thermal decomposition commences, so ATH cannot be used in material requiring higher temperatures for processing. ATH loses 34.5% of the original weight by 350°C, by releasing water in an endothermic decomposition. This has the effect of both reducing the heat within the system and diluting the surrounding gases, which can reduce the rate of combustion to the point of self extinguishment. It is this process that renders ATH a genuine fire retardant, not simply inert filler relying on polymer dilution to inhibit the burning behaviour of the mixture. The downside of the high loading of this material is a worsening of the physical properties [134].

Fewer studies have been reported with examples of polyisoprene using endothermic decomposing mineral fillers other than ATH. As ATH starts to decompose at 180°C, the fuel dilution benefit is lost at the peak decomposition temperature of polyisoprene, around 380°C, before which all the water will have been lost. Other endothermic fillers with a higher decomposition temperature may be more effective, either alone or as a blend with ATH.

Magnesium hydroxide (MH)

$$Mg(OH)_2\,(s) \xrightarrow{300\text{–}320°C} MgO(s) + H_2O(g)$$

Magnesium hydroxide, (MH) works in a similar manner to ATH, but decomposition commences at around 300°C which enables use in higher temperature processes. MH is also used in similarly high loadings to ATH. It seems likely that magnesium hydroxide could be added to polyisoprene, but no examples were found in the literature.

Lawson [58] shows examples of the use of magnesium hydroxide in conjunction with ATH in both EPDM and ethylene-acrylic elastomers. Unfortunately comparison of ATH to MH cannot be made because the MH modified recipes also contained phosphate plasticiser. Lawson [64] also investigated smoke inhibition by ATH, MH and calcium carbonate in SBR foam. In this case MH was found to yield significantly lower levels of smoke than ATH, which in turn was significantly better than calcium carbonate. The effect of LOI was also reported, with calcium carbonate having no benefit over an unfilled rubber compound at 18.5%, and ATH / MH both having an LOI of 24%. Mouseman [13] continues work with calcium carbonate, soft clay, ATH and MH but in EPDM compounds at the higher level of 200 pphr (64% by weight). In the NBS smoke chamber the compounds performed similarly in the non-flaming test with high smoke density observed. In the flaming test however MH significantly outperformed the other fillers, with ATH performing worst with the most visual obscuration. In EPDM, the highest LOI value of 34% was obtained with MH, compared to 31% for ATH.

A wide range of other fire retardant additives have been found to work synergistically with hydrated fillers, including zinc borate, red phosphorus, metal nitrates and nano-clays [135]. Synergism is valuable with hydrated fillers such as ATH and MH, since this can allow a reduction in the overall filler loading improving flexibility or impact resistance for an equivalent fire test performance.

Huntite and Hydromagnesite

Huntite and hydromagnesite occur together naturally as minerals, marketed as a low cost effective alternative to aluminium and magnesium hydroxides. These two minerals decompose endothermically through the following reactions, reviewed by Hollingbery [131], [136] and summarised below. Commercial grades typically contain a ratio of between 60:40 - 40:60 hydromagnesite/huntite.

Hydromagnesite

$$Mg_5(CO_3)_4(OH)_2.4H_2O \xrightarrow{220°C} Mg_5(CO_3)_4(OH)_2 + 4H_2O \xrightarrow{395°C} 5MgO + 4CO_2 + H_2O$$

Huntite

$$Mg_3Ca(CO_3)_4 \xrightarrow{450°C} 3MgO + CaCO_3 + 3CO_2 \xrightarrow{720°C} CaO + CO_2(g)$$

The mixture decomposes over a range of temperature from 220 to 800°C, releasing water vapour and carbon dioxide. The endothermic stages are shown in the DSC trace in Figure 11. The first two peaks are caused by decomposition of the hydromagnesite, and the second two peaks by the decomposition of the huntite. The hydromagnesite decomposition matches that of most polymers more closely than huntite, suggesting that hydromagnesite is more effective as a fire retardant. However, the platy huntite remains intact until higher temperatures are achieved, and appears to form an effective barrier layer. It has been suggested that this residue and the wide decomposition temperature range leads to enhanced performance in comparison with ATH.

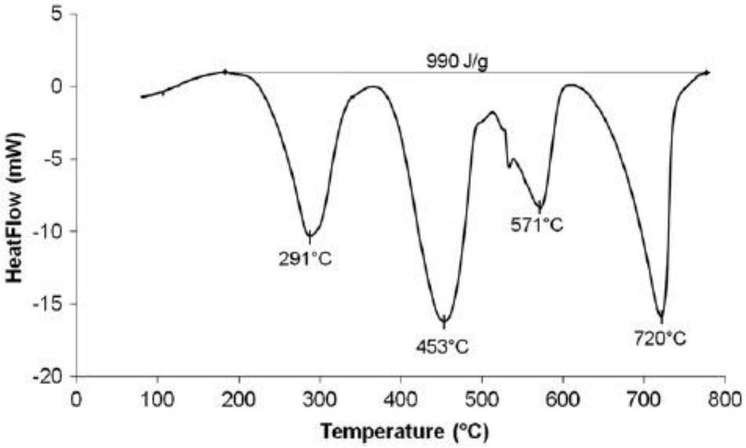


Figure 11 DSC profile of a mix of huntite and hydromagnesite

To be effective in ethylene vinyl acetate (EVA), an elastomeric copolymer, it needs to be loaded at levels of over 50% by weight. In addition to the action by endothermic decomposition to remove heat from the system, the gas and vapour can function as a blowing agent to create intumescent char comprised of the remaining metal oxides. In an EPM rubber compound, use of 20 pphr huntite/hydromagnesite with 150 pphr ATH gave an LOI of 30.5%, around 2% higher than with 170 pphr ATH [137].

1.10.12 Tin compounds as synergists

Inorganic tin compounds have been investigated by Cusack for use as secondary fire retardants, leading to the commercial introduction of zinc hydroxystannate (ZHS) and zinc stannate (ZS). Whilst initially discovered to be alternative synergists to antimony trioxide in halogenated polymers, they are also considered useful in halogen-free systems to promote char and suppress smoke [138]. Although both decompose with the release of water, this is not the main mechanism for their fire retardant action.

zinc hydroxystannate

$$ZnSn(OH)_6\,(s) \xrightarrow{180°C} ZnSnO_3\,(s) + 3\,H_2O\,(g)$$

zinc stannate

$$ZnSnO_3\,(s) \xrightarrow{570°C} ZnSnO_3\,(s) + 3\,H_2O\,(g)$$

In a report by the International Tin Research Institute (ITRI) examples are given of ZHS in natural rubber [139], added in addition to ATH in a carbon-black filled recipe with a conventional sulphur cure system, showing an increase in LOI and reduction in smoke (Table 14). Reductions in smoke yield are of particular interest for polyisoprene.

Sample	LOI %	NBS smoke $D_{mc/g}$ (flaming mode)	Smoke reduction %
Control	18.1	54.0	-
50% ATH	28.9	14.5	73
50% ATH + 2.5% ZHS	30.7	9.7	82

Table 14 Effects of ZHS and ATH on the LOI and smoke density of NR (ITRI)

Natural rubber (NR) compounds were evaluated using a range of fire retardants by Ismawi [62]. Two themes were explored, organo-halogens and hydrated fillers. In the halogen containing recipes, both chlorinated paraffin wax (CP) and decabromodiphenyl oxide (DBDPO) were evaluated in combination with zinc hydroxystannate (ZHS), zinc stannate (ZS) and antimony trioxide (Sb_2O_3) to investigate possible synergism for the reduction of flammability and smoke generation. Burning behaviour was measured using UL94 vertical test and LOI. For comparison purposes, an unfilled NR recipe was characterised with a resultant LOI of 18.2% and no rating in the UL94. The individual additions of 20 pphr ZHS, ZS and Sb_2O_3 had no effect on these results, as may be expected from materials typically used as synergists with other FR additives. Considering CP, the use of 40 pphr gave an LOI of 20.8%, but when 4 phr of ZHS was also added, the LOI rose to 22.4%, indicating some beneficial effect as a combination. When DBBO was used with Sb_2O_3 at a loading of 22.3 and 7.5 pphr respectively, an LOI of 22.6 was measured, achieving UL94 V1.

Considering alumina hydroxide (ATH) and zinc hydroxystannate (ZHS), a range of formulations and burning test results are shown in Table 15.

ATH pphr	ZHS pphr	LOI %	UL-94 rating
0	0	18.2	No classification
0	20	18.2	No classification
60	0	20.8	No classification
100	0	23.8	V1
140	0	26.2	V1
130	10	26.6	V1
125	15	26.4	V1

Table 15 Effect of ATH and ZHS loading on LOI and UL94

It can be seen that increasing levels of ATH increase LOI modestly. At 10 pphr ZHS a small improvement was noted, less so at 15 pphr, indicating an optimum loading below 15 pphr. Cloisite 20A was also evaluated within this study, at 10 pphr using 130 pphr ATH, an LOI of 28% was achieved, along with the only UL94 V0 rating in this study for a zero halogen compound. This is particularly interesting because nanoclays are often considered to only impart useful fire retardance when excellent levels of particle dispersion are achieved. Using standard rubber processing equipment it is unlikely that sufficient shear can be imparted to the material for this level of dispersion without agglomeration, as SEM work undertaken indicated poor dispersion of the hydrated filler and reducing tensile strength. However, it has been argued that such excellent dispersion need not be present in the compound, provided it occurs in the decomposing melt prior to ignition [140]. It is difficult to fully assess the contribution of these additions without comparison to a reference compound in order to eliminate the effect of reducing the fire load.

1.10.13 Boron Compounds

Zinc borate is the most commonly used boron based fire retardant, and is used typically as a secondary additive to increase the efficiency of fire retarded systems and as a smoke suppressant. In halogenated systems it is often used in conjunction with antimony oxide, whilst in halogen free systems it is often used with hydrated fillers or phosphorus compounds. The most commonly used grade and extensively reviewed by Shen [141] has the following structure, marketed by Rio Tinto as Firebrake® ZB.

$2\ ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$

Upon heating zinc borate dissolves in its own water of hydration [142], and then eliminates the water to form boric acid. This then further decomposes in the two steps below.

$$2H_3BO_3(s) \xrightarrow{180\text{–}200°C} 2\ HBO_2(s) + H_2O(g) \xrightarrow{260\text{–}270°C} B_2O_3(s) + H_2O(s)$$

In some applications zinc borate can be used alone, but this is less common. It is thought that in halogenated systems zinc borate works by decomposing upon heating to form a zinc halide or zinc oxyhalide that accelerates the decomposition of halogen sources producing gas phase halogen sources and leaving unsaturated hydrocarbon residues to promote char formation. From the release of the B_2O_3 functional group, a low melting point glass is generated that can stabilise the char. This boron compound can also promote the formation of ceramic structures in systems containing ATH or magnesium hydroxide. In addition the release of water can also promote the formation of foamy char. In the presence of a silica source such as a silicone polymer or SiO_2, zinc borate is also believed to form a borosilicate glass at polymer combustion temperatures [143], resulting in an impermeable barrier to heat and gases.

In a study of boron compounds [61] in selected materials, ammonium pentaborate was found to be an effective secondary fire retardant in thermoplastic polyurethanes and nylon 6,6. Ammonium pentaborate (APB) decomposes when heated to produce several products, including ammonia and water vapour which work as inorganic blowing agents, and forming a boric acid glass. A proposed decomposition scheme is outlined below:

$$2\ NH_4B_5O_8 \cdot 4H_2O\ (s) \xrightarrow{100\text{-}450°C} 2\ NH_3\ (g) + 9\ H_2O\ (g) + 5\ B_2O_3\ (s)$$

This combined product is claimed to yield an effective intumescent but rigid char, represented in Figure 12.

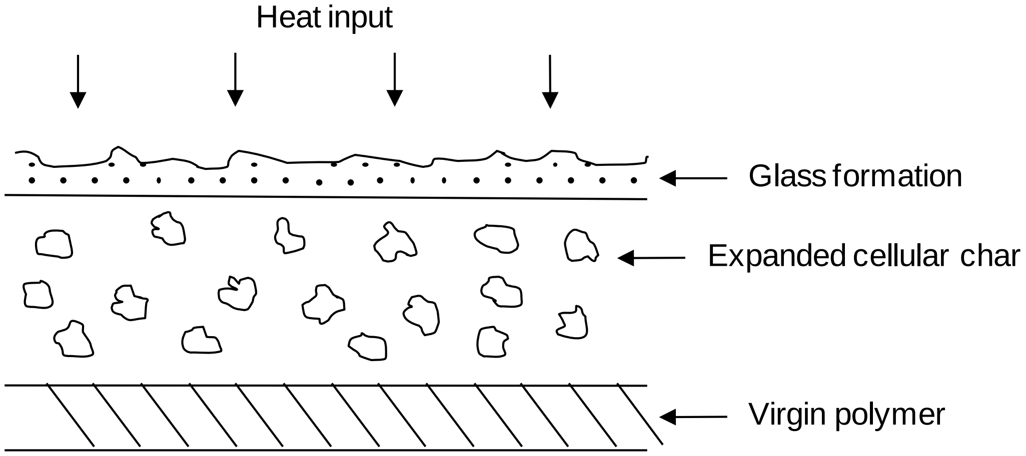


Figure 12 Scheme for intumescent char layer development for APB

APB was also evaluated within a carbon black filled sulphur cross-linked natural rubber in the same study. It was added at 25 pphr, and compared to equal additions of materials including zinc borate, aluminium hydroxide and calcium carbonate. All of the additives had a modest effect on flammability as measured by LOI. The unmodified formulation had an LOI of 17.5%, with $CaCO_3$ and zinc borate raising the LOI to 18.0%, and APB and ATH having a slightly improved benefit with an LOI of 19.0%. In the study it was observed that for APB some intumescence occurred for the rubber compound, but it was short-lived. It was suggested that the carbon black bulk may be interfering with the intumescence. Considering the decomposition products, ammonia and water vapour would be able to produce the necessary intumescence, but the boric acid alone would not be enough to produce a hard char.

1.10.14 **Expandable Graphite (EG)**

Expandable graphite is an interesting material produced by the intercalation of acid, typically sulphuric, between layers of graphite. When heated to around 200°C, gas and vapour is released resulting in rapid expansion between the layers to produce graphitic worm-like growths visible to the naked eye. It has been proposed [144] that the gas expansion that causes the volume expansion is due to a redox reaction between the sulphuric acid and the graphite.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2\,H_2O + 2\,SO_2$$

Since all the evolved gases and water vapour are non-flammable, they will dilute the fuel within the gas phase. The main benefit of EG however is considered to be the production of a fluffy intumescent layer of carbon which functions as a barrier to heat and gas, so slowing down the typical cycle of heat from flaming combustion generating more gaseous fuel. Lyon [46] has observed that elastomers are well suited to modification with EG because at the expansion temperature they are sufficiently soft to allow high volumetric expansion. He evaluated 20% EG in polyurethane rubber (PU) and polyphosphazene rubber (PZR). The residues from cone calorimetry (Figure 13) vividly illustrate the high levels of expansion possible from EG compared to unmodified materials. Significant reductions in the peak heat release rate were observed following EG modification for both polymers, including the already ‘fire resistant’ polymer PZR.

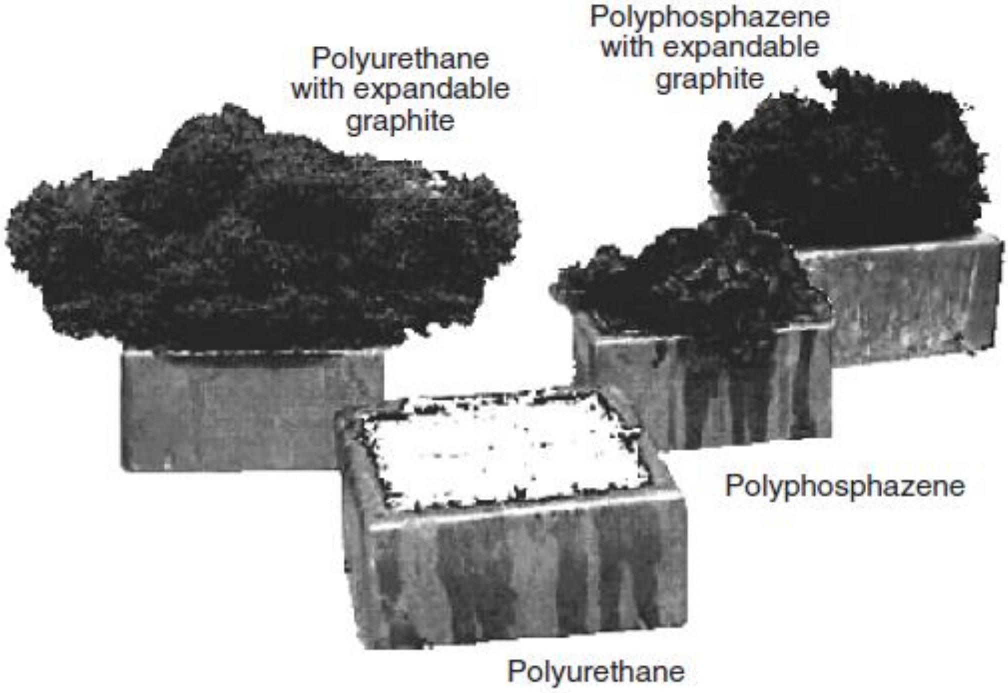


Figure 13 Images of residue following cone calorimetry (Lyon)

Moon [95] investigated formulations based on an NBR foam filled with 195 pphr ATH, with the addition of 10-30 pphr red phosphorus (RP), APP and EG. For RP and APP an optimum level of 10 pphr yielded a good reduction in peak HRR, but at 30 pphr of EG the most significant improvement in burning behaviour and smoke production was reported.

Considering that expandable graphite functions as a physical barrier to burning, it may be suitable in polyisoprene. A potential problem will be the large particle size necessary to cause the high expansion rates, which is likely to have a detrimental effect on physical properties such as tear and tensile strength.

1.10.15 **Nanocomposites**

The use of nano-scale fire retardants are now widely reported, where a small amount of material is added to produce a nanocomposite, which has a significant impact on both the mechanical properties and fire performance of the polymer. The majority of work has been reported in the use of clays, particularly montmorillonite clay [145], but is also being applied using materials including graphites, carbon nanotubes and polyhedral oligosilsequioxanes (POSS) [146].

Montmorillonite organoclay (MMT) was evaluated by Liu [147] in natural rubber, with conventional bench scale mill mixing employed as a means of filler incorporation and dispersion. MMT was also reacted with tributyl phosphate to produce a modified organoclay (TMMT), with the intention of increasing the interlayer spacing and therefore the level of intercalation. This appeared successful from TEM observations and X-ray diffraction patterns, where the use of 10 - 20 pphr MMT gave a useful reduction to around 70-80% average HRR, and the use of TMMT at equal levels yielded further improvements to 60-75% reduction of average HRR as measured by cone calorimeter. A significant review of elastomer nanocomposites has been reported by Maiti [148], examining the literature available for a range of nano-fillers in various elastomers. Of the 519 papers cited however, only a small number make reference to the assessment of nano-fillers as fire retardants. Kumar [149] also makes a comprehensive review of nano-fillers and application in polymers for various purposes, including fire retardancy. EPDM compounded with montmorillonite clay is considered, and problems with increased degradation of product are reported. It is proposed that the usual level of antioxidant incorporated may be partly consumed by the organic coating of the clay during melt processing.

The possible synergism between magnesium hydroxide and multi-walled carbon nanotubes (MWNT) was considered by Ye [150] in EVA. Starting with 50% magnesium hydroxide, MWNT was added at low levels from 1-3%, whilst retaining the same overall percentage of additive. An optimum level of 2% was determined, at which the LOI rose from 34 to 39%, and a significant reduction of the peak heat release was measured on a cone calorimeter. This improvement was attributed to several factors relating to the MWNT presence. These include an increase in the melt viscosity of the polymer due to MWNT network structures formed and a subsequent improvement in the resistance to oxidation during thermal decomposition, due to the improved barrier properties of the charred layer. It was noted from visual observations that the char layer was a continuous and robust surface without the cracks and voids noted in the polymer modified with magnesium hydroxide only. These studies demonstrate the potential for nanocomposites based on polyisoprene, with the general aim of reducing loading for a given level of burning performance.

More recently work has been carried out in elastomers with nano-scale fillers, such as single-wall carbon nanotubes (SWNT) [24] and carbon nanofibrils [25]. Small additions of such materials can impart significant changes to the compound's physical properties, far beyond that of micron sized filler, provided they are able to be fully dispersed within the polymer matrix. Since nanofillers can have significant effects at low loading levels, they appear to be the ideal choice of fire retardants. Unfortunately they are difficult to disperse at the levels necessary to achieve the desired modification of physical properties [151]. The potential is limited by the ability to disperse these materials at the nano-scale whilst working at the industrial processing scale.

1.11 Conclusions

A review of relevant background literature in relation to polymers and additives, decomposition, industry tests, fire retardants and fire retardance of rubber was undertaken. This was focussed on fire retardant approaches to rubber compounds, polyisoprene being the target polymer for protection.

With the growth of mass transportation systems and tunnels there is increased demand for fire retarded rubber, and for some applications only polyisoprene will meet the physical demands for low damping and durability. Rubbers are complex, functional composite materials, where interaction of the elastomer with the carbon black imparts desirable mechanical properties; and maintaining this functionality while reducing flammability is crucial to the success of this project. Polyisoprene rubbers ignite easily with high heat release and smoke levels, but relatively low toxicity of fume. Halogenated rubbers have lower ignitability and are often self-extinguishing, but under forced burning conditions release high levels of smoke, corrosive gas and toxic fume.

Although natural rubber can be considered one of the most sustainable and ‘carbon-neutral’ polymers, any attempt at fire retardancy also needs to address the issues of environmental sustainability avoiding halogenated additives. There are a wide range of potential approaches available for polyisoprene rubber compounds to reduce the flammability. Jincheng [93] showed that intumescent additives based on phosphorus and nitrogen chemistry can show effective reductions in heat release without excessive sacrifice of physical properties, so such chemistry shows potential for industrial application.

Inorganic endothermically decomposing fillers are likely to remain the mainstay of halogen-free systems for some time, combining economy, a reduction in flammability, smoke inhibition with low toxicity of fume. Looking beyond aluminium hydroxide, however, there is significant scope for increased effectiveness from various options. Firstly the use of magnesium hydroxide and natural blends of huntite/hydromagnesite can be evaluated. In addition, additives such as zinc hydroxystannate show improved LOI and smoke reduction in polyisoprene. Where mixture homogeneity is less critical, large particles of expandable graphite can create an effective voluminous barrier to burning, most suitable for thicker rubber articles. Nano-sized additives offer the potential of the greatest fire retardant effect for the lowest loading level. These materials have shown excellent effects in the laboratory for other polymers, but the break-through for nano-materials needs to be in the industrialisation of the high dispersion levels required.

CHAPTER 2. EXPERIMENTAL

2.1 Application of candidate fire retardants for use in polyisoprene

This project sets out to make use of fire retardants (FR) to modify the fire behaviour, but maintain the physical properties required for satisfactory performance. In order to meet this it is necessary to define clearly the properties of the ideal FR additive.

2.1.1 Specification for an ideal fire retardant

Fire retardancy

The additive must reduce flammability to a specified level. The fire retardancy must be retained throughout the lifetime of the product, so additives that decompose significantly, leach or migrate in the working environment of the product are not satisfactory.

Additive level

To maintain the elasticity, and resistance to permanent set (non-elastic deformation) of a rubber compound, it is not possible to add large quantities of additives which will excessively dilute the polymeric content. Additive levels of above 100 pphr (50% by mass of rubber) are likely to have adverse effects on required physical properties. Ideally, the fire retardant needs to be active at low levels of addition, and sufficiently cheap at the effective loading.

Compatibility

Any additive needs to be chemically inert within the rubber compound, during cross-linking, and at the service temperatures encountered. During the mixing process it can be added as a powder or a liquid. As a powder, it must be both sufficiently small in particle size and fully compatible with the polymer to fully disperse within the polymeric matrix so as not to disrupt the physical properties such as tear strength, or melt below the mixing temperature. It must easily process in the equipment usual to the polymer.

Environmental aspects and legislation

Any candidate fire retardant should be considered in terms of health and environmental legislation. The European Union has been instrumental in bringing forward a series of directives to reduce the environmental impact of industry. Previous examples of these instruments include the End of Life Vehicle (ELV) directive 2000/53/EC and the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment Regulations 2008 “the RoHS regulations”, EU Directive 2002/95. In both cases there has been a general approach to reduce or eliminate the environmental release of toxic and bio-accumulative materials such as heavy metals such as cadmium. In addition, within RoHS polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) fire retardants are also banned. This has been a particular problem for the electronics industry, who have made extensive use of polymers containing brominated fire retardants [152]. On a pragmatic level it is of little sense to invest in the development of an additive that may be restricted within a few years. Many international companies have also published ‘black’ and ‘grey’ lists for suppliers of products and components. A ‘black’ list details chemicals that are banned for supply. Many of these materials may be restricted for use in one industrial area, but the ban often covers all business areas to apply a consistent approach. A ‘grey’ list will have materials which are not banned, but may be suspected of health or environmental concerns, and therefore should be avoided. The Volvo Black List STD100-0002 and Volvo Grey List STD100-0003 are typical of this approach, which include all brominated organic fire retardants, not just PBB and PBDE.

The 1907/2006 EC REACH (Registration, Evaluation, Authorisation & restriction of Chemicals) regulation establishes obligations for the manufacturers, importers and downstream users of chemical substances to ensure that chemicals in use are registered and evaluated for toxicity and environmental impact. In addition, the EU agency responsible for implementation of this directive, the European Chemicals Agency (ECHA), have published a list of “Substances of Very High Concern” (SVHC) [153]. This includes materials defined as carcinogenic, mutagenic or toxic to reproduction, persistent, bioaccumulative and toxic, and/or identified from scientific evidence as causing probable serious effects to human health or the environment (e.g. endocrine disrupters). Within the SVHC list are chemicals used as fire retardants; hexabromocyclododecane (HBCDD), tris (2-chloroethyl) phosphate (TCEP) and short chain chlorinated paraffin waxes. Any user of materials on the SVHC list is now obliged by law to inform their customers of the presence of these chemicals in products. This approach is likely to significantly reduce the use of this class of materials without an actual ban being imposed.

2.1.2 Initial selection of fire retardants for evaluation in polyisoprene

By eliminating all of the types of additives that do not comply with the basic specification for an ideal fire retardant, a range of candidate materials should remain for consideration. The additive levels are from the literature reviewed and Horrocks [154].

Base chemistry	Type of retardant	Additive level %	Compatibility	Environmental concern
Halogen	Primary	8-15	Fair	High
Phosphorus/nitrogen	Primary	20-30	Fair	Moderate
Hydrated Fillers	Primary	> 50	Good	Low
Boron synergists	Secondary	5-10	Good	Low
Zinc hydroxystannate	Secondary	2	Good	Low
Nanomaterials	Secondary	1-5	Poor	Moderate
Expandable Graphite	Primary	<20	Poor	low

Table 16: comparison of candidate fire retardants for polyisoprene

Halogen based fire retardants

Whilst halogen based compounds are known to be highly effective gas phase fire retardants they are likely to become unavailable in the present forms in the medium to long term. Within the new requirements of REACH the cost of registering new materials based on halogens is likely reduce the long term commercial interest in these materials, and some existing materials are being banned. An additional problem with halogenated additives is that whilst they can reduce flammability and render materials self-extinguishing, they will emit higher levels of smoke and toxic fumes during thermal decomposition. Based on these considerations halogenated materials will not be used in this work.

Phosphorus based fire retardants

The large family of phosphorus compounds are suitable candidate materials for investigation in polyisoprene. They have acceptable environmental aspects, and are reported to be effective at lower loading levels. Phosphate esters investigated in natural rubber has limited benefit, but may be useful as a substitute for flammable plasticisers such as mineral oils. Ammonium polyphosphate, often in combination with a blowing agent and a char former, is worth consideration. Synergists are often used to increase the efficacy of the fire retardancy, so will require evaluation. Nitrogen based retardants are also often used in combination with phosphorus based chemistry, so will be evaluated within this study.

Hydrated fillers

Fillers which decompose endothermically to release water and inert gases appear very attractive as fire retardants, with low toxicity and low smoke. The drawback of these materials, such as aluminium and magnesium hydroxide, is that they need to be added at high quantities to be effective. The necessarily high levels of loading may give a reduction in the elastomeric physical properties, but will be investigated with this limitation in mind. In addition the huntite/hydromagnesite blend UltraCarb will be investigated as alternative hydrated fillers with an increased residue strength promoted.

Boron

Boron compounds are typically used as secondary fire retardants in conjunction with hydrated filler, so will be considered.

Zinc hydroxystannate

With some literature showing improvements in burning behaviour when used in conjunction with ATH, this material will also be investigated experimentally.

Nanomaterials

Since nanofillers can have significant effects a low loading levels, and can enhance mechanical properties in polymers, they appear to be the ideal family of fire retardants. Unfortunately they have proven difficult to disperse at the levels necessary to achieve the desired reduction in burning behaviour.

2.1.3 Fire retardant additives, synergists and fillers

Table 17 lists the additives used in the fire retardant formulations in this study, with commercial trade names and suppliers.

Chemical name	Trade name	Supplier
calcium carbonate	Snowcal 80	Omya
precipitated amorphous silica	Ultrasil 360	Evonik
ammonium polyphosphate	Exolit AP422	Clariant
Melamine	Melamine	Acros Organics
Pentaerythritol	Pentaerythritol	Acros Organics
expandable graphite (EG)	Firecarb TEG-315	Minelco
triethyl phosphate (TEP)	Triethyl phosphate 99%	Acros Organics
aluminium hydroxide (ATH)	Apyral 40CD	Nabaltec AG
aluminium hydroxide coated with 10% Zinc hydroxystannate	Storflam ZAH	Joseph Storey
magnesium hydroxide (MH)	Magnifin H14C	Omya
magnesium hydroxide coated with 10% Zinc hydroxystannate	Storflam ZMH	Joseph Storey
60% huntite / 40% hydromagnesite	UltraCarb 1291	Minelco
40% huntite / 60% hydromagnesite	UltraCarb LH15C	Minelco
zinc borate (ZB)	Storlflam ZB2335	Joseph Storey
zinc hydroxystannate (ZHS)	Storflam ZHS	Joseph Storey
red phosphorus 50% on castor oil (RP)	Exolit RP 6500	Clariant

Table 17 Fire retardant additives used in project

2.2 Formulation and preparation of rubber compounds

2.2.1 Formulation of rubber compounds

The rubber industry uses a convention for the formulation of compounds based around 100 parts of elastomer. This is known as ‘parts per hundred resin’ (or in the case of rubber ‘parts per hundred rubber’), abbreviated as PPHR or PHR. This is in contrast to many thermoplastic formulations which are expressed in terms of percentage, and care must be taken not to confuse percentage with pphr when noting additives levels employed. The reason for this with rubber is that the basis of formulations is the elastomer, so all additions are at known proportions to elastomer regardless of the other additives. This allows new formulations to be assembled rapidly applying conventional practice to additive levels; zinc oxide is typically added at 5 pphr in most sulphur cured rubbers, for example.

For the experimental work a model rubber formulation was developed as a typical non-fire retarded benchmark for comparison purposes. The model formulation in Table 18 was based on available literature [29] with some modifications noted.

Additive	Composition (pphr)	Function
synthetic polyisoprene	100	Polymer
carbon black N550	40	Filler
naphthenic process oil	2	Plasticiser
zinc oxide	5	Cross-link activator
stearic acid	2	Cross-link activator
TMQ [1]	2	Antioxidant
antiozonant wax	2	Protection from ozone
Sulphur	0.25	Cross-linking agent
MBS [2]	2.1	Accelerator
TMTD [3]	1	Accelerator
Total	156.35	

Table 18 Model polyisoprene rubber formulation B40

[1] Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline

[2] 2-(4-morpholinothio) benzthiazole

[3] tetramethyl thiuram disulfide

In the literature formulation, the polymer used is natural rubber, grade SMRCV60. This was substituted for a synthetic grade of polyisoprene, with a cis-1,4 isoprene content of 99%. This grade was chosen because it has several advantages over natural rubber; polyisoprene has a higher purity compared to natural rubber, so was considered more stable for purposes of comparison, and produces lower levels of compression set than natural rubber for an equal formulation. Since the addition of fire retardant additives may cause an undesirable increase in compression set, it seemed prudent to start with a formulation with the best properties available.

Carbon black (trade name Cabot Sterling SO) was added at 40 pphr for the base formulation in accordance with the literature. The grade used is denoted N550 in ASTM D1765, also known in the industry as FEF (fast extrusion furnace). This a medium reinforcing filler with a particle size area of around 39-55 nm diameter and a corresponding surface area of around 45 m^2/g [16]. This reinforcing filler increases modulus to give a vulcanised hardness value of around 54° IRHD in the same literature.

Naphthenic process oil (grade Shell Carnea oil 46) was added at 2 pphr as a processing aid, allowing the easy incorporation of carbon black. The literature formulation noted 4 pphr, but this was considered a higher than necessary addition of a flammable additive.

Zinc oxide (trade name Alchem Red Seal Zinc Oxide Powder) was added at 5pphr in accordance with the literature. A Red Seal grade has a purity of 99.5%, with special attention in the process ensure a low residue of lead oxide (<0.1%), a known contaminant in naturally occurring zinc oxide.

Stearic (octadecanoic) acid (trade name Foster 1801 beads) was used in accordance with the literature formulation as part of the cross-linking activation system.

TMQ (Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline, trade name Safic Alcan TMQ) was used at 2 pphr. This is a general purpose antioxidant commonly used in diene elastomers to reduce the deterioration of physical properties from ageing and slow the rate flex cracking.

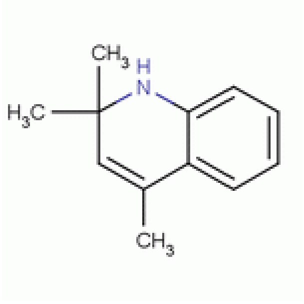


Figure 14 Chemical structure of TMQ antioxidant

Antiozonant wax (trade name Safic Alcan Alchem 3467) is a microcrystalline paraffin wax with a melting point of around 66°C, and is able to migrate to the surface of the product over time. This surface bloom provides a physical barrier to attack from ozone in static applications.

Ground sulphur (Trade name Hays sulphur powder 120 mesh) is added as the cross-linking agent at 0.25 pphr as part of an efficient vulcanisation (EV) cure system. This low level of sulphur will lead to a rubber compound with improved heat resistance and lower compression set compared to a conventional high sulphur cure.

2-(4-morpholinothio) benzthiazole (IUPAC name 4-(1,3-benzothiazol-2-sulfanyl)morpholine, $C_{11}H_{12}N_2OS_2$), (trade name Flexys Santocure MBS) is added as an accelerator to speed up the vulcanisation time but imparting a longer scorch time (time to the onset of vulcanisation), so imparting processing safety.

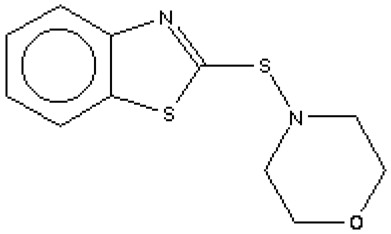


Figure 15 Chemical structure of MBS accelerator

Tetramethyl thiuram disulfide (TMTD), (trade name Flexys Perkacit TMTD) is a secondary accelerator added to boost the rate of cure and increase state of cure, so improving physical properties.

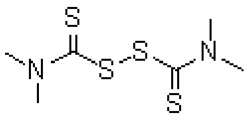


Figure 16 Chemical structure of TMTD accelerator

2.2.2 Preparation of compounds

Mixer formulation

Rubber mixing formulations are calculated based on total pphr, mix density (expressed as specific gravity), mixer free volume (litres) and fill factor. This is calculated as follows for an internal mixer.

Total batch weight (kg) = mixer free volume (litres) x fill factor x mix SG

Fill factor is a term for the percentage loading of a mixer for optimum mixing efficiency. An internal mixer is never 100% filled, because an air space is necessary to allow the movement of material around the mixing chamber between and around the mixer rotors.

The weight for each addition is then calculated using the following formula.

$$\text{Additive weight (Kg)} = \frac{\text{pphr additive x total batch weight}}{\text{Total mix pphr}}$$

Mixing process

Equipment

Francis Shaw K1 Intermix internal mixer capacity 5.5 litres

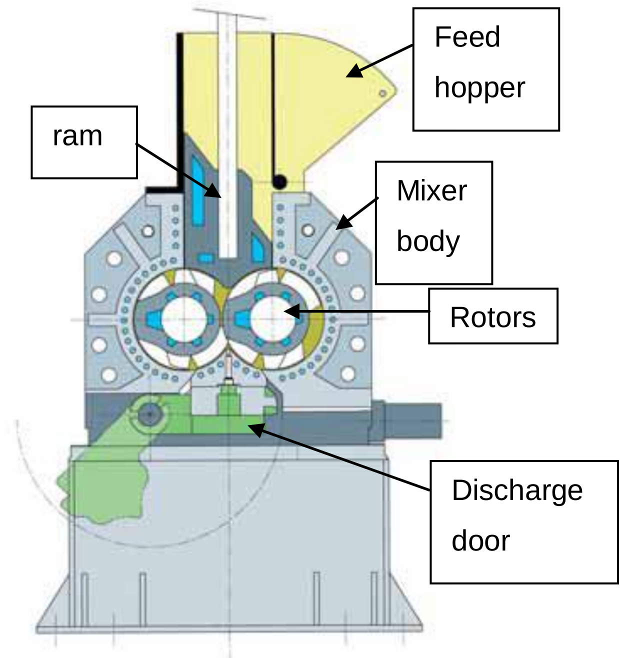


Figure 17 Cross-sectional schematic view of a typical internal mixer

This is a larger laboratory scale mixer, using two contra-rotating intermeshing rotors. This is used for producing the first stage mix, often known as a masterbatch. It comprises a mixing chamber, with a water cooled body and rotors, pneumatic ram and hydraulically operated discharge door underneath, driven by a variable speed controlled DC motor through a reducing gearbox. Typical mixing rotor speed 60 RPM. Lubrication oil is supplied by a pump system to the rotor bearings and gland seals, and is a potential source of rotor contamination. A manually operated hopper door serves to allow charging of the mixer chamber when open, and when closed allows the ram to lift and descend without risk of injury to the operator. The state of mix is monitored using mix temperature, motor current and time.

Procedure

Dust extraction is turned on. Prior to a mixing run, a ‘cleaner’ batch is put through to warm up the mixer chamber and ensure no excess lubrication oil has built up. A general mixing procedure is followed according to Table 19, although this will vary depending on the formulation.

Operation	Time (mins)	Temperature (°C)
Load polymer	0	
Load small powders, oil and filler	1	
Add half fire retardant	2	60
Add remaining fire retardant	3	70
Sweep down ram and hopper door	4	80
Discharge door open, ram up	6	100

Table 19 Typical lab scale mixing sequence

The mixed rubber is discharged into the dump tray, check-weighed and loaded onto the two-roll mill.

Milling process

Equipment

Two roll mill, bowl size 450mm long x 225mm diameter. Water cooled by flood cooling via rotary joints. Drive: Variable speed AC drive though reducing gearbox to fixed ratio bowls at a front-back ratio of 1 to 1.03.

Procedure

Personal protective equipment is worn, such as lab-coat, gloves, safety glasses and a dust mask where necessary. Dust extraction is turned on. The two in-running rolls present a hazard so are protected by a cage, three E-stops and the ‘Lunn’ safety bars, which all cause an electronic dead-stop. Rubber compound is loaded onto the front bowl and formed into a rolling band. A masterbatch is milled for approximately five minutes to cool, blend the compound and form a useable sheet form.

The mill is also used for second stage mixing of rubber compounds, where additional additives are incorporated and dispersed into the rubber compound (Table 20).

Operation	Time (mins)
Load masterbatch, form rolling band	0
Blend and warm up	1
Add curatives to rolling band	2
Sweep tray and add to mill	3
Blend thoroughly	5
Remove in sheet form	10

Table 20 Typical lab mill second stage operation timings

2.2.3 Vulcanisation (cross-linking) of samples

Equipment

Hydraulic press with electrically heated platens, adjustable pressure 200-1500 kN and steel moulds with cavities in accordance with relevant standards and an allowance for mould shrinkage.

Procedure

Moulds are heated in the press until the cavity temperature has stabilised. Sample pre-forms, typically 5-10% heavier than the final sample mass are prepared from freshly milled rubber. Where necessary metal tokens for bonding are prepared by grit blasting and coating with a proprietary bonding agent. Lord Chemosil 211 was sprayed on as a metal primer and Lord Chemosil 411NL as an adhesive layer, a common system for IR. Test samples are compression moulded using standardised cure times at 153°C. Bonded test pieces are transfer moulded to ensure an even and sufficient cavity pressure, important to attain good rubber to metal bonding. Moulded samples are cleaned to remove flash (loose rubber) and conditioned for a minimum of 24 hours.

2.3 Physical and rheological characterisation

Characterisation of Physical Properties

A key aspect of this project was to ensure that any new fire retarded rubbers maintained their physical performance, characterised using the following industry standard tests.

2.3.1 Rheological and vulcanising properties

Equipment

Alpha Technologies MDR2000A

Procedure

The effect on rheological and vulcanising properties will be measured using a Moving Die Rheometer (MDR). An uncured sample is compressed between heated oscillating dies in accordance with ASTM D5289 [155] for 18 minutes at 160°C. The resultant torque developed within the dies due to the resistance exerted by the test material is measured and plotted against time. Software performs an automatic analysis of the plot and extracts key information (Figure 18).

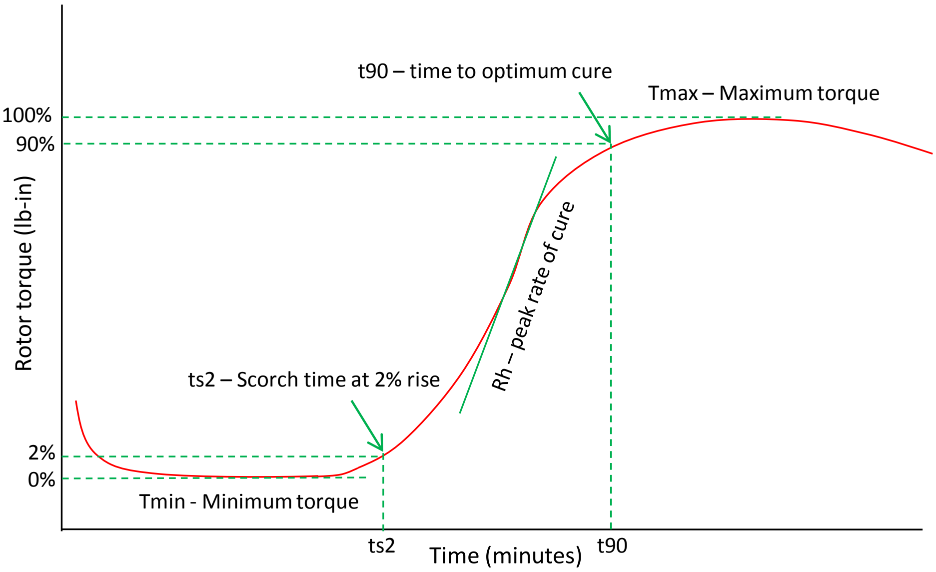


Figure 18 Simplified MDR plot showing key data points

T_{min} minimum torque is a simple measure of viscosity at processing temperature so can be used to predict ease of injection. This is considered in conjunction with ts_2, commonly known as scorch time, the point where no more flow of the rubber is possible due to the onset of cross-linking. If the material is forced to flow after this point then the product will have cured lumps resulting in a rough looking or incomplete product. T_{max} maximum torque measures the torsional modulus at this temperature, and t_{90} (time to 90% cure) is calculated to indicate when the ‘optimum’ cure has been completed, and may be used with some success in thinner section articles to estimate the cure time for the best compromise of physical properties. More often it is used for quality control to ensure that the curatives are well incorporated and dispersed. R_h, the rate of cure, measures the maximum rate of cross-linking; a high (fast) cure rate is often sought to minimise cycle times.

2.3.2 Hardness

Hardness is a comparative indicator of modulus at low deflections, and can be measured using several systems, the most popular for rubber being Shore A and IRHD, the latter being used in these studies.

Equipment

Wallace Cogenix bench hardness tester in accordance with ISO 48 [156].

Procedure

The hardness of a 6mm thick cross-linked sample is measured using a vibrating needle under a mass for 30 seconds. The displacement of the needle is correlated to the IRHD (International Rubber Hardness Degree) scale, with typical rubber compounds being within the range of 40 (low hardness) – 80 IRHD (high hardness).

2.3.3 Specific Gravity (SG)

Specific gravity is usually quoted as the unit-less measure of density for cured rubber compounds, a most common quality control measure for rubber compounds. SG is used to calculate product mass based on the product dimensions.

Equipment

Laboratory scale equipped with distilled water beaker for weighing in water

Procedure

Testing is in accordance with BS ISO 2781 [157]. A 2mm thick sample is cut into a 25mm square and the volume is determined by weighing in water and air.

SG is calculated as follows-

$$\text{Specific Gravity} = \frac{\text{mass}}{\text{mass - weight in water}}$$

2.3.4 Tensile stress / strain properties

Tensile strength and elongation at break minimum values are common requirements in most rubber specifications indicating a basic quality of strength and elasticity. Poor additive dispersion and high filler loadings will reduce these properties.

Equipment

Hounsfield vertical tensometer with 5KN tension load cell and laser extensometer

Procedure

Tensile strength and elongation at break is measured in accordance with ISO 37 [158]. A type 1 defined dumb-bell shaped specimen is stamped from 2+/-0.2 mm thick moulded sheet and measured accurately, with a section 25mm is marked on the middle section of the specimen using reflective tape for tracking by the laser extensometer (Figure 19). The sample is loaded between grips and pulled in tension at 500 mm/minute until a break is detected. The maximum force in Newton’s is divided by the starting point surface area to yield a result in Nmm^{-2} (commonly expressed as the equal unit MPa). The maximum yield is recorded, and expressed as a percentage of the original length.

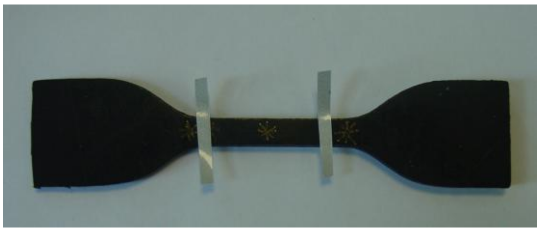


Figure 19 Dumb-bell test piece with reflective tape indicating extension section

2.3.5 Tear Strength

Tear strength is a useful indicator of the resistance of a rubbery material to cuts and cut propagation, and a low value may indicate poor additive dispersion and low product durability.

Equipment

Hounsfield vertical tensometer with 5KN tension load cell and laser extensometer

Tear strength is another destructive tensile property, but using a different sample types to deliberately determine the resistance of cured rubber to tearing. This is determined in accordance with BS ISO 34[159] for both method A (Crescent tear) and method B (Trouser tear), which describe the sample geometry (Figure 19). The samples are stamped from 2+/-0.2 mm thick moulded sheet and pulled at a rate of 500 mm/minute until a break is detected. The maximum force in Newtons is divided by the measured thickness to give a result in KNm^{-1} (sometimes expressed as the equal unit Nmm^{-1})

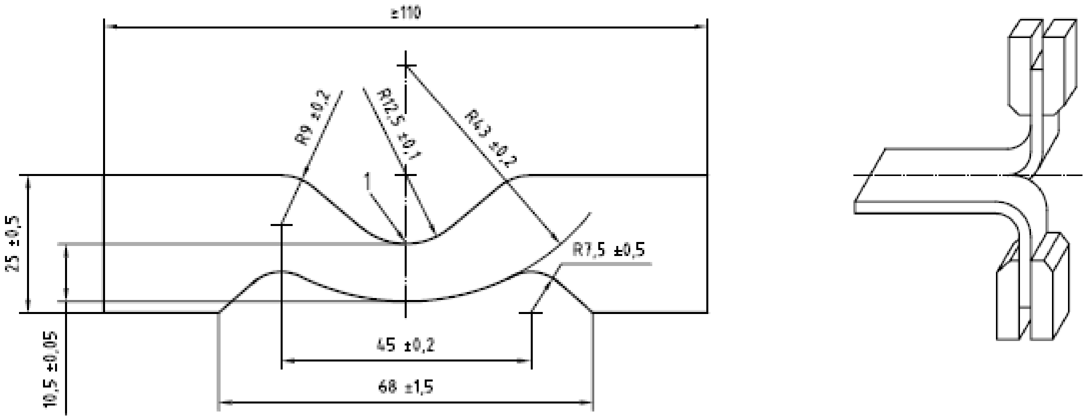


Figure 20 Crescent and Trouser tear test piece shapes

2.3.6 Accelerated ageing in hot air

Equipment

Gallenkamp electrically heated circulating air laboratory oven with accurate temperature control.

Procedure

A timed exposure to hot air [160] is employed to estimate the comparative resistance to long term ageing. Test Samples are aged in an oven at 70°C for 72 hours, and tested afterwards in accordance with the relevant ISO standard. Changes in tensile strength and elongation at break are expressed as percentage change from original value, and changes in hardness simply expressed in IRHD degrees change.

2.3.7 Compression set

Compression set [161] is an important measure of rubber compounds to withstand deformations without permanent set, and is used to establish both optimum formulation design and to check the state of cure of a product.

Equipment

Steel clamps of with a flat polished surface and spacers, and hot air oven.

Accurate dial gauge indicator.

Procedure

Disc shaped samples are compression moulded of approximate dimensions 29mm in diameter and thickness 12.5mm, compressed by 25% in steel clamps and then placed in an oven for 24 hours at 70°C. The clamp is then removed and the samples removed, and allowed to relax for 30 minutes. The compression set is then calculated based on the initial and final height.

$$\text{Compression set \%} = \frac{\text{Original height} - \text{Final height x 100}}{\text{Original height} - \text{Compressed height}}$$

2.3.8 Water absorption

Excessive additives of a hygroscopic nature however may cause swelling which can reduce product life and change the material modulus for instance. A test in boiling water is used as an accelerated test for water absorbance.

Equipment

Thermostatically controlled heating plate

Glass flask with air cooled condensing column

Laboratory scale equipped with distilled water beaker for weighing in water

Procedure

Testing is in accordance with ISO 1817 [162]. A 2mm thick sample is cut into a 25mm square and the volume is determined by weighing in water and air. The sample is then boiled in distilled water for 70 hours. After cooling and surface drying the volume is re-measured.

The percentage volume change is calculated as follows-

$$\text{Volume change \%} = \frac{\text{final mass - weight in water x 100}}{\text{original mass - weight in water}}$$

2.3.9 Dispersion

The dispersion of powders incorporated within the vulcanised rubber samples was determined in accordance with ISO 11345 method B [163]. This uses video microscopy of a clean cut edge of rubber linked with interpretive computer software. The values cannot be determined for un-vulcanised rubber, since entrapped air within the compound will yield a false result. The good micro-scale dispersion of additives is important to obtain the optimum physical properties for a given formulation. Whilst physical properties can suggest low dispersion, this method shows a direct measure. If an additive has a large particle size, or shows poor compatibility within the polymer matrix, then the dispersion test will usually highlight this.

Equipment

Optigrade Dispergrader

Procedure

A cured sample is cut into 3mm section and presented to a 100X scale video microscope, and built in software scans the image for white points of light which indicate light scattering by filler or other visible agglomerates. This determines the X value (filler dispersion) and Y value (agglomerate count), and then combines them into an overall dispersion rating, an ‘E’ rating from 0 to 10.

2.3.10 Dynamic behaviour

When rubber is used within a dynamic application such as an engine mounting, it is useful to be able to evaluate the effect of additives within a material test for dynamic behaviour. Dilution of the polymer with fillers will tend to increase the modulus and particularly increase the dynamic stiffness. This can lead to increased transmissibility of vibration. In addition the resilience will typically drop, indicating a higher damping characteristic. This can lead to greater heat build-up in the product, leading to a reduced service life through physical or chemical degradation.

Equipment

Yerzley Oscillograph

Procedure

This method employs a rubber to metal bonded sample allowing the rubber to be deflected in shear in accordance with ASTM D945 [164], with measured and calculated properties in Table 21.

Test	Units of measure	Characteristic
Shear modulus (SM)	MPa	Modulus of material at quasi-static load
Dynamic modulus (DM)	MPa	Modulus of material under dynamic condition
Dynamic/Static ratio	N/A	Used to calculate dynamic modulus increase
Resilience	%	Reciprocal of damping, assesses ‘bounce’
Phase angle	Degrees	Measure of tan δ (loss angle)
Creep	%	Short-term measure of recoverable compression

Table 21 Summary of Yerzley data points calculated from test

2.3.11 Bond strength

The effect of formulation modification can be evaluated for the rubber to metal bond strength [165], of importance for bonded suspension components. A defined test piece comprising of two circular plates with a flat surface for bonding to a 3mm thick rubber section and threaded fittings for mounting in tension is used.

Equipment

Hounsfield vertical tensometer fitted with 50KN tension load cell

Procedure

Samples are pulled in tension at a rate of 25mm/minute until failure, and the maximum load in KN recorded and divided by the surface area to give a bond test value in MPa.

2.4 Chemical characterisation

2.4.1 Determination of cross-link density using equilibrium solvent swelling

Cross-link density was determined using a solvent equilibrium swelling method to assess the level of cross-links formed between the polymer chains.

Equipment

Laboratory weigh scale

Procedure

Samples of dimension 50 x 25 x 2mm cross-linked rubber sheet are weighed in air and water, and immersed in toluene at 25°C until equilibrium swelling is attained. The sample is reweighed after wiping off excess solvent but not allowing the surface to dry out. The sample is then allowed to fully dry out, and then re-weighed after 10 days at 25°C.

The cross-link density can then be calculated using the Flory-Rehner equation [166]

$$v = \frac{1}{V_s}\left[\frac{\ln(1 - V_r) + V_r + \chi V_r^{2}}{V_r^{1/3} - \frac{1}{2}V_r}\right]$$

Where

ν	cross-link density (moles)
V_s	molecular volume of solvent
V_r	volume fraction of rubber in the swollen gel
χ	Interaction constant (usually given as 0.4 for natural rubber)

2.5 Microscale Thermal Decomposition

2.5.1 Thermogravimetric Analysis (TGA) / Derivative Thermogravimetry (DTG)

Equipment

Stanton Redcroft TGA 1000, with feeds of laboratory grade nitrogen and air

Procedure

Testing was carried out in adherence to ISO 11358 [167] (TGA general principles) and BS ISO 9924[168], written specifically in relation to some common hydrocarbon elastomers including polyisoprene. A one-piece sample of mass 10 +/-0.5mg is weighed on an accurate lab balance. Liquids or powders were weighed directly into the hanging platinum crucible. When testing in nitrogen following use in air, the unit is purged for a minimum of two hours to ensure that the large volume of gas within the balance head is oxygen free, validated using an oxygen analyser.

Runs were undertaken separately in atmospheres of air and nitrogen using from 25 to 900°C at a heating rate of 10°C per minute and a gas flow rate of 25 ml/minute unless stated otherwise. Data was captured using a model TC-08 Pico data-logger and software. A subsequent .CSV file was exported into Microsoft Excel for analysis. A correction factor was applied for buoyancy encountered with this apparatus, where a false increase of mass is measured due to the expansion of gas within the furnace, resulting in an increased downwards force on the pan. This is dependant upon gas flow rate, and a run was made with an empty pan at the same flow rate to measure the false increase, which is then subtracted from the apparent mass loss percentage. Plots of TGA and DTG are then produced for analysis.

2.6 Burning tests

2.6.1 Limiting Oxygen Index (LOI)

Equipment

Stanton Redcroft Flammability Apparatus (FTA)
Gas burner using propane/methane canister (Labtherm scientific)

Procedure

Limiting Oxygen Index (LOI) in accordance with BS EN ISO 4589 part 2 [39] was used as a simple industry test for flammability by variation of the proportion of oxygen to nitrogen in the test atmosphere. Rubber samples are not always self-supporting, so moulded strips 3 x 52 x 140mm were mounted in a vertical support frame accessory. The oxygen/nitrogen flow rates are set by adjusting needle valves to maintain a flow rate of 17+/-0.85 litres per minute, and measured using a paramagnetic oxygen analyser. A gas flame (16mm) is placed just on the top edge of the sample in 5 second intervals (up to 30 seconds) until a flame is established. The sample flame is then timed to check for self extinguishing behaviour with 3 minutes. If the sample self extinguishes then a new run is made at a higher O_2 concentration, and if burning persists then the O_2 concentration is reduced. This is continued until confidence is gained through repeats in changes of 0.2 % O_2 concentration to give a calculated result for the final LOI value.

2.6.2 Horizontal burning flammability test

A small scale flammability test was also carried out in accordance with ISO 1210 method A [38]. This method is equivalent to the Underwriter Laboratory test UL94HB, but with some differences with respect to the expression of results.

Equipment

Lab gas burner and sample holder.

Procedure

A sample 3 x 13 x 125mm is mounted horizontally in an apparatus with the facility to support the sample to maintain the necessary flatness whilst tilted edge-on at 30° and exposed to to a small (19mm) gas flame at an angle of 45° for 30 seconds. The burning behaviour is then observed and timed. A sample may self extinguish when the flame is withdrawn, self extinguish between 25 and 125mm, or continue to burn until the flame reaches 125mm. The results are then classified as follows in Table 22. FH is an abbreviation of Flaming Horizontal.

Designation	Suffix to designation	Burning behaviour observed
FH-1	N/A	Self Extinguishing, no combustion beyond first 25mm mark
FH-2	Length of burnt area (mm)	Self Extinguishes between 25 and 100 mm mark
FH-3	Burning rate (mm/min)	Does not Self Extinguish, burning rate <40mm/min for samples 3-12mm thick or <75mm/min for samples <3mm thick
FH-4	Burning rate (mm/min)	Does not Self Extinguish, burning rate > FH-3 maximum values

Table 22 Result categories ISO 1210 method A

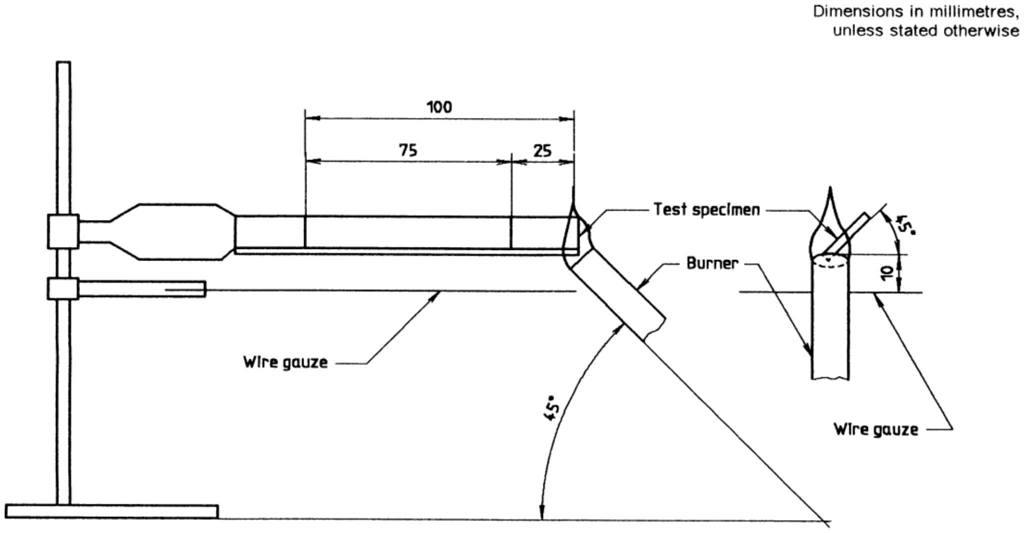


Figure 21 Test sample configuration ISO 1210 method A

2.6.3 Cone calorimetry

Cone calorimetry in accordance with ISO 5660 part 1[169] was used to assess burning behaviour, smoke and CO/CO_2 emissions.

Equipment

Fire Testing Technology (FTT) cone calorimeter

Calibration

Gas analysers are calibrated using known feed gases. The CO/CO_2 is calibrated using nitrogen for a zero point and a span gas mix of typically 8% CO_2 and 2000 ppm CO in nitrogen. The oxygen analyser is calibrated using nitrogen for a zero point and surrounding air as a span gas of 20.95% oxygen. Heat release is checked by use of a methane gas burner set at 5KW using an accurate gas flow meter and calculated into heat release by the 'CONECALC' software. From the oxygen depletion and CO, CO_2 measured a calibration constant 'C' is determined, and must lie within the range 0.038 to 0.042. The cone heater is set to an established temperature, and the resultant heat flux measured using a thermopile. Optical density measured by a laser beam and detectors is calibrated by use of standard filters. The mass load-cell can be calibrated by use of a known mass. To validate the cone performance black pigmented cast polymethylmethacrylate (PMMA) is tested and values are checked against a published value for the effective heat of combustion and heat release curves from previous successful calibrations.

Procedure

For each day running a series of checks are made of the instruments on-board the cone calorimeter. A key element to reliable performance is the maintenance and configuration of the filters within the gas stream drawn from the sampling ring within the horizontal run of the exhaust stack. In a modification to extend filter life and maintain good air flow from the gas sampling point to the gas analysers, a glass wool soot filter was incorporated into the line between the sampling ring and the 'Balston' filter. After this point the gas stream enters the pump, which must also be cleaned regularly to ensure reliability. The gas stream then is split two ways: one line feeds the CO/CO_2 analyser through a compact filter unit. The second stream is then dried and can be stripped of CO_2 before entering the paramagnetic oxygen analyser. A schematic view of sample gas flow is in Figure 22.

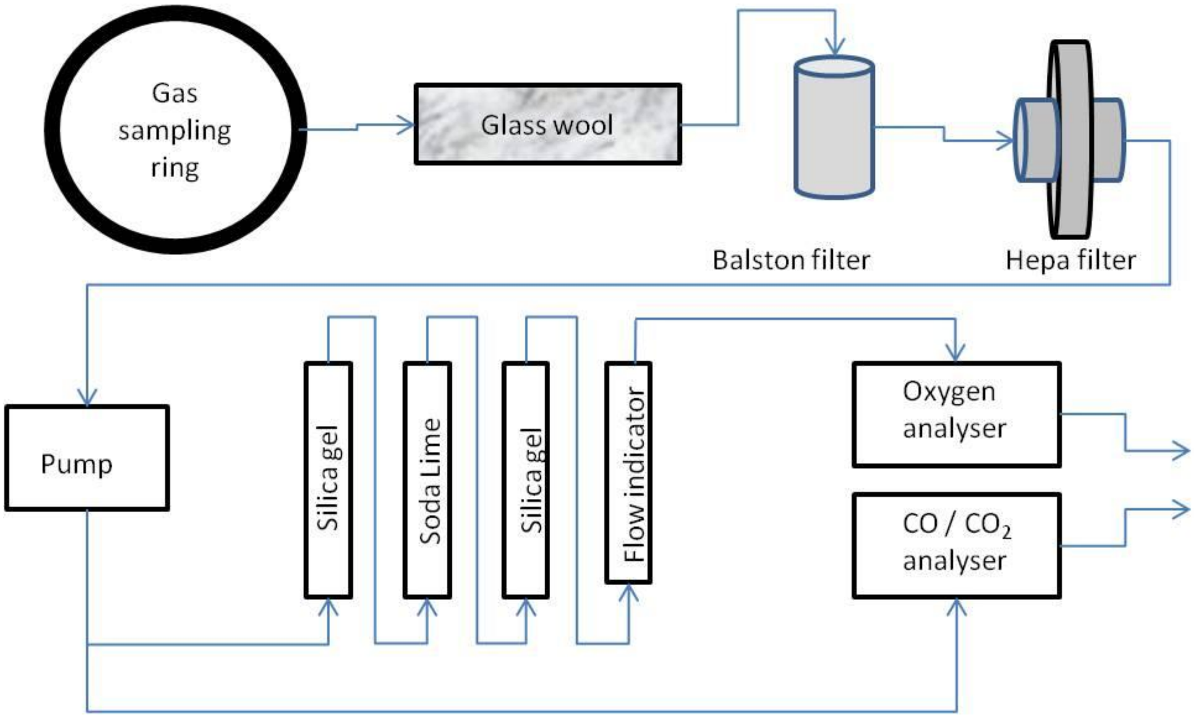


Figure 22 Schematic view of sample gas flow in cone calorimeter

For each material, three samples 100 x 100 x 6mm were tested on the Cone Calorimeter at an imposed heat flux of 35 or 50kW/m^2, mounted on a mineral wool insulated sample holder, contained by aluminium foil on the base and sides. The removable sample holder sits on a pedestal which has a load cell at the base to record the mass during the test. The use of a steel side-frame was used in some instances where significant spalling has occurred following intumescent behaviour. The sample is exposed to a cone shaped radiant heater, with an electrical spark operating until flaming combustion. Observations of behaviour can be made throughout the run for changes such as surface bubbling and intumescence particularly before a large flame is developed, but can be difficult to observe more subtle changes due to the obscuration by the flame. When flaming combustion ceases then the test is deemed complete, but some continued smouldering combustion may be taking place leading to some residual heat release being measured at the end of the test, often leading to high CO levels being noted at the end of test.

Smoke and mass loss has a negligible time delay, but a delay of up to 20 seconds may be noted from the gas analysers. This delay is observed during the test when the smoke and heat release rate is displayed live on the Conecalc PC software, with smoke rising ahead of HRR. Once the run is complete the software applies a correction factor to off-set the time lag. To avoid (and detect) any problems with reproducibility of results, the three samples are not run concurrently, but sequentially as part of a set of materials, with the runs for each repeat run apart by several hours as a minimum.

Analysis of Cone Calorimeter data points

A summary report is produced with the software with values including peak and average heat release, but the strength of the cone lies with the consideration of the burning behaviour as a function of time. From the three runs per material, average plots are produced using Microsoft Excel to allow overlay comparisons of the following key features - percentage mass remaining, Heat Release Rate, Rate of Smoke Release (RSR), Total Heat Evolved (THE), CO_2 and CO production rate. Schartel [100] describes a commonly considered set of typical HRR curves (Figure 23). This overall view of the heat release rate can be used to help identify the type of burning behaviour encountered in addition to the values gathered.

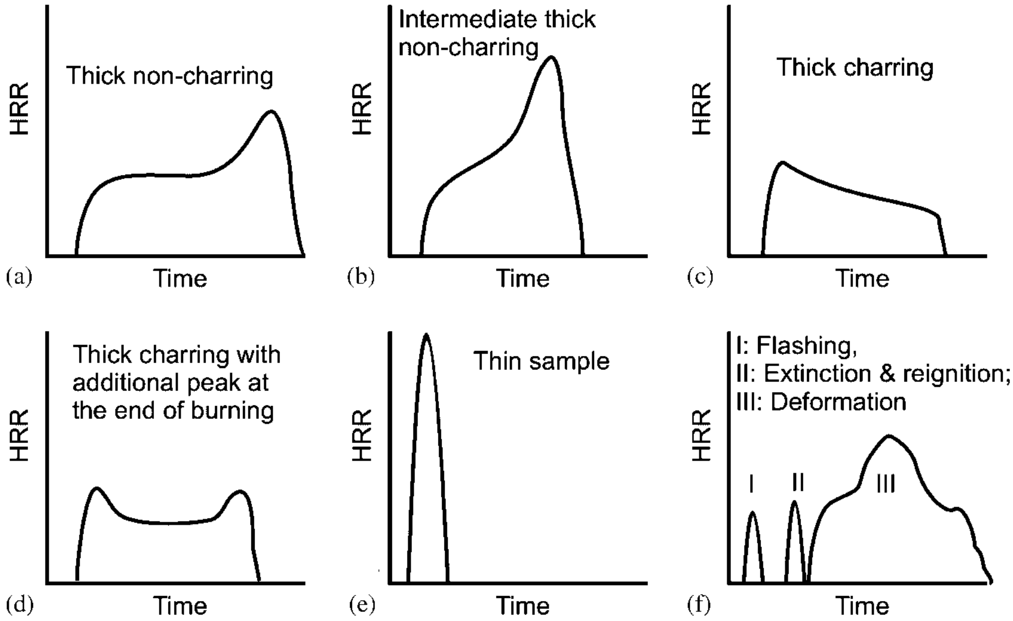


Figure 23 Typical HRR curves for different characteristic burning behaviours

Further analyses may be made of the HRR data, in an attempt to consolidate the heat release curve into a single measure of burning performance to satisfy a defined industry requirement. One example of this is the Maximum Average Rate of Heat Emission (MARHE), specified with TS EN45545-part 2 [170]. This measure is calculated using the cumulative heat emission from t=0 to t=t where t is the time and q is the heat release rate.

$$ARHE(t_n) = \frac{\sum_2^n (t_n - t_{n-1}) \text{ X } \frac{\dot{q}_n + \dot{q}_{n-1}}{2}}{t_n - t_{n-1}}$$

2.7 Objectives of experimental work undertaken

Two objectives (highlighted in bold below) were set for the experimental work within this project. The tasks undertaken to achieve these objectives are itemised below.

Investigate practically the thermal decomposition and burning behaviour of rubbers, and identify the relationships between them.

TGA of polyisoprene and single additives was undertaken to study the effects on thermal stability of typical materials used in a polyisoprene rubber compound.

Simple rubber mixtures were produced and TGA undertaken to investigate any interaction.

Rubber formulations with a variation of cross-link density and type were investigated by TGA and flammability tests.

Rubber formulations with different fillers were produced and characterised for TGA, physical properties and flammability tests.

A detailed study of the effect of varying levels of carbon black in rubber was investigated using TGA, physical properties and flammability tests.

Study the physical properties, thermal decomposition and fire performance of formulations containing fire retardants.

Rubber compounds were prepared and physical and flammability properties evaluated using ammonium polyphosphate, and in combination with pentaerythritol, melamine and expandable graphite.

Rubber compounds were prepared and characterised using expandable graphite at various levels.

The effects of hydrated fillers and additives in a polyisoprene rubber compound were investigated; aluminium hydroxide (ATH); Ultracarb (a blend of huntite of hydromagnesite); magnesium hydroxide (MH); and calcium carbonate.

The effects of zinc hydroxystannate as a proposed synergist in ATH and MH, both as an additive and a coating onto the filler, were investigated using TGA, physical properties and flammability tests.

Zinc borate, red phosphorus, and expandable graphite were incorporated into ATH containing formulations and investigated using TGA, physical properties and flammability tests.

Following positive results from an equal blend of ATH and MH, further mixtures were investigated at a range of mixtures, and investigated using TGA, physical properties and flammability tests.

CHAPTER 3. RESULTS AND DISCUSSION – POLYISOPRENE AND ADDITIVES

3.1 Thermogravimetric analysis of polyisoprene and additives

3.1.1 Introduction

Since a rubber compound contains additives, it was considered useful to carry out TGA/DTG on the chemicals used within these and further planned studies. These materials are fully detailed in section 2.2.1.

3.1.2 Results

Each additive was heated at a rate of 10°C per minute in nitrogen and air to 900°C. The results are plotted in Figure 24 and Figure 25 respectively for the first stage materials, and Figure 26 and Figure 27 for the cross-linking additives.

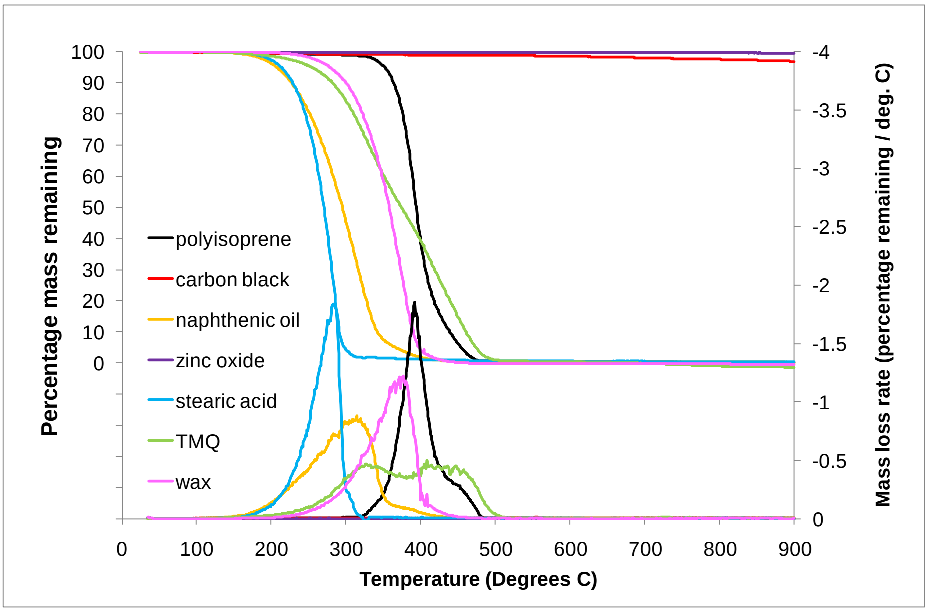


Figure 24 TGA and DTG curves for IR polymer and typical additives in nitrogen

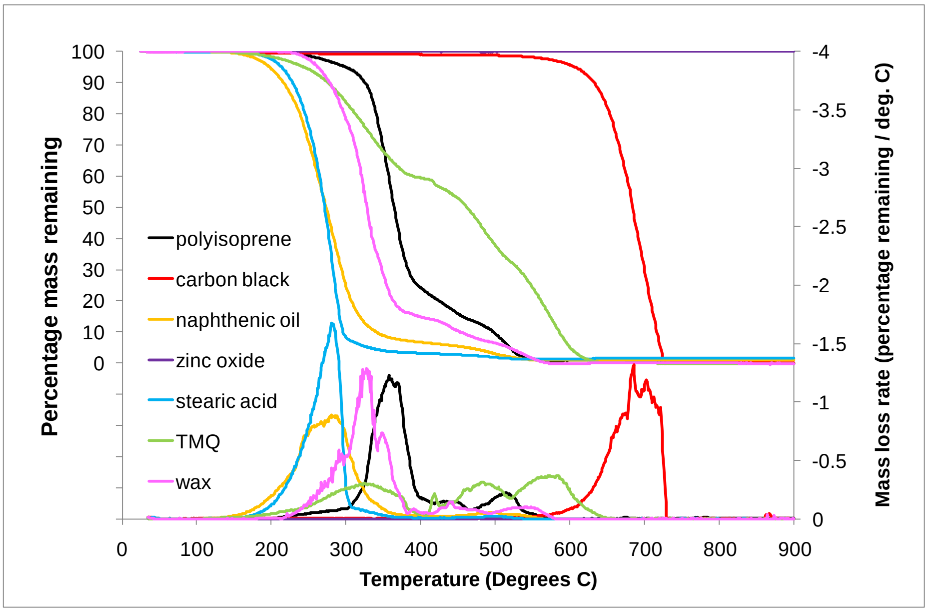


Figure 25 TGA and DTG curves for IR polymer and typical additives in air

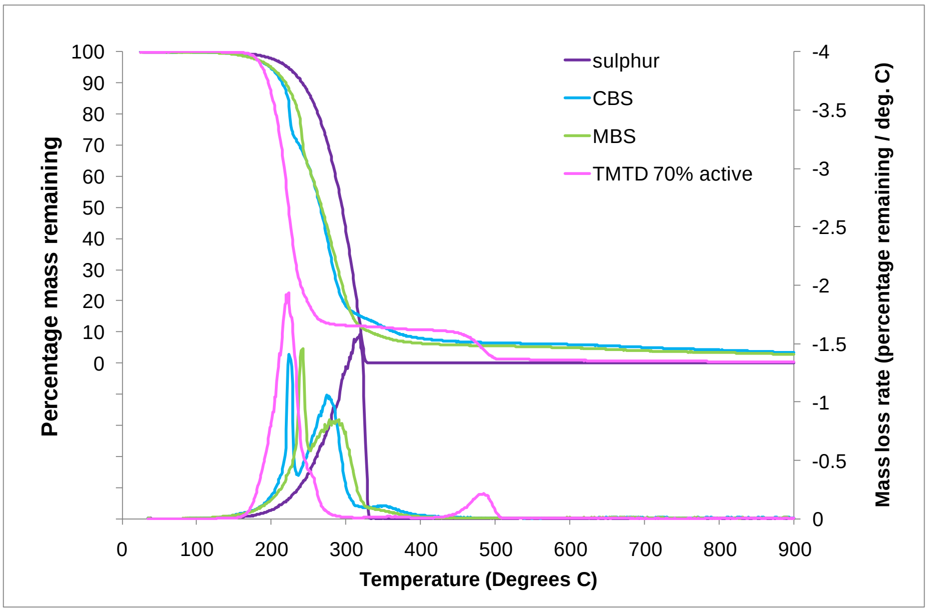


Figure 26 TGA and DTG curves for cross-linking additives in nitrogen

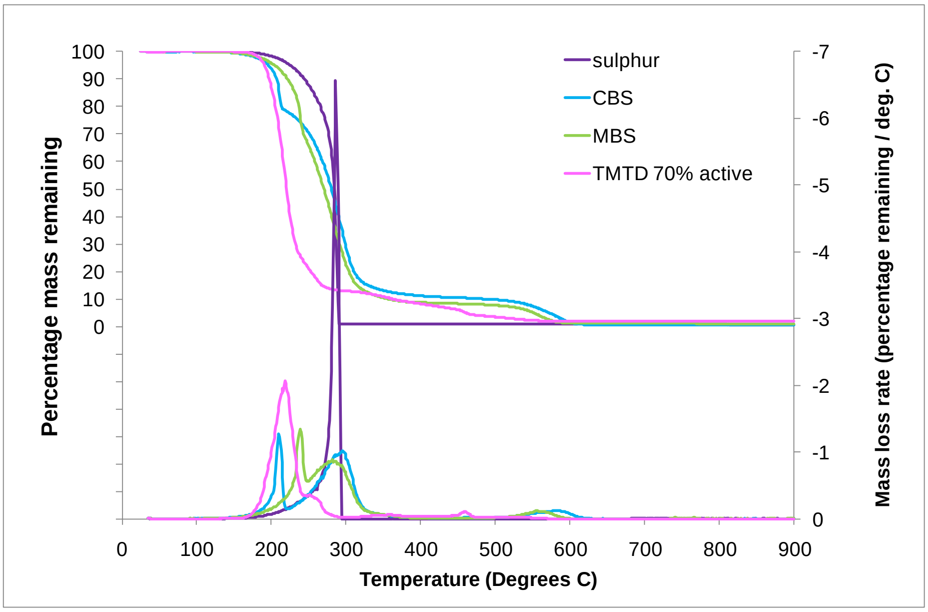


Figure 27 TGA and DTG curves for cross-linking additives in air

Using DTG data the temperature for each peak rate of mass loss was compiled into Table 23 for ease of comparison. In the case of some materials no peak was recorded due to a lack of significant mass loss in these additives.

Material	Air °C	Nitrogen °C
High cis 1,4 Synthetic Polyisoprene	357	392
Carbon black N550	685	no peak
Naphthenic process oil	287	314
zinc oxide	no peak	no peak
Stearic Acid	280	277
TMQ	572	327
Wax	327	377
Sulphur	286	318
CBS	294	278
MBS	285	242
TMTD 70% active	218	223

Table 23 TGA mass loss peak temperatures for additives

For polyisoprene in nitrogen there is a significant mass loss at a peak of 392°C, in fair agreement with literature, with figures of 365, 377, 368 and 388°C quoted depending on test conditions[171]. The process is in one rapid step complete by 470°C, indicating no stable char development. In contrast the mass loss in air starts at an earlier temperature indicating some oxidative reactions, with an earlier peak mass loss temperature of 357°C. Approaching 30% residual mass however, some char residue developed with an improved thermal stability up to around 540°C.

Carbon black is the most stable organic additive, with significant mass loss commencing in air at over 600°C and the peak rate of mass loss occurring at 685°C.

Zinc oxide is unaffected by the heating, with a negligible loss of mass in both atmospheres. Alone it is therefore acting as an inert additive, which will lead to a reduced fuel load. It is not known if the presence of this metal oxide can affect the thermal stability of other additives.

The naphthenic process oil and stearic acid both decompose at a temperature much lower than the polymer, so can be considered to add to the volatility of the rubber compounds. Whilst added at low levels, these materials may reduce the time to ignition by readily volatilising into flammable vapour at well below 300°C. This indicates that the elimination of process oils or replacement with less flammable additives reduces ignitability. It is less clear of the final effect of stearic acid, since this is partly consumed with the cross-linking reactions, reacting with zinc oxide during vulcanisation to give zinc stearate.

The microcrystalline paraffin wax is more stable than the oil in both air and nitrogen. In air the mass loss is reduced in the latter stages, indicating some temporary char development, in a similar manner to polyisoprene. Antioxidant TMQ (Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline) loses mass from around 200°C, but proceeds slowly. This additive is designed to mop up oxygen free-radicals, but is not able to prevent polymer decomposition. Sulphur is unstable, with a rapid mass loss complete by 287°C in air and 314°C in nitrogen. This indicates that a rubber compound with unreacted sulphur, undergoing more rapid thermal decomposition, and suggests a low thermal stability to sulphur cross-links. The organic additives CBS, TMTD and MBS all decompose in a similar manner, with a sudden loss of mass at between 250 and 350°C, followed by a slower mass loss being complete at between 500 and 600°C.

All of the curing additives are added in small proportions compared to the polymer and filler, but if not fully reacted during vulcanisation could lead to the evolution of organic volatiles at lower temperatures than the polymer, thus reducing the time to ignition.

3.1.3 Summary

It is clear that the presence of additives will have some influence on the overall thermal decomposition of a rubber compound and by implication may affect the burning behaviour. It confirms the suggestion that the addition of mineral oil will be detrimental when fire retarding rubber, and the use of less volatile alternatives such as zinc soaps should be sought. Most of the curatives are highly unstable, but these are mostly reacted during cross-linking. Both zinc oxide and carbon black are stabilising factors, but any effects on the decomposition process within the polymer would be worthwhile investigating. The decomposition of most of the additives was unaffected by the presence of the rubber components (as measured by TGA). However, the presence of polyisoprene alters the decomposition of carbon black, as discussed later in section 3.2.

3.2 Decomposition study of base formulation

3.2.1 Introduction

In this study basic rubber mixtures were prepared to attempt to better understand the interactions between some important additives under microscale thermal decomposition with TGA.

3.2.2 Experimental section

3.2.2.1 Materials

Simple rubber compounds (Table 24) were evaluated using TGA in nitrogen and air.

additives pphr	IB40	IBZ	BZ	IZ	IB5	IB20	IB60	IS
polyisoprene	100	100		100	100	100	100	100
Carbon black	40	40	40		5	20	60	
Precipitated silica								40
zinc oxide		5	5	5				
Total pphr	140	145	45	105	105	120	160	140

Table 24 Simple rubber formulations in pphr

3.2.2.2 TGA results

TGA runs were carried out at a heating rate of 10°C per minute and a gas flow rate of 50 ml/minute. For ease of comparison the formulation and final TGA residues are in Table 25.

Additive % (by wt.)	IB40	IBZ	BZ	IZ	IB5	IB20	IB60	IS
polyisoprene	71.4	69.0	0.0	95.2	95.2	83.3	62.5	71.4
Carbon black	28.6	27.6	88.9	0.0	4.8	16.7	37.5	0.0
Precipitated silica								28.6
zinc oxide		3.4	11.1	4.8				
total non-polymer %	28.6	31.0	100	4.8	4.8	16.7	37.5	28.6
TGA residue								
Final % air	0.2	4.3	11.3	5.4	0.0	0.4	0.8	26.0
Final % N2	27.4	30.7	97.1	5.3	4.2	15.7	37.2	25.8

Table 25 Simple rubber formulations percentage additives and TGA residues

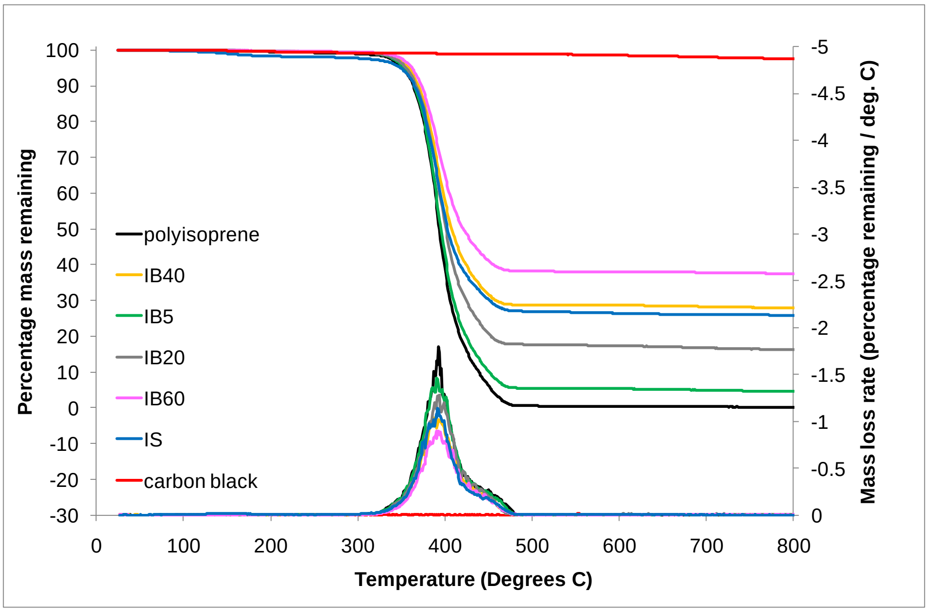


Figure 28 TGA and DTG curves for the variation of filler level and type in nitrogen

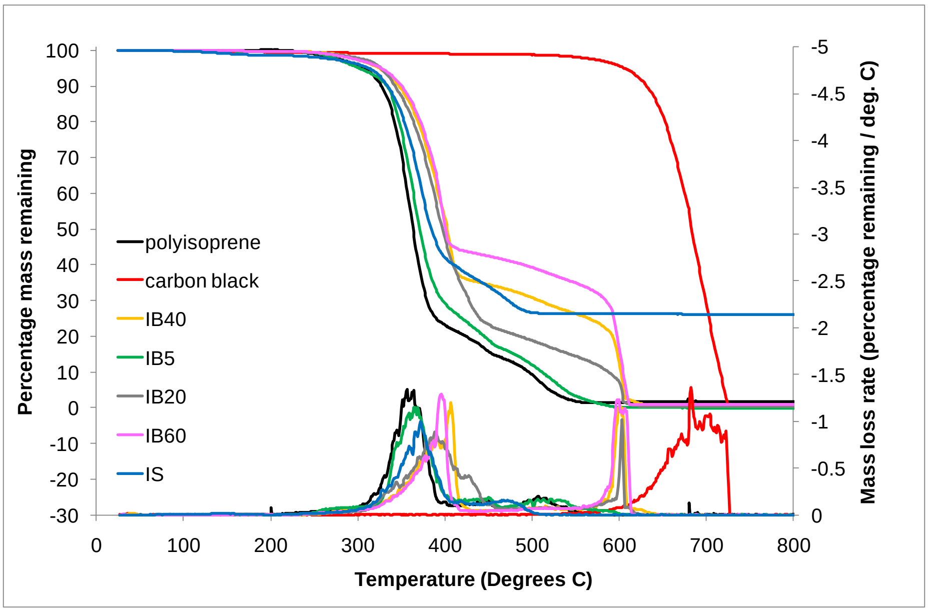


Figure 29 TGA and DTG curves for the variation of filler level and type in air

The effect of carbon black and silica in rubber is considered without any other additives in nitrogen (Figure 28) and air (Figure 29). In nitrogen carbon black levels have little effect on the decomposition of the polymer. In air, as the level of carbon black is increased, the mass loss is slower with a delayed DTG peak. The presence of increasing levels of carbon black may therefore be considered to improve the thermal oxidative stability of the rubber compound beyond the simple decrease of polymer. This indicates that an oxidative process is controlling the stability imparted by carbon black. It may be that either the carbon black is either chemically absorbing free radicals so slowing the rate of random chain scission, or that the carbon black is a physical barrier to either oxygen absorption or the volatilisation of small species. Considering the mass loss of pure polymer, compared to a carbon black filled compound, it may be considered that the level of char development for the compound is higher in the presence of carbon black than as a pure polymer. It may be that the rate of oxidation is lower due to the presence of carbon black blocking gas migration, or that the carbon black may absorb free radicals. A constructed TGA and DTG curve (using the proportional addition of the single material curves) (Figure 30) highlights the effect of carbon black to increase the thermal stability of the polyisoprene under air – and conversely the reduction in the thermal stability of the carbon black.

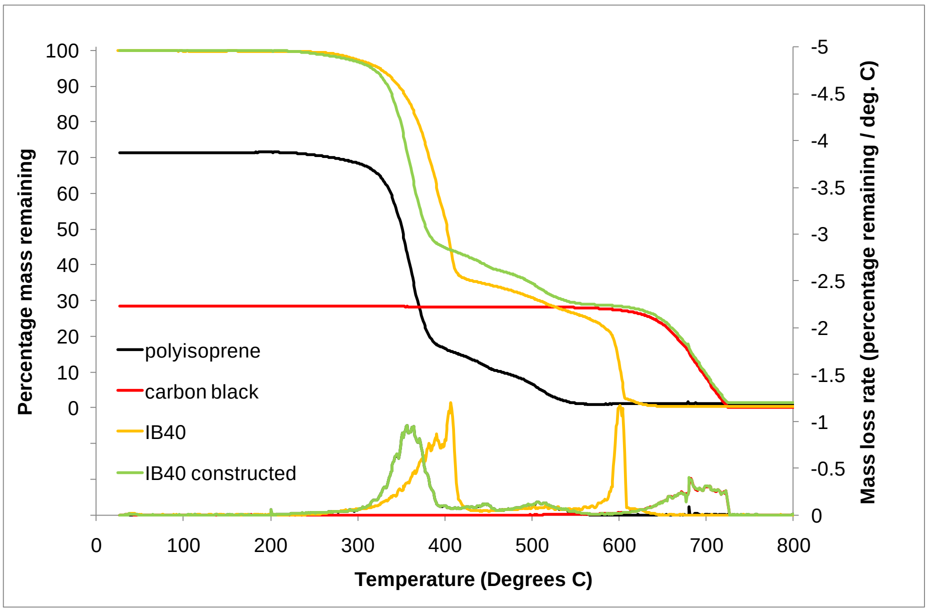


Figure 30 Constructed and actual TGA and DTG curves for IB40 in air

To separate the degradation of the polymer, and the carbon black, a formulation was prepared using precipitated silica at 40 pphr (IS), so that the mass loss can be compared to IB (40 pphr carbon black). The addition of silica leads to a low level of mass loss (around 2%) between 120 and 200°C, related to water loss from the filler. In a nitrogen atmosphere there seems to be little difference between carbon black and silica, whereas in air the carbon black imparts more stability to oxidation of the polymer than the precipitated silica. This is noticeable both in the early stages of mass loss and over 400°C where char may be developed. Char development in the silica filled formulation is less apparent with a faster rate of mass loss from 400 to 500°C. From 550°C the carbon black starts to oxidise, whereas the silica is resistant to thermal decomposition within the range of experimentation.

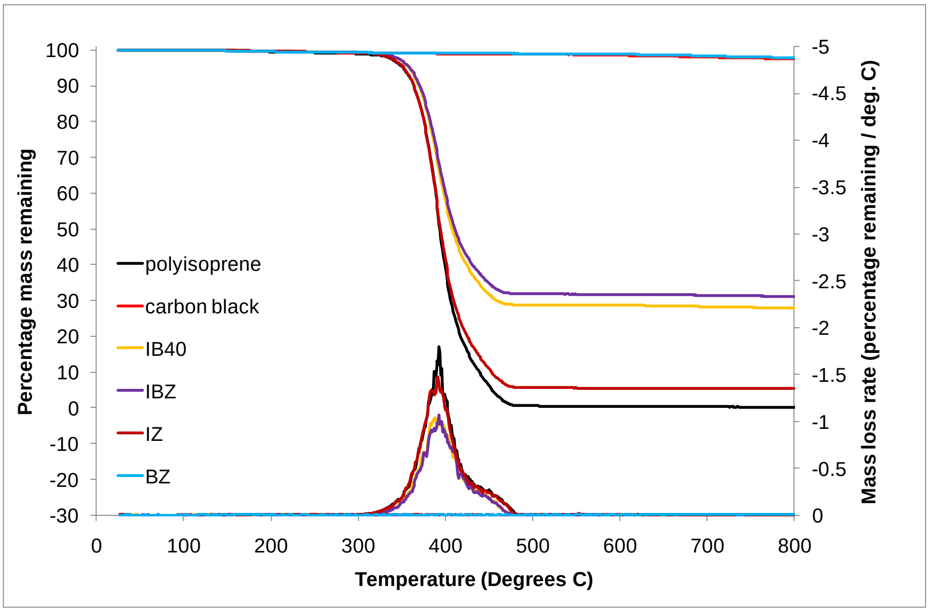


Figure 31 TGA and DTG curves comparing the influence of zinc oxide in nitrogen

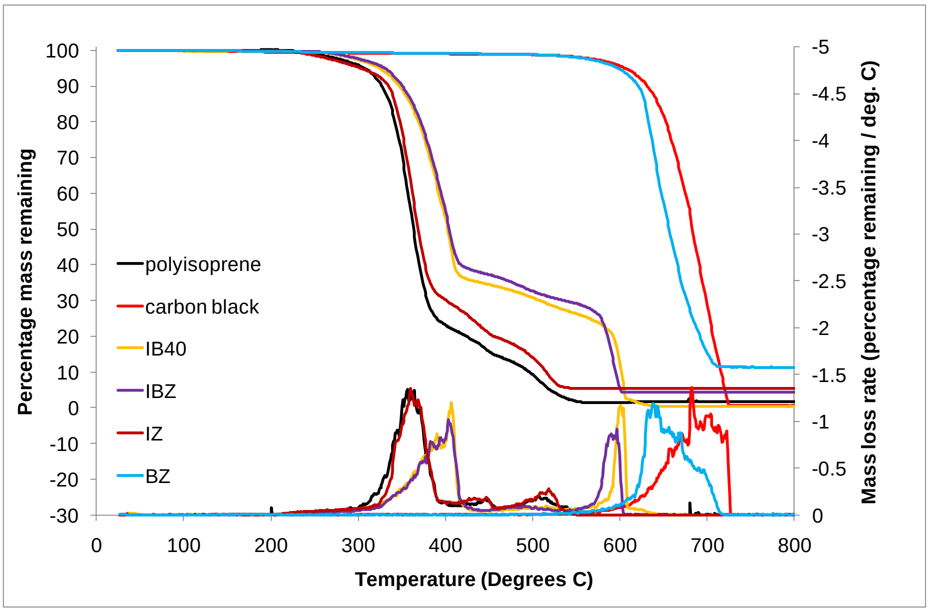


Figure 32 TGA and DTG curves comparing the influence of zinc oxide in air

TGA in nitrogen (Figure 31) and air (Figure 32) evaluates the presence of zinc oxide on the mass loss of polyisoprene and carbon black. In some materials, metals or their oxides can act as catalysts with the ability to either promote formations of new structures, so aiding thermal stability; or conversely to promote degradation processes such as chain stripping leading to increased rates of volatile production. No significant differences in the rubber compounds were observed, suggesting that zinc oxide has little effect on thermal decomposition. In a simple ground mixture of zinc oxide and carbon black however (Figure 32), it appears that the presence of zinc oxide leads to a more rapid mass loss in air compared to pristine carbon black. This raises a few possibilities; either that zinc oxide reduces the thermal stability, or that the action of mixing together the materials modified the carbon black. Since carbon black is a pelletised agglomeration of particles, it is possible that the latter explanation of mixing has increased the available surface area of carbon black for oxidation, so increasing the rate of mass loss. This may be confirmed by the similar temperatures for the start and finish of the mass loss for carbon black.

3.2.3 Summary

Basic rubber mixtures were prepared to attempt to better understand the interactions between commonly used additives under microscale thermal decomposition with TGA. Zinc oxide has a minimal effect on thermal decomposition other than by simple dilution. Precipitated silica as a filler in polyisoprene creates less stability than carbon black in the region of 400 to 550°C, but yields a final inorganic residue resistant to decomposition within the conditions employed. Increasing levels of carbon black yield reduced rates of mass loss in the polymer decomposition phase, when decomposed in an atmosphere of air, but has little effect in nitrogen. Carbon black has a peak decomposition temperature of around 685°C, but when mixed with rubber this value is reduced to around 600°C. Fillers are of interest for further study of decomposition and burning in compounds, so are explored in sections 3.4 and 3.5. In addition, it would be useful to consider the effect of some of the functional additives, including cross-linking agents, explored in section 3.3.

3.3 Effects of cross-linking

3.3.1 Introduction

The effect of cross-link density and type on the thermal decomposition was measured by TGA, while the corresponding influence on the flammability was determined by cone calorimetry and limiting oxygen index (LOI).

3.3.2 Experimental section

3.3.2.1 Materials

The base formulation in Table 26 and the final conversion compounds in Table 27 were based on available literature [29].

Base formulation	Composition (pphr)
synthetic polyisoprene	100
carbon black N550	40
naphthenic process oil	2
zinc oxide	5
stearic acid	2
TMQ	2
antiozonant wax	2

Table 26 Base rubber formulation for cross-linking formulations

	Composition (pphr)					
Formulation Number	N	S	SV	S-EV	EV	P
Cure system	None	Sulphur Only	High Sulphur	Semi-EV	EV	Peroxide
Sulphur	-	2.5	2.5	1.5	0.25	-
CBS	-	-	0.6	1.5	-	-
MBS	-	-	-	-	2.1	-
TMTD	-	-	-	-	1	-
dicumyl peroxide	-	-	-	-	-	3

Table 27 Additives used in cross-linking formulations

Samples from formulation N and S were formed at room temperature to the same shape as the formulations with a full cross-linking system, with the remaining samples vulcanised as described in section 2.2.3.

3.3.3 Results and discussion

3.3.3.1 Rheological and physical tests

Property	Units	N	S	SV	S-EV	EV	P
Vulcanised		no	No	yes	yes	yes	yes
Cure system		None	sulphur only	High sulphur	Semi-EV	EV	Peroxide
Cross-link Density	Moles	N/A	N/A	6.39	7.40	6.17	3.17
MDR MH (160°C)	lb/in	1.14	2.86	11.4	12.43	10.62	6.65
MDR MH (200°C)	lb/in	0.68	4.46	7.66	10.12	8.77	5.16
Hardness	IRHD	37	37	53	56	56	43

Table 28 Physical test results for cross-linking formulations

* The values cannot be determined for un-vulcanised rubber, since entrapped air within the compound will yield a false result.

For formulations N and S, a result for cross-link density was not obtained because without cross-links, the rubber compound dissolved fully within the solvent. The semi-EV cure system within formulation S-EV produced the highest cross-link density, followed by the remaining sulphur cross-linked formulations, S and EV. A lower level of cross-link density was measured for formulation P using the organic peroxide curative.

Maximum MDR torque (MH) at 160°C showed that that formulation N with no sulphur did not vulcanise at all, as expected. Formulation S with added sulphur but no accelerator started to vulcanise, albeit very slowly. The relative values of maximum torque for the remaining formulations can be compared in rank with the cross-link densities measured, where formulation S-EV gave the highest torque and formulation P gave the lowest. Testing at 200°C led to a reduction in maximum torque for the cross-linking formulations, indicative of a lower level of cross-linking. This is usually explained as an increasing level of reversion, a term used to describe the destruction of cross-links at higher vulcanising temperatures. S achieves a higher level of cross-linking at 200°C, since the increased energy input has increased the speed of the formation of cross-links relevant for any thermal decomposition testing, since some cross-linking may occur during these tests.

Hardness values broadly follow MH and cross-link density, with sulphur cured formulations giving similar results, but the peroxide cured formulation gave a lower level of hardness

3.3.4 TGA results

TGA Gas flow rate of 50 ml/minute, heating rate of 10°C/minute.

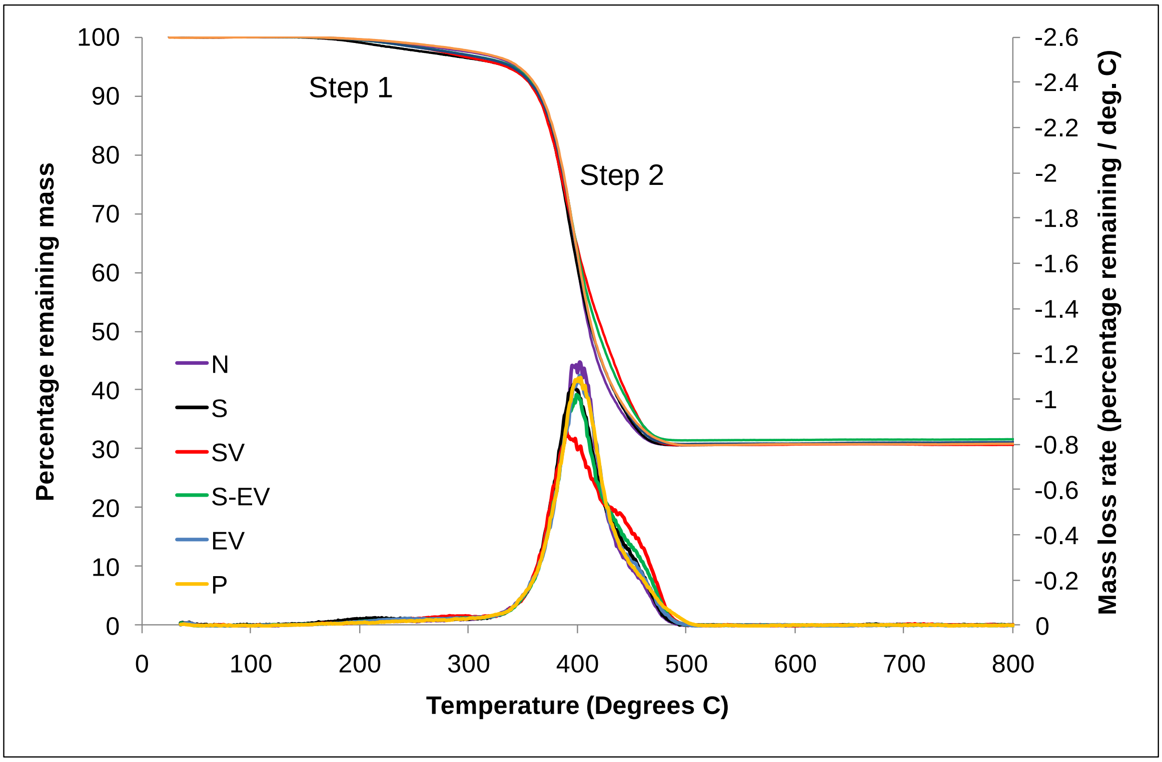


Figure 33 TGA and DTG curves for cross-linking formulations in nitrogen

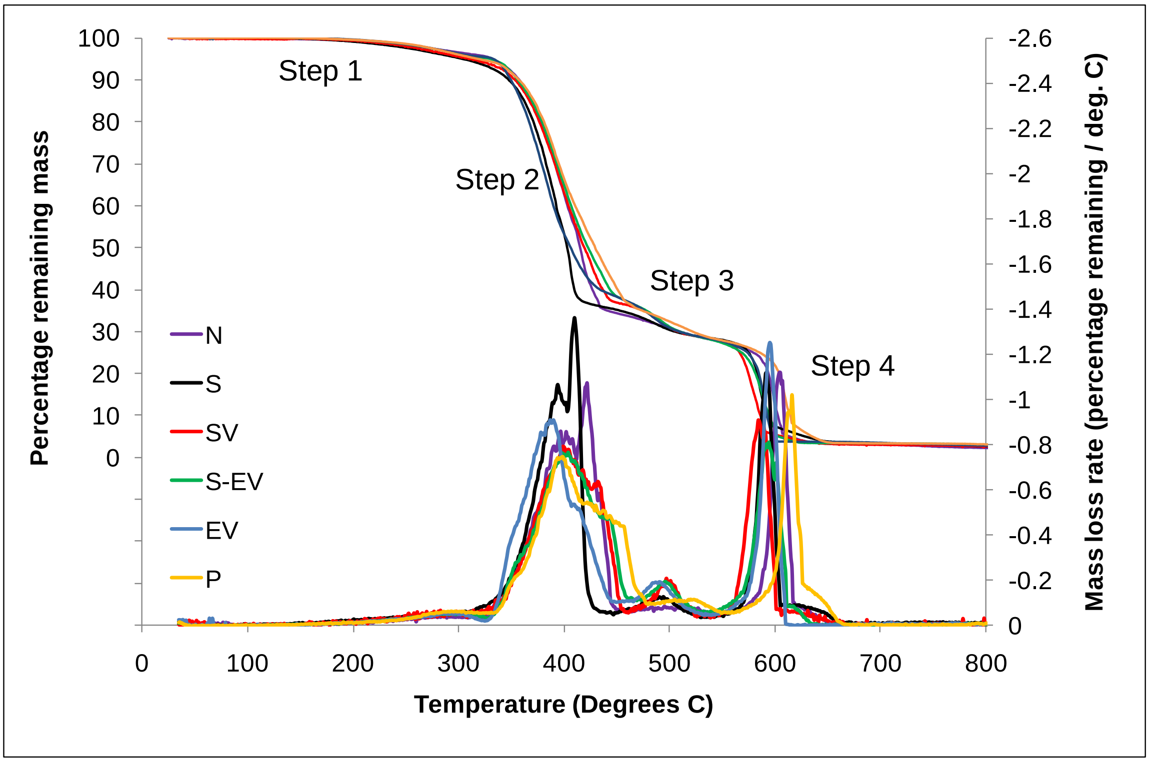


Figure 34 TGA and DTG curves for cross-linking formulations in air

Formulation code	N	S	SV	S-EV	EV	P
Nitrogen	402	396	390	399	402	401
Air	422	410	399	397	390	399

Table 29 DTG peak decomposition temperatures for cross-linking formulations

Two clear steps are noticeable when TGA is carried out in nitrogen (Figure 33). Step 1 is almost indistinguishable between the formulations, this mass loss associated with the loss of materials of lower molecular weight. In step 2 the compound decomposes at a common peak temperature of just below 400°C (Table 29). The lowest rate of mass loss is formulation SV with the highest level of additive sulphur, with a lower rate of mass loss between 440 and 480°C, indicating some temporary polymer charring. The mass remaining however is broadly equal for all of the formulations, indicating that cross-linking does not influence any substantial yield within nitrogen. The remaining mass percentage of approximately 29% in nitrogen indicates that the polymer and other additives with the exception of carbon black and zinc oxide have been fully decomposed and volatilised. This percentage is comparable to the residue from the cone calorimeter, suggesting that TGA in nitrogen for these compounds can give a good prediction of the remaining mass generated in the cone.

The TGA / DTG data in air is plotted in Figure 34. There is a gradual mass loss of volatiles from around 150 to 350°C (step 1) similar to nitrogen, followed by polymer decomposition from 350 to around 430°C (step 2). A gradual mass loss until around 580°C (step 3) then changes to a final pyrolysis stage (step 4), at which the mass loss is complete by 660°C. The polymer decomposition in step 2 is very similar for all the cross-linked compounds, peaking at a similar temperature and rate. Formulation N decomposes in two steps, which are distinguishable in Figure 34. It can be observed that cross-linking has reduced the rate of mass loss in the first part of step 2, and given a significant reduction in the height of the second associated peak of step 2.
Step 3 is considerably shorter however for the cross-linked formulations, with an early onset of the final mass loss phase. Formulation P remained the most stable with the lowest rate of mass loss in the polymer charring phase and in the final stage of carbon black mass loss, indicating that the peroxide cure system has promoted char development and graphitisation throughout the temperature range. This indicates that whilst sulphur cross-linking stabilises the rubber in the lower temperatures of decomposition, the residue is less stable at higher temperatures. This suggests that sulphur cross-links can reduce the levels of char development. This agrees with previous literature that suggests that whilst cross-links provide some stability at lower temperatures, they are ineffective at pyrolysis temperatures. This is proposed by

Straus [83], who suggests that the sulphur bonding to the pendant carbon can hinder cyclization of the polymer chain.

To assess the influence of the additives on the overall thermal decomposition of compound SV, a constructed TGA (sum of the proportional mass loss of the individual components) was plotted against the actual decomposition. TGA in nitrogen is displayed in Figure 35, with a slightly increased rate of mass loss for the cross-linked compound from around 400 to 450°C and a small increase in residue to the formulated TGA. The increased thermal stability of the final compound may be due to the cross-linking, or hindrance of the volatilisation of the decomposed polymer fragments by the presence of the carbon black. In air (Figure 36) the difference is substantial, with the cross-linked compound more stable than the constructed TGA curve. This difference shows that the thermal stability of the polyisoprene is increased by the presence of additives, most likely carbon black.

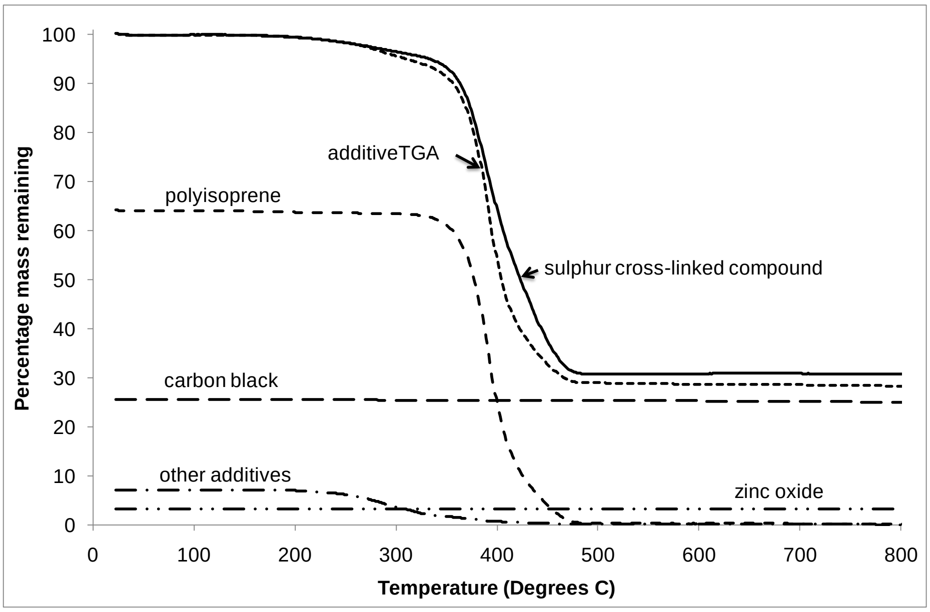


Figure 35 TGA curves for compound SV - actual and additive in nitrogen

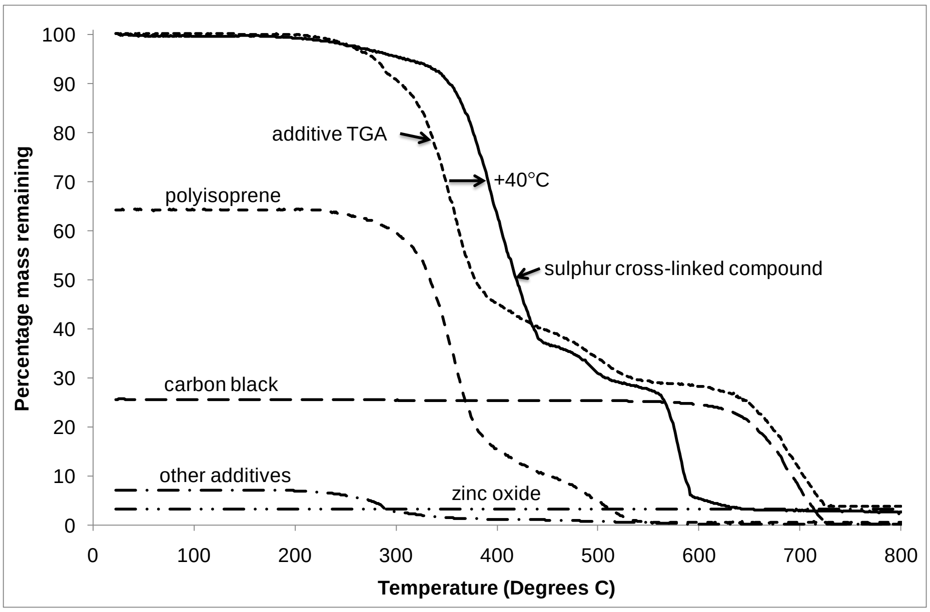


Figure 36 TGA curves for compound SV - actual and additive in air

During the mixing process, the additives within the rubber, whilst dispersed at a fine level, are not chemically bonded or modified by addition but remain as a simple mixture. A number of possibilities could be advanced to explain this difference:

The carbon black within the rubber mixture may reduce the rate that the oxygen can diffuse into the polymer so retarding polymer decomposition. The carbon black may be absorbing free radicals during polymer decomposition. Finally, the mass loss occurs at a significantly temperature than when tested as a separate additives. This indicates that the carbon black is fully oxidised at a lower temperature within the compounds than as a separate additive. At the final stage of decomposition it is likely that the only remaining additives of significance are the zinc oxide and the carbon black. This raises the possibility that the carbon black is reduced in particle size, so increasing in available surface area, by the mixing process, so the early gasification may relate to the availability of oxygen to the surface.

3.3.5 Burning behaviour

Limiting Oxygen Index (LOI)

There was little variation between the different levels of cross-linking. The highest value of 19.8% (Table 30) was obtained for the highest level of cross-linking (S-EV), but the next highest value of 19.5% was for the formulation with no cross-linking.

Property	Units	N	S	SV	S-EV	EV	P
Vulcanised		no	No	yes	yes	yes	yes
Cure system		None	sulphur only	High sulphur	Semi-EV	EV	Peroxide
LOI	% O_2	19.5	19.3	19.3	19.8	19.1	19.2

Table 30 LOI values for cross-linking formulations

Burning behaviour Cone Calorimeter

Three samples 100 x 100 x 6mm per formulation were tested on the Cone Calorimeter at an imposed heat flux of 35 kW/m^2.

Property	Units	N	S	SV	S-EV	EV	P
Time to ignition	secs	70	65	59	56	57	63
Time to flameout	secs	1062	641	689	707	865	851
Total Heat evolved	MJ/m^2	145.6	145.6	137.1	136.5	140.8	141.4
HRR average	KW/m^2	147	256	220	211	175	179
HRR peak	KW/m^2	505	628	578	489	584	541
HRR peak at time	secs	100	93	97	90	93	103
Mass remaining	%	30.4	29.6	29.6	28.9	29.6	29.0

Table 31 Mean values from cone calorimeter for cross-linking formulations

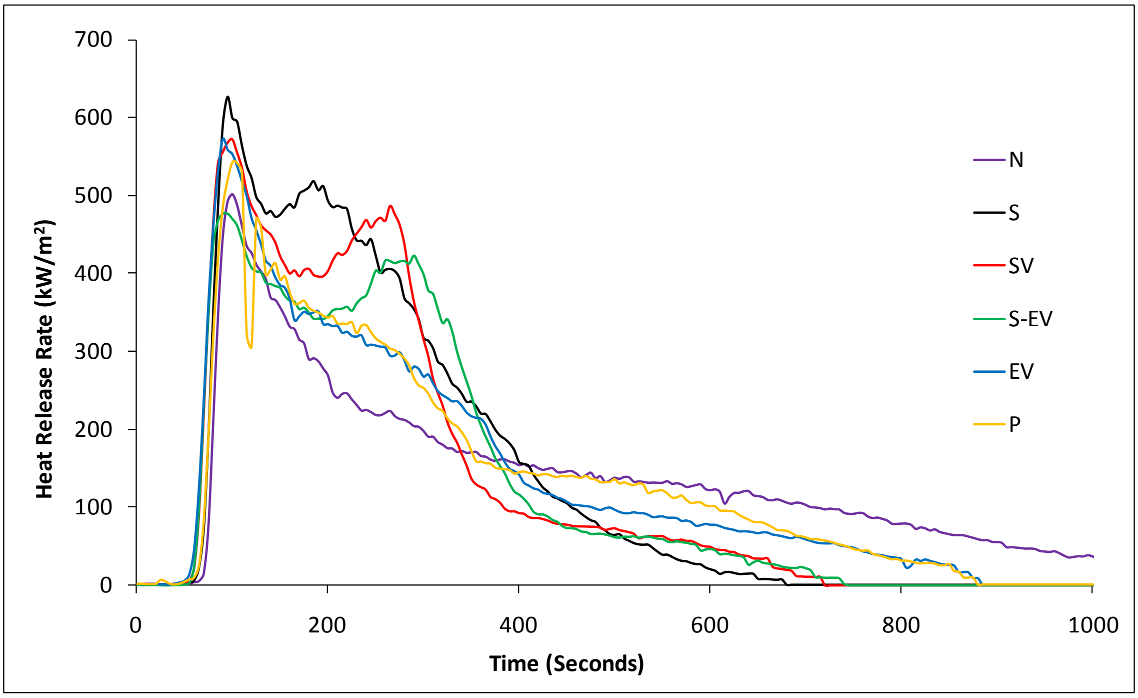


Figure 37 Heat release rate from cone calorimeter for cross-linking formulations

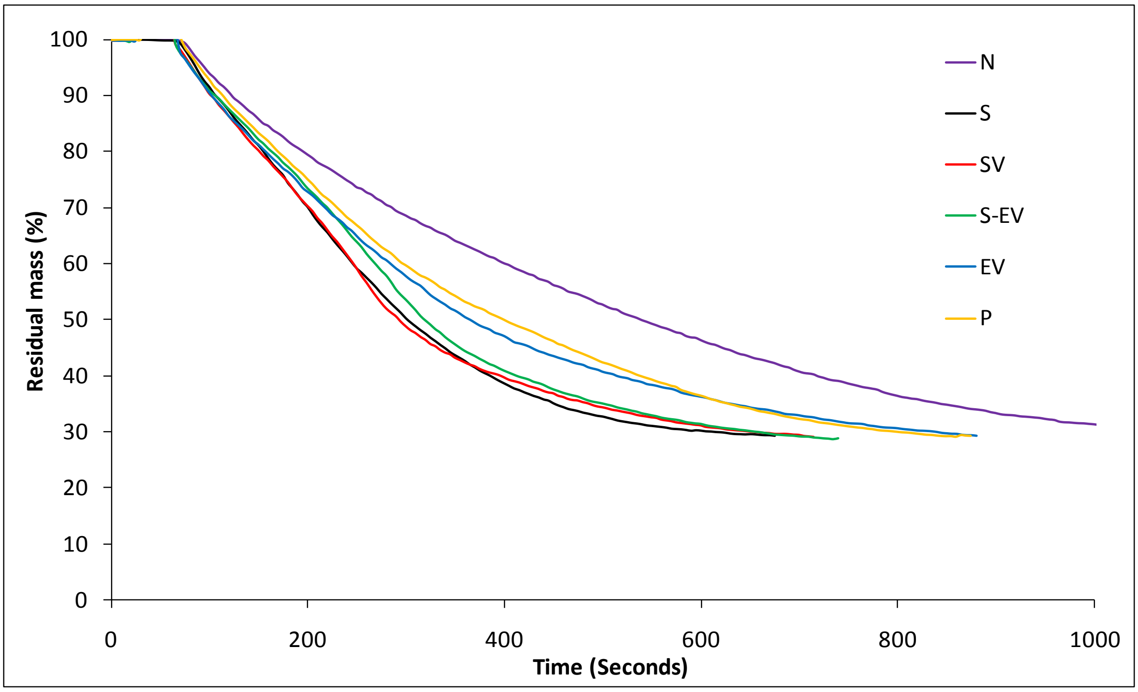


Figure 38 Residual mass from cone calorimeter for cross-linking formulations

Considering the heat release graph in Figure 37, there are significant differences in the burning behaviour between the formulations. The time to ignition (T_{ig}) was longest for the unvulcanized formulations N and S, and the shortest times to ignition for the compounds with the highest level of cross-linking. No relationship is apparent between T_{ig} and LOI for these materials. This can be examined is Figure 39, where all of the indicators of cross-linking show that reduced time to ignition is linked to increased cross-linking.

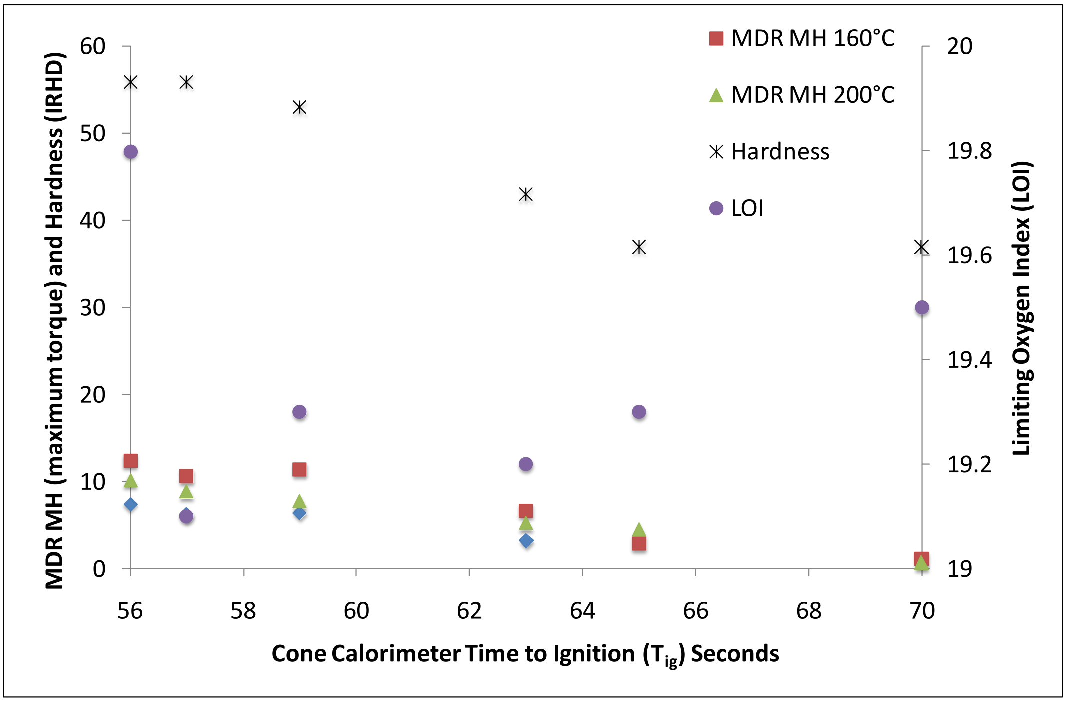


Figure 39 Comparison of Time to Ignition to cross-linking data for cross-linking formulations

The peak HRR for S was significantly higher than for the other compounds. Comparing it with formulation N, the only difference is the addition of sulphur. Sulphur is also present in formulations SV, S-EV and EV, but is predominantly bound within cross-links. S-EV with the highest level of cross-linking had the lowest level of peak HRR. Interestingly, the HRR after the peak release shows the most variation with formulation. Formulation N with no cross-linking agents added shows a rapid drop off in HRR, so taking the longest time to flameout. Formulation S with the high level of free sulphur is the most rapid to flameout, followed closely by formulation SV with a high sulphur cure. Time to flameout appears to vary in line with the level of added sulphur. Considering Figure 38 a similar relationship with the sulphur level is noted, where the compound with no added sulphur has a significantly lower rate of mass loss. The level of cross-linking however does not appear to relate to mass loss.

Considering the mass remaining, it can be compared with the percentage mass of carbon black and zinc oxide. Each formulation has a similar level of remaining mass, at around 29 to 30%. This indicates that the polymer and most of the other organic additives are fully decomposed into volatiles, whilst the carbon black and zinc oxide remain predominantly unchanged. Considering the TGA results for the raw ingredients in Figure 25, the zinc oxide mass is unaffected by heating up to 900°C, whilst the carbon black loses mass from around 550°C onwards. At a heat flux of 35kW/m^2 within the cone calorimeter, the heater will attain a temperature of around 625°C, for which the sample is likely to reach similar levels initially. When the sample attains a peak level of heat release, in this case over 500kW/m^2, the temperature would be expected to be somewhat higher.

Consideration of the shape of the heat release curve indicates a rapid rise to the maximum HRR for all of the formulations, and a second lower peak for the compounds containing higher levels of sulphur. As the sulphur level drops, so does the height of the second peak. With no added sulphur there is no second peak and a subsequent long tail of heat release. A commonly considered set of typical HRR curves (Figure 23) can be compared to the HRR curves in Figure 37; the closest is c) Thick charring for the zero and sulphur addition, and d) thick charring with an additional peak at the end of burning for the higher sulphur levels. This is an interesting observation since polyisoprene is not considered to be capable of charring to any significant degree [172]. Carbon black however is a stable agglomerated particle produced from soot so can be considered comparable to char particles. It is fair therefore to conclude that the carbon black is acting like a stabilising residue within the condensed phase. In this role it is not adding to the available fuel load with the conditions of the cone, and will act as an insulating barrier to reduce the rate heat flow to the underlying decomposing polymer.

Figure 40 Image of cone residue from formulation N

The residues were all of a similar appearance (Figure 40). Examination of the residue shows a delicate, friable structure considered to be carbon black and zinc oxide based on the mass remaining, which is within one percent of the combined value within the formulations, as shown in Table 32. Towards the periphery, of the sample some white residue can be seen, which indicates zinc oxide on the surface. This indicates that there may have been a small level of burning of the carbon black to allow the disclosure of the zinc oxide, which is otherwise hidden within the carbon black. This suggests some smouldering combustion within the carbon black, but was at such a slow rate that the oxidation was not allowed to continue since the test is stopped at flameout.

Formulation Number	Units	N	S	SV	S-EV	EV	P
Carbon black content	%	26.1	25.7	25.6	25.6	25.5	24.9
Zinc oxide content	%	3.3	3.2	3.2	3.2	3.2	3.1
Carbon black and zinc oxide content	%	29.4	28.9	28.8	28.8	28.7	28.0
Mass remaining cone calorimeter	%	30.4	29.6	29.6	28.9	29.6	29
Additional (non-inorganic) mass	%	1.0	0.7	0.8	0.1	0.9	1.0
Mass remaining TGA in air at 900°C	%	3.0	2.7	2.1	3.4	2.8	2.4

Table 32 Percentage residue comparison for cross-linking formulations

3.3.6 Summary

The MDR maximum torque (MH) of the vulcanised compounds gave a more convenient indication of the ranking of cross-link density compared with equilibrium swelling. The addition of curatives, vulcanisation and cross-link density had little effect on LOI, a measure of ease of extinction at low imposed heat flux.

Increasing cross-link density tends to reduce the time to ignition in the cone. The unvulcanised rubber compound with sulphur added has the highest rate of heat release and the lowest thermal stability during the TGA polymer decomposition phase in air.

Time to flameout appears to reduce in line with increased levels of added sulphur. Formulation N with no cross-linking agents added shows a rapid drop off in HRR, so taking the longest time to flameout.

In nitrogen the polymer decomposes rapidly between 350 and 450°C, leaving the carbon black and zinc oxide. In air, the polymer begins decomposition at a lower temperature but at a slower rate, indicating that oxidation may play a role in some char development. The cross-linked compounds have a greater stability to decomposition below 450°C, in agreement with literature [83]. The addition of sulphur to rubber causes a general reduction in thermal stability as a simple addition, when vulcanised causes a limited increase in the resistance to thermal decomposition in the TGA and in the early stages of burning, but causes reduced stability once the fire is well developed. TGA in nitrogen for these compounds can give a good prediction of the remaining mass generated in the cone.

The purpose of this study was to improve the understanding of the effects of cross-linking additives in the rubber compound to aid future design of fire retardant formulations. The key conclusions are apparent from this: The necessary process of cross-linking decreases the time to ignition and gives higher heat release, but the effect is less acute if the system contains lower levels of available sulphur. The best systems from the perspective of reduced burning are in the form of organic peroxide or an Efficient Vulcanisation (EV) system.

3.4 Fire Retardant Effect of Selected Fillers

3.4.1 Introduction

A search of the literature has found limited studies that evaluate the burning behaviour of different fillers in polyisoprene rubber compounds. The addition of carbon black will reduce the fuel available for flaming combustion, since carbon black will only burn by smouldering at the fire conditions found in a cone calorimeter. The thermal conductivity and stability of the layer of char residue under forced combustion in the cone could be strongly influenced by the choice of filler. In this work this possibility is investigated by the full and partial substitution of carbon black with both precipitated amorphous silica and calcium carbonate, common inorganic fillers. For the purpose of this study both of these inorganic fillers are considered to be inert within the range of polymer decomposition. Untreated silica (structure SiO_2) is thermally stable, although may absorb some water on storage (approximately 5%) which will be liberated on heating. Calcium carbonate decomposes under heating (typically over 650°C) to calcium oxide and carbon dioxide, in molar mass proportions of 56 and 44% respectively. At this temperature it is unlikely to provide any useful fire retardant action from the endothermic decomposition and CO_2 liberation since this is much higher than the polyisoprene decomposition temperature.

3.4.2 Experimental section

Material formulations were formulated at equal levels of polymer and overall filler loading in Table 33.

Ingredient (values in pphr)	B	SB	S	CB	C
Synthetic polyisoprene	100	100	100	100	100
Carbon black N550	40	20		20	
Precipitated amorphous silica		20	40		
Calcium carbonate				20	40
Naphthenic process oil	2	2	2	2	2
Zinc Oxide	5	5	5	5	5
Stearic Acid	2	2	2	2	2
Antioxidant TMQ	2	2	2	2	2
Antiozonant wax	2	2	2	2	2
Sulphur	0.25	0.25	0.25	0.25	0.25
MBS	2.1	2.1	2.1	2.1	2.1
TMTD	1.25	1.25	1.25	1.25	1.25
Total	156.6	156.6	156.6	156.6	156.6

Table 33 Polyisoprene formulations varied by filler type with equal total pphr

3.4.3 Results

3.4.3.1 Physical properties

Formulation code		B	SB	S	CB	C
Tensile stress / strain properties						
Tensile Strength	MPa	23.1	21.1	20.4	21.4	15.6
Elongation at Break	%	509	504	595	554	659
Hardness	IRHD	56	49	46	47	41
Specific Gravity		1.08	1.09	1.1	1.11	1.14
Yerzley properties						
Static modulus (SM)	MPa	0.72	0.55	0.51	0.52	0.38
Dynamic modulus (DM)	MPa	1.13	0.75	0.83	0.66	0.51
DM/SM Ratio		1.57	1.36	1.63	1.27	1.34
Angle Loss	%	5.8	4.8	5.6	3.3	3.1
Phase Angle	%	8.1	5.5	5.2	3.1	1.1
Resilience	%	72	73	72	83	87
Creep	%	4.4	6.3	8.9	4.0	3.9
Compression Set 22hrs at 70°C	%	5.0	1.2	4.6	7.7	11.2
Dispersion indices						
X value (filler dispersion)		6.9	6.8	*	3.1	*
Y value (agglomerate count)		9.5	9.7	*	6.8	*
E rating		7	7	*	3	*
Moving Die Rheometer (MDR)						
Minimum torque (ML)	lb-in	0.86	0.56	0.73	0.38	0.21
Maximum Torque (MH)	lb-in	11.17	9.32	9.7	8.52	6.84
Time to Scorch (ts2)	min	4.04	4.65	4.32	5.38	6.86
Time to 90% cure (t90)	min	9.74	9.21	8.28	10.8	12.61
Peak rate of cure (Rh)	lb-in/min	1.96	2.14	2.7	1.53	1.15

Table 34 Physical properties for varied filler formulations

* The values cannot be determined for rubber containing only white fillers.

Tensile strength (Table 34) is mostly unaffected for filler combinations except formulation C, associated with an increase of elongation at break, indicative of a lower modulus. Hardness values indicate that the silica and calcium carbonate do not provide the same level of modulus increase afforded by the carbon black. The static modulus values confirm the effect of filler on the hardness values measured, with the inorganic fillers leading to reduced material modulus. The DM/SM ratio was seen to vary considerably with different filler combinations, and the formulations with half loadings tended to lower levels of DM/SM ratios than the 100% mixes. This may be that mixtures tended to disrupt the formation of significant filler-filler structures within the matrix, which can lead to a higher dynamic response in rubber compounds. The use of carbon black and silica yields comparable resilience values, whereas the use of calcium carbonate gives an extremely high resilience. The use of silica was seen to produce an increase in Yerzley creep, with a doubling of the value for 100% silica in comparison with carbon black or calcium carbonate.

Compression set shows an extremely low value for SB and a general increase when using calcium carbonate in CB and C. The dispersion of formulation CB was at a lower level, so it may be that the calcium carbonate had poor compatibility with the polymer in these formulations.

The use of inorganic fillers reduces viscosity, with the calcium carbonate giving the lowest value. The maximum torque indirectly indicates the state of cure attained for a given formulation, and is comparable in rank to hardness as an indication of modulus. Calcium carbonate gave an increase in the time to scorch ts2, whereas silica had less impact. The use of silica gave a reduction in the time t90, where the use of calcium carbonate increased the cure time. This is a result of the change in the rate of cure, as measured by Rh, with higher values for silica and lower for $CaCO_3$.

Overall the use of silica as a replacement for carbon black could be considered as a practical possibility with optimisation of the compound formulation to suit the filler type. This would include the likely use of a silane coupling agent whether reacted within the mixer or as a coating on the silica to improve the polymer/filler interaction. In addition the use of polyethylene glycol (PEG) which is commonly used in silica filled rubber formulations [173] to maintain the state of cure by reacting with silanol groups on the silica, to reduce reactions with the organic accelerators.

3.4.3.2 TGA results

TGA runs were carried at a heating rate of 10°C per minute and a gas flow rate of 25 ml/minute.

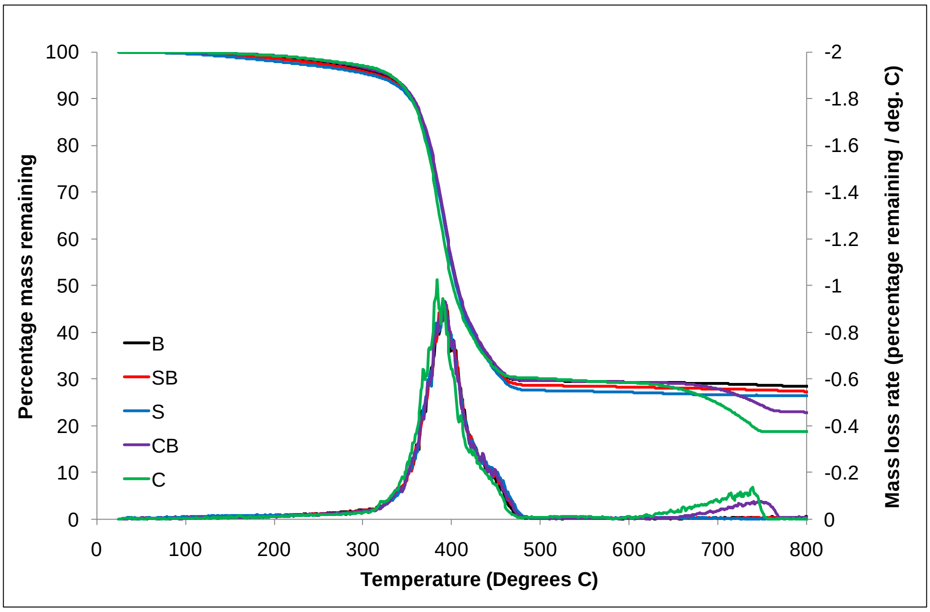


Figure 41 TGA and DTG curves for varied filler formulations in nitrogen

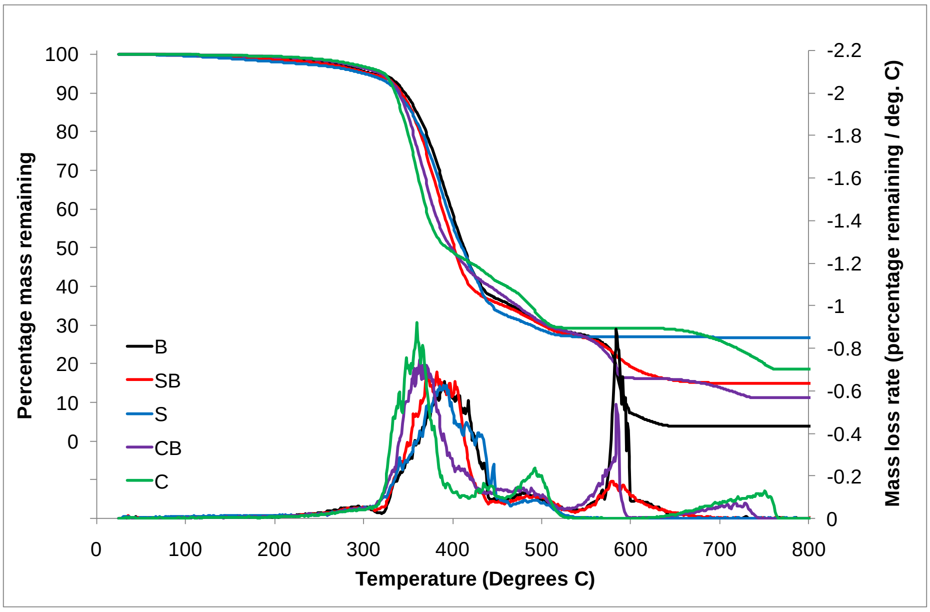


Figure 42 TGA and DTG curves for varied filler formulations in air

Formulation	B	SB	S	CB	C
Nitrogen (°C)	391	392	392	392	384
Air (°C)	391	384	390	363	360

Table 35 Maximum polymer DTG value for varied filler formulations

The mass loss from thermal decomposition of the cross-linked polyisoprene in nitrogen (Figure 41) is mostly unaffected by different fillers apart from a moderate reduction for formulation C (Table 35). The plots are similar until approximately 650°C, at which point formulations CB and C show mass loss, associated with the loss of CO_2 from the decomposition of calcium carbonate. The same materials when tested in air however show more variation due to filler types and loading (Figure 42). In the first step the rate of polymer decomposition is markedly more rapid for formulations C and CB which contain calcium carbonate. This is confirmed in Table 35 with significantly lower temperatures for the maximum rate of polymer decomposition in comparison with formulation B, indicating a strong influence of oxygen in the decomposition mechanism. This mass loss continues until approximately 400°C, at which point the rate is significantly slower until around 500°C. This indicates that some temporary char behaviour may be occurring as a result of oxidation.

Comparing the relative effect of carbon black and silica fillers, less difference on the polymer decomposition and charring is noted by filler substitution. Formulation B (40pphr carbon black) and formulation S (40pphr silica) both lost mass equally, indicating no influence of the filler on the polymer decomposition. The blend of silica and black was less stable in air however, with a reduction to 384°C for the maximum DTG value for the polymer.

At approximately 580°C the carbon black begins to oxidise for all of the formulations containing this filler. SB with silica and black shows a significantly lower rate of carbon black oxidation than formulation CB. Formulation CB exhibits a rapid rate of mass loss almost equal to the rate of mass loss for formulation B. It is proposed that the presence of silica has some stabilising effect on the carbon black to reduce the rate of oxidation.

3.4.3.3 Limiting Oxygen Index (LOI)

Formulation code		B	SB	S	CB	C
LOI	% oxygen	19.3	19.5	19.5	19.5	17.9

Table 36 LOI values for varied filler formulations

In Table 36 the LOI values determined show that the partial and full substitution of silica for carbon black had little effect on this measure of flammability. Formulation CB with a partial substitution of carbon black with calcium carbonate was also unaffected, but when fully replaced in formulation C, the burning behaviour was significantly modified. The value of 17.9% oxygen is more comparable to values quoted for polyisoprene in the form of unmodified natural rubber in standard texts of 18.5% [48]. The value may be even lower due to the presence of volatile additives in the compound such as mineral oil. This indicates that the dilution of polymer by the presence of calcium carbonate does not increase the LOI value. It does indicate however, that the addition of carbon black and silica does enhance the LOI value by a modest amount. During the LOI test it was observed that the carbon black and silica mostly remained in place on the burnt samples, which would tend to reduce the efficiency of the flame by absorbing heat. In the case of formulation C, the burnt residue was weak and collapsed rapidly, exposing further rubber for flame spread.

3.4.3.4 Cone calorimetry

Samples 100 x 100 x 6mm were tested on the Cone Calorimeter at an imposed heat flux of 50kW/m^2. Samples were tested without a steel side frame, and were covered with aluminium foil on the base and sides.

Property	Units	B	SB	S	CB	C
Time to ignition	secs	21	22	20	15	22
Time to flameout	secs	404	520	437	387	310
Total Heat evolved	MJ/m^2	133.2	143.4	137.6	122.4	126.4
Total smoke released	m^2/m^2	5057	5203	5037	4921	4695
HRR average	kW/m^2	349	289	331	321	402
HRR peak	kW/m^2	588	686	687	534	600
HRR peak at time	secs	230	203	158	213	207
Mass remaining	%	27.2	24.3	24.1	28.3	23.9

Table 37 Summary of Cone Calorimeter values for varied filler formulations

Time to ignition values (Table 37), a measure of ignitability, might be expected to be longer for the white surfaces of S and C than for the carbon black containing formulations B, SB and CB. This is not the case, with most values similar except for the lower value for CB, which presents no obvious explanation. These test results are the mean of three samples, and with a low range of t_{ig} variation for each formulation were considered valid.

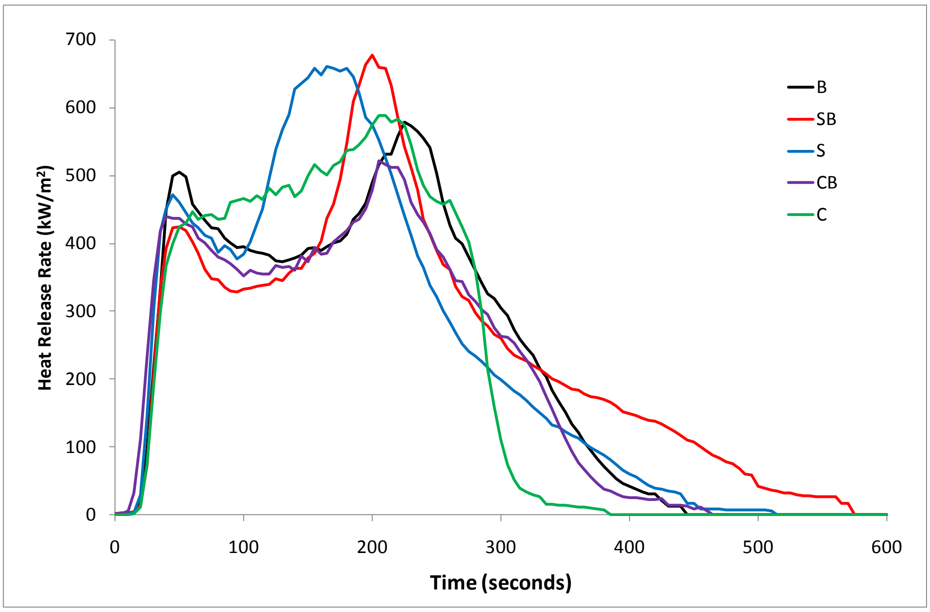


Figure 43 Heat release rate from cone calorimeter for varied filler formulations

Figure 43 plots the heat release rate (HRR) against time. The carbon black only filled formulation B has two peaks of heat release, with a higher second peak. When silica is added in formulations SB and S, the first peak is slightly reduced, but has a shorter interval to a second, higher, peak value, most apparent when the carbon black is entirely replaced with silica. When calcium carbonate is partially added, the HRR curve is comparable to the carbon black filled formulation, but when the black is entirely replaced the curve is significantly different. The initial peak heat release value is at a similar level, but unlike the other formulations, continues to rise to a second peak HRR comparable with formulation B. The presence of carbon black in this compound, and to a lesser degree silica, promotes the suppression of heat release after an initial peak, comparable to the development of a char layer. In contrast the addition of calcium carbonate alone does not produce this effect.

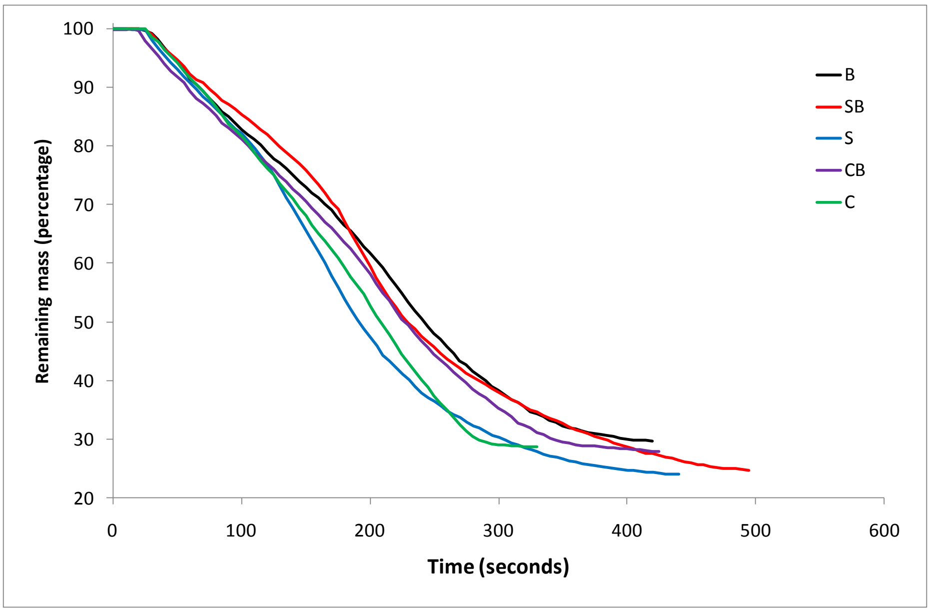


Figure 44 Residual mass from cone for varied filler formulations

Figure 44 plots the comparative mean mass loss against time. Up to the first 2 minutes the mass loss is similar, comparable to the early stage HRR curves.

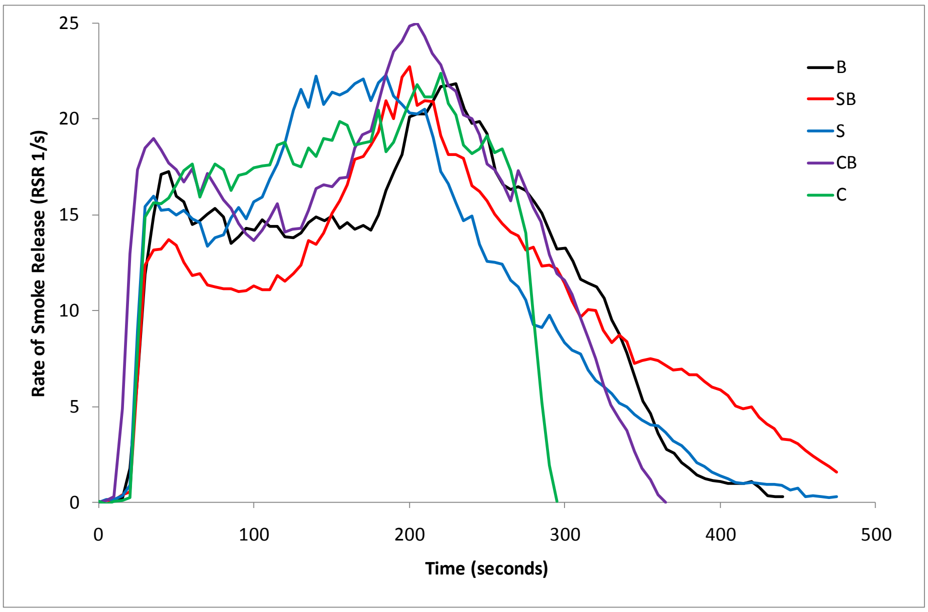


Figure 45 Mean rate of smoke release from cone for varied filler formulations

CO_2 emission and CO emission all broadly follow the heat release curves. Smoke release (Figure 45) is less straightforward; with the silica / carbon black blend SB resulting in the lowest rate of smoke emission in the first two minutes of burning.

3.4.4 Summary

Rubber compounds were prepared and tested using carbon black, precipitated silica and calcium carbonate. The presence of filler within a rubber compound will tend to reduce heat release and act like a stabilising residue within the condensed phase. The partial substitution of carbon black with inorganic fillers did not cause excessive detrimental changes in the physical properties, polymer thermal decomposition and burning behaviour. The elimination of carbon black results in a rubber compound with inferior physical and burning behaviour, most notably for calcium carbonate. The partial use of silica caused some improvement in smoke yield in the earlier stages of burning.

Carbon black plays a useful role in the burning behaviour of rubber compounds so should be retained within a fire retarded formulation. The effect of the level of carbon black addition on burning is not understood, however; so this is investigated in section 3.5.

3.5 Effect of carbon black on burning and thermal decomposition

3.5.1 Introduction

To investigate the effect of varying levels of carbon black rubber compounds were prepared with the incorporation of carbon black from 0 to 80 pphr in steps of 20 pphr.

3.5.2 Experimental section

Material formulations were formulated with increasing levels of filler loading in Table 38.

Ingredient (values in pphr)	B0	B20	B40	B60	B80
synthetic polyisoprene	100	100	100	100	100
carbon black N550	0	20	40	60	80
naphthenic process oil	2	2	2	2	2
zinc oxide	5	5	5	5	5
stearic acid	2	2	2	2	2
antioxidant TMQ	2	2	2	2	2
antiozonant wax	2	2	2	2	2
sulphur	0.25	0.25	0.25	0.25	0.25
MBS	2.1	2.1	2.1	2.1	2.1
TMTD 80%	1.25	1.25	1.25	1.25	1.25
Total	116.6	136.6	156.6	176.6	196.6

Table 38 Polyisoprene formulations with variation of carbon black loading

3.5.3 Results

3.5.3.1 Physical properties

Formulation code	Units	B0	B20	B40	B60	B80
Hardness	IRHD	37	45	54	63	71
Specific Gravity		1.00	1.02	1.08	1.13	1.17
Tensile stress / strain properties						
Tensile Strength	MPa	18.1	22.9	24.9	22.6	20.1
Elongation at Break	%	634	502	465	370	268
Trouser tear	KN/m	6.24	5.06	12.62	8.62	9.83
Crescent tear	N/2mm	93.38	109.8	206.4	206.2	193
Aged 70h at 70°C						
Change in tensile strength	%	12.4	15.0	0.0	-10.6	-1.3
Change in E@B	%	-11.0	-6.8	-14.2	-18.9	-5.7
Change in hardness	IRHD	+2.0	+1.2	+3.3	+3.0	+1.9
Compression Set 22hrs 70°C	%	4.2	4.2	4.9	4.4	1.9
Yerzley properties						
Static modulus (SM)	MPa	0.32	0.46	0.66	0.97	1.43
Dynamic modulus (DM)	MPa	0.37	0.56	0.91	1.38	2.01
DM/SM Ratio		1.16	1.22	1.38	1.42	1.41
Resilience	%	83.6	81.5	78.6	68.7	55.3
Creep	%	2.86	3.67	4.09	4.77	5.42
70h at 100°C Volume Change water	%	1.9	1.6	0.4	1.3	1.8
Adhesion tensile test	MPa	1.3	8.5	11.5	9.18	7.76
Moving Die Rheometer (MDR)						
Minimum torque (ML)	lb-in	0.56	0.59	0.64	1.02	1.76
Maximum Torque (MH)	lb-in	5.76	7.89	10.67	14.43	17.88
Time to Scorch (ts2)	min	7.31	5.24	4.01	2.84	2.23
Time to 90% cure (t90)	min	12.93	10.63	9.69	8.59	9.34
Peak rate of cure (Rh)	lb-in/min	0.79	1.26	1.86	2.68	2.93

Table 39 Physical properties for formulations with variation of carbon black loading

As carbon black levels increase the rubber hardness increases from 37 to 71 IRHD (Table 39), and can be considered typical for general purpose rubber compounds. The tensile strength is typical for a polyisoprene or natural rubber mix, where the addition of carbon black only confers a minor improvement. Formulation B0 still has good physical strength because polyisoprene strain-crystallises, so is not entirely dependant upon carbon black for strength. The increase in carbon black can be associated with a reduction of elongation at break from the modulus increase.

The effect of hot air ageing on tensile properties and hardness shows that the compounds all show good resistance, with less than 20% reduction of tensile properties, and less than 4 IRHD change in hardness. The DM/SM ratio was seen to increase broadly in line with the dilution of polymer, also reducing resilience.

The effect of boiling water on the material volume was also tested, with no significant change incurred through the use of carbon black. The absence of filler in B0 notably gave a poor bond value of 1.3 MPa, which would be unacceptable in a product. The increasing levels of carbon black predictably increase ML, rate of cure and MH, and reduce t_2, t_{90}.

3.5.4 TGA results

TGA / DTG was undertaken at a heating rate of 10°C/minute with flowing gas at 25ml/minute.

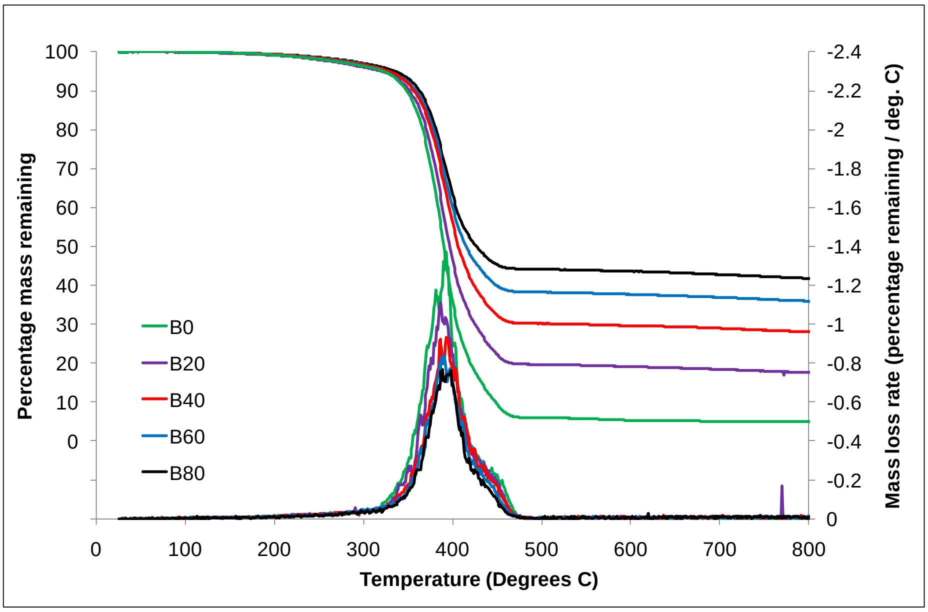


Figure 46 TGA and DTG curves for carbon black formulations in nitrogen

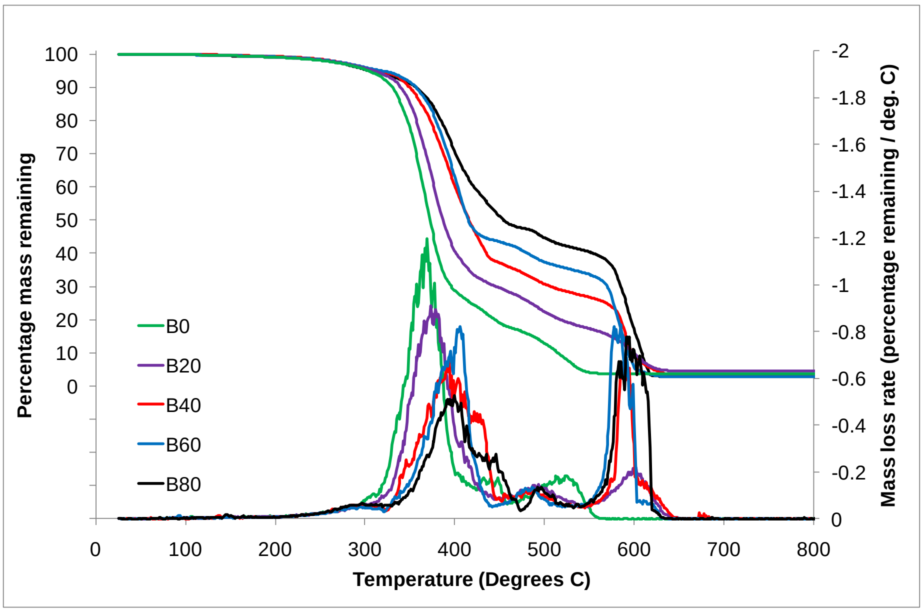


Figure 47 TGA and DTG curves for carbon black formulations in air

Formulation code	B0	B20	B40	B60	B80
Nitrogen (°C)	392	387	393	390	389
Air (°C)	369	373	393	406	400

Table 40 Maximum polymer DTG value for carbon black formulations

Formulation code	B0	B20	B40	B60	B80
TGA mass % residue at 500˚C	5.4	19.1	29.6	37.6	44.7
TGA mass % residue at 900˚C	4.8	16.9	27.5	35.4	41.2
Formulation mass % carbon black + zinc oxide	4.3	18.3	28.7	36.8	43.2

Table 41 Final residues in nitrogen for carbon black formulations

Figure 46 plots the TGA / DTG in nitrogen, with the temperature of maximum DTG values in Table 40. The presence and level of carbon black has little effect on the thermal stability of the polymer at the microscale, with the residue increasing correspondingly with increasing loading levels of carbon black. A comparison of remaining residues is made with the formulated combined percentage of carbon black and zinc oxide in Table 41. At 500°C the percentage residue shows a fair correlation with the level of carbon black and zinc oxide. From 500 to 900°C a very low rate of mass loss is observed. This could be either a further mass loss of carbon black in nitrogen due to a further decomposition process, or that the nitrogen atmosphere has some trace of oxygen contamination, so allowing limited oxidation of the residue.

Figure 47 plots the TGA / DTG in air and Table 40 the peak temperatures of decomposition. In contrast with nitrogen, in an oxidising atmosphere the level of carbon black has an impact on the peak temperature of decomposition. In B0 the peak temperature is lowest, at just over 20°C below the value in N_2. Increasing levels of carbon black confer improved thermal stability, with B40 in air comparable with nitrogen. With the highest loading of carbon black B80, the thermal stability in air is around 10°C higher than in nitrogen, showing an approximate range of 30°C. This indicates that an oxidative process is controlling the stability imparted by carbon black. It may be that either the carbon black is either chemically absorbing free radicals so slowing the rate of random chain scission, or that the carbon black is a physical barrier to either oxygen absorption or the volatilisation of small species.

3.5.5 Burning behaviour

Small scale flammability tests

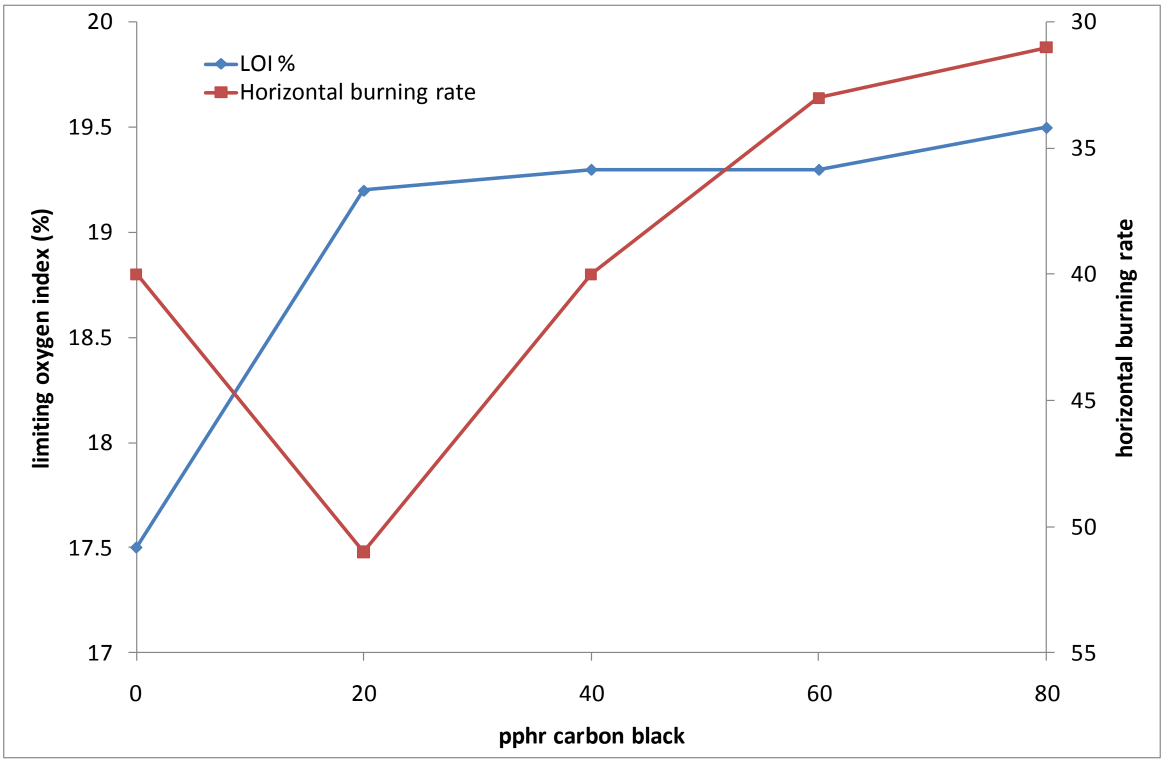


Figure 48 LOI and horizontal burning values for carbon black formulations

In Figure 48 the LOI values show that the absence of carbon black causes a significant reduction, with the value of 17.5% oxygen somewhat lower than values quoted for polyisoprene polymer in by Van Krevelen at 18.5% [48]. This value may be even lower due to the presence of volatile additives in the compound such as mineral oil. Between 20 and 80 pphr of carbon black added, the LOI value remains very similar, between 19.2 and 19.5%. This requires some explanation, since it may be reasonable to assume that progressive dilution of the polymer could increase LOI in some proportion. A visual observation of the LOI testing is of some benefit here. In formulation B0, once the sample was alight, the burning led to the melting and dripping of the polymer, with no residue remaining to provide any obstacle to burning or absorb heat.

In contrast, in all of the black filled formulations the behaviour was approximately the same. Once ignited from the pilot flame, the burning would be steady with a residue building up. The flame would still be able to spread easily, but would have to provide heat to the developing residue, so requiring a higher oxygen level to maintain flaming combustion. Whilst the polymer may still melt, it did not have the opportunity to drip and rapidly transfer heat to the underlying mass. The carbon black therefore can be seen to have a modest stabilising benefit from a fairly low level, but has little benefit at higher loadings.

Comparing the ratings with the carbon black level, the highest level of horizontal burning rate was for B20, which progressively improves as the carbon black level is increased. For B60 and B80 the burning rate is sufficiently low to merit the FH3 rating. The unfilled material yields the same result as that for 40 pphr carbon black, in contrast to the LOI values. Observing the carbon black filled compounds, the material, once burnt, leaves a moderately stable carbon black residue which seems to retard burning by providing a physical barrier to flame spread, hence the modest improvement at higher loading rates. For the unfilled compound however, the polymer liquefies once ignited with flaming drips. Whilst burning is therefore rapid, the rate of flame spread is disrupted by dripping so removing heat and fuel from the flame front, explaining why the unfilled material B0 is slower to spread flame than the lightly filled B20.

Cone calorimetry

Property	Units	B0	B20	B40	B60	B80
Time to ignition	secs	15	18	19	29	34
Time to flameout	secs	311	358	453	440	427
Total Heat Evolved	MJ/m^2	225	161	146	133	127
Total smoke released	m^2/m^2	7267	6977	6272	5693	5142
HRR average	KW/m^2	815	479	337	324	324
HRR peak	KW/m^2	2475	686	569	638	611
HRR peak at time	secs	137	213	173	235	230
Mass remaining	%	6.6	18.9	28.8	36.5	39.4
MARHE	KW/m^2	1213	514	406	380	365

Table 42 Summary of mean cone calorimeter values for carbon black formulations

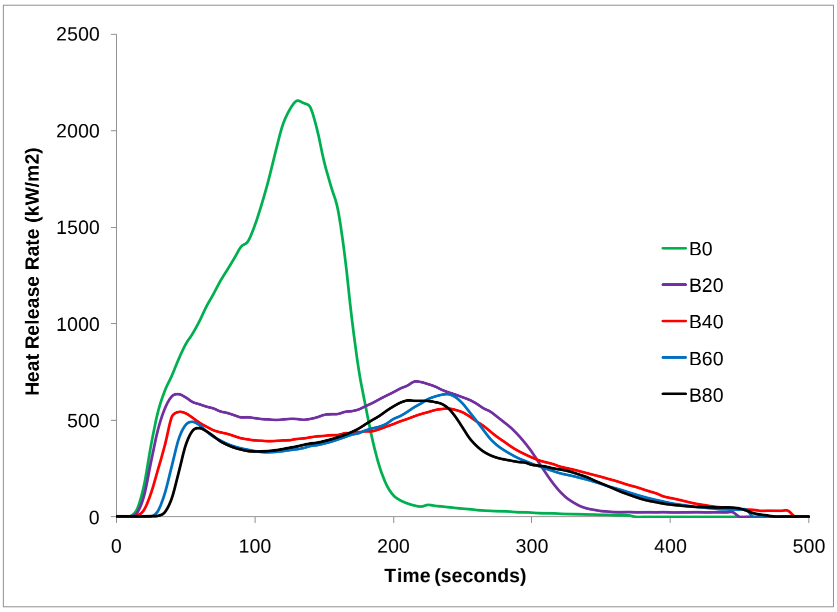


Figure 49 Heat release rate from cone calorimeter for carbon black formulations

Figure 49 plots the heat release rate, with a summary of cone data in Table 42. The omission of carbon black gave a very high peak heat release value with a rapid consumption of the fuel. The polymer surface was seen to decompose to a liquid once ignited. This would allow a more rapid transfer of heat to the underlying material through the more effective transfer of heat than conduction alone. For all of the carbon black filled formulations a vigorous but steadier burning was encountered, with an initial peak followed by a steady period of burning until a second peak was encountered. This contrast in behaviour indicates that the presence of carbon black is performing some function in regulating the release of fuel available for combustion. Whilst the heat release is generally highest for B20, any additional carbon black level above 40 pphr has superficially a less important contribution to fire retardance, but there are some benefits to be noted. Increasing levels of carbon black increase times to ignition from 15 seconds for B0 to 34 seconds for B80. There are three potential explanations for this significant increase. Firstly, TGA data in air showed an increase in the thermal stability of the formulations with increased levels of carbon black. Secondly, the increase in carbon black will increase the thermal conductivity of the material, to reducing the rate of temperature build-up at the sample surface from the imposed radiant heat. Lastly, the dilution of the elastomer with carbon black will increase the time to achieve a sufficient concentration of volatiles for ignition.

Comparing the two HRR peaks, increasing black levels yield a significant reduction in the first peak HRR and these are also delayed in proportion to the delay in ignition time. Conversely however the highest second peak heat release values are not in proportion to black loadings. The lightly filled B20 has the highest peak, but B60 and

B80 have higher peak HRR values than B40. During the initial burning, the black filled compounds all had a similar reaction to the radiant heat imposed apart from the above HRR values with time, where after approximately 200 seconds however the higher filled formulations exhibited intumescent behaviour, with a high level of swelling which opened up fissures in the remaining material plaque, so increasing the available surface area for burning and yielding high heat release. Images of the cone residue (Figure 52) show that the remaining mass retains a degree of the expanded height.

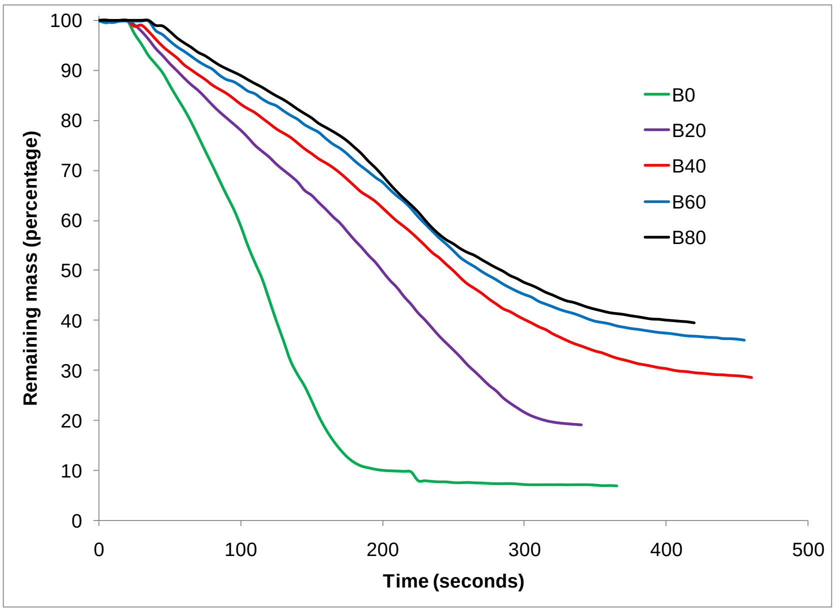


Figure 50 Residual mass from cone calorimeter for carbon black formulations

Figure 50 plots the mass loss curve in the cone. Clearly the incorporation of carbon black has a beneficial effect on reducing mass loss under imposed flaming combustion. The rates of CO_2 and CO emission mirror the rate of heat release.

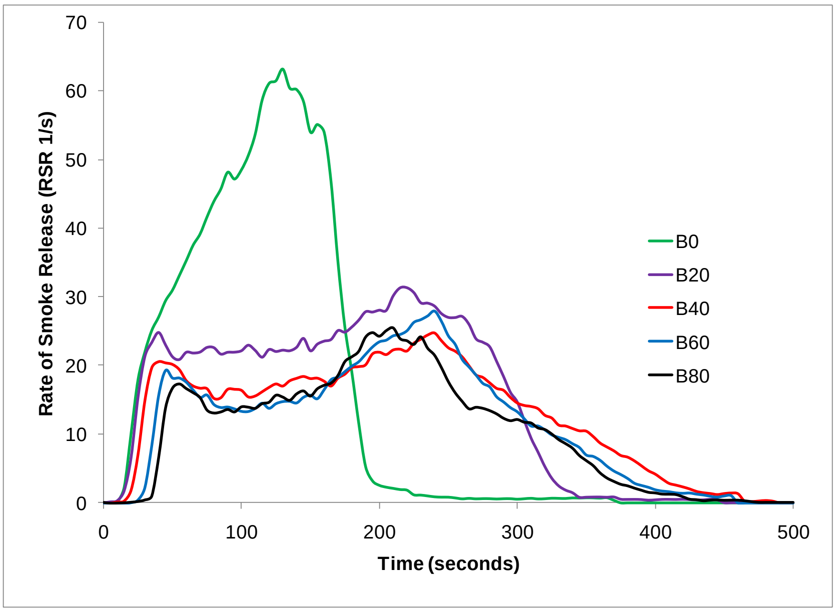


Figure 51 Mean rate of smoke release for carbon black formulations

In Figure 51 the rate of smoke release can be considered within the cone calorimeter, with the reduction of HRR from carbon black reflected within smoke emission. This indicates that the fine sooty particles within carbon black are not contributing to the smoke yield.

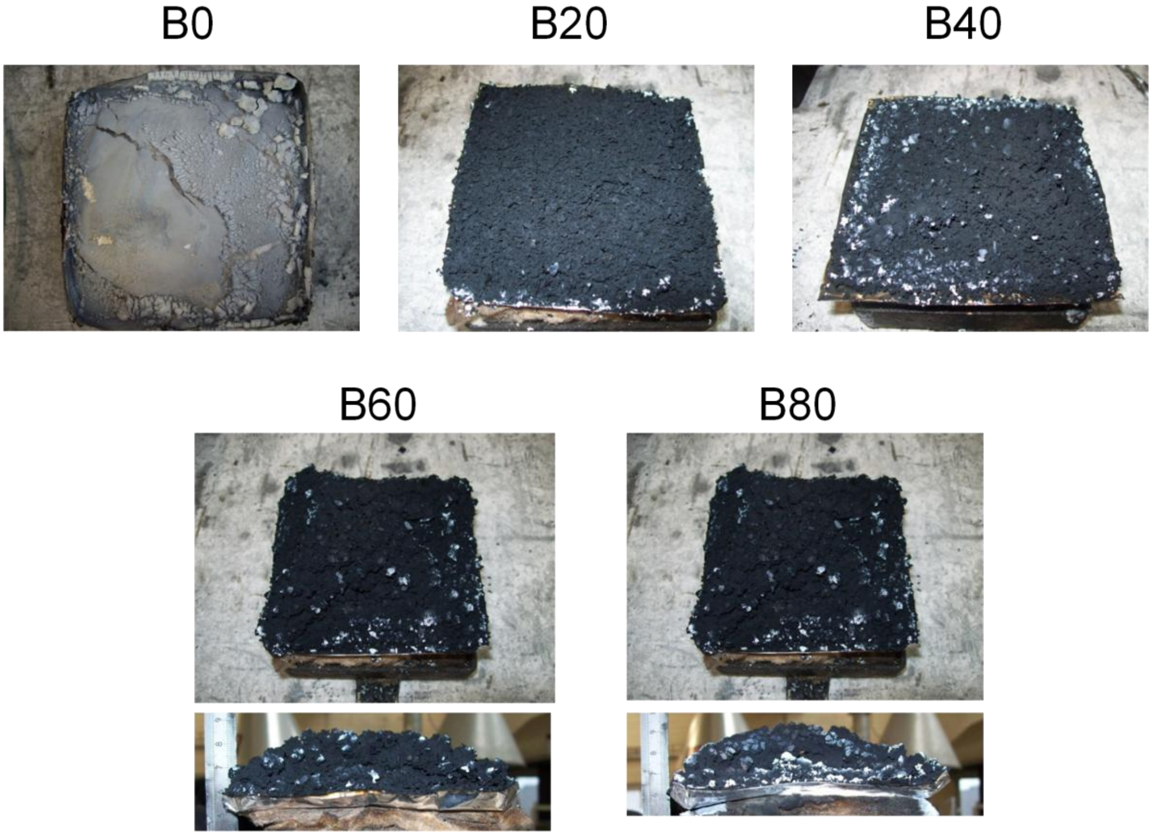


Figure 52 Images of typical cone residues for carbon black formulations

3.5.6 Summary

An unfilled IR compound displays a low level of LOI and burns with melting and dripping. When submitted to the high imposed heat flux of the cone calorimeter it ignites quickly and burns very rapidly, releasing a very high level of heat release, smoke, carbon monoxide and carbon dioxide in a short period.

The addition of carbon black from 20 to 80 pphr gives a modest improvement in LOI, and a minor improvement in horizontal flame spread at higher levels. Any level of addition gives a dramatic reduction in the rates of heat, smoke CO and CO_2 release when subjected to cone calorimetry, in comparison with the unfilled formulation B0. Increasing levels of carbon black gave a useful increase in the time to ignition, from 15 seconds for unfilled up to 34 seconds for B80. The remaining mass in the cone was in broad agreement with the combined level of zinc oxide and carbon black, indicating that little combustion of the carbon black had occurred, and that no appreciable level of charring had occurred within the polymer.

CHAPTER 4. RESULTS AND DISCUSSION - FIRE RETARDED POLYISOPRENE

4.1 Fire retardancy of ammonium polyphosphate

4.1.1 Experimental section

Rubber compounds were prepared and evaluated using ammonium polyphosphate (APP) and in combination with pentaerythritol (PER) and melamine. The percentage polymer remains the same, with the carbon black filler removed in proportion to the fire retardant added (Table 43). This should maintain an equal fuel load to provide a fair comparison of burning behaviour. One exception to this is A15 P5 B40, with the same carbon black as B40 but with APP and pentaerythritol, to evaluate the effect of an increased level of carbon black within an APP system. In formulation A15 E10 B15, the use of expandable graphite (EG) in a combination with APP was evaluated.

Additive (pphr)	B40	A15 B25	A15 P5 B20	A15 P5 B40	A15 M5 B20	A15 P5 M5 B15	A15 E10 B15
Base formulation B0	116.6	116.6	116.6	116.6	116.6	116.6	116.6
carbon black N550	40	25	20	40	20	15	15
ammonium polyphosphate		15	15	15	15	15	15
pentaerythritol			5	5		5	
melamine					5	5	
expandable graphite							10
Total	156.6	156.6	156.6	176.6	156.6	156.6	156.6

Table 43 APP based polyisoprene formulations

4.1.2 **Results**

4.1.2.1 Physical properties

Formulation code	Units	B40	A15 B25	A15 P5 B20	A15 P5 B40	A15 M5 B20	A15 P5 M5 B15	A15 E10 B15
Hardness	IRHD	54	52	50	59	51	48	52
Specific Gravity		1.08	1.08	1.07	1.13	1.08	1.07	1.09
Tensile Strength	MPa	24.9	18.3	15.4	18.1	15.3	9.5	18.3
Elongation at Break	%	465	500	467	364	426	512	513
Trouser tear	KN/m	12.6	4.5	5.0	9.3	6.4	5.8	4.9
Crescent tear	N/2mm	206	101	80	139	86	83	79
Aged 70h at 70°C								
Change in tensile strength	%	0.0	3.4	-19.2	-31.8	7.6	60.3	-10.4
Change in E@B	%	-14.2	-13.4	-6.2	-9.3	7.5	-10.4	-15.2
Change in hardness	IRHD	+3	+2	+3	+4	+3	+2	+4
Comp. Set 22hrs 70°C	%	4.9	10.0	11.5	13.0	11.8	15.1	14.4
Static modulus (SM)	MPa	0.66	0.6	0.54	0.82	0.59	0.50	0.62
Dynamic modulus (DM)	MPa	0.91	0.8	0.72	1.21	0.72	0.65	1.16
DM/SM Ratio		1.38	1.33	1.33	1.48	1.22	1.30	1.87
Resilience	%	79	81	83	71	85	82	84
Creep	%	4.09	5.42	3.22	4.69	3.7	3.26	3.17
Volume change water 70h at 100°C	%	+0.4	+40.7	+5.2	+33.3	+12.3	+47.9	+44.0
Adhesion tensile test	MPa	11.5	6.62	5.72	7.99	5.46	4.12	3.81
filler dispersion	X	7.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
agglomerate count	Y	9.8	3.8	2.6	2.9	2.6	0.6	<0.5
Dispersion E rating		7	1	1	1	1	1	1
Minimum torque (ML)	lb-in	0.64	0.62	0.56	0.83	0.56	0.50	0.7
Maximum Torque (MH)	lb-in	10.67	9.96	9.13	12.56	9.64	8.20	9.14
Time to Scorch (ts2)	min	4.01	4.58	4.80	3.74	4.57	5.17	5.07
Time to 90% cure (t90)	min	9.69	10.30	9.91	8.77	9.60	10.70	10.29
Peak rate of cure (Rh)	lb-in/min	1.86	1.93	2.05	3.43	2.16	1.76	1.72

Table 44 Physical properties for APP formulations

Using the unmodified B40 as a benchmark (Table 44), hardness is reduced as carbon black is substituted with additives. To change a rubber compound by 1 point of hardness, a change of around 2.5 pphr of carbon black is typical for this base formulation. In this case it may be expected that a reduction to 25 pphr carbon black such as in A15 B25 would lead to a hardness value of 48 IRHD. Tensile strength drops acceptably from 25 to 18 MPa with the addition of APP, but below acceptable levels when PER and melamine are also added. All of the FR modified compounds suffer a high loss of tear strength, which is often indicative of poor filler dispersion, confirmed within the dispersion indices.

The effect of hot air ageing on tensile properties and hardness shows that the addition of APP alone has led to a no particular change in tensile and elongation properties, and hardness change. The presence of APP with other additives did lead to some reduction in aged tensile properties, but this may be an artefact of the low dispersion. For the APP filled materials there is an increase to compression set, detrimental for some applications. The use of APP led to little change in resilience measured, and no effect on creep.

There was an increase in the volume of water absorbed through the use of APP, which has a high level of water solubility in standard grades. Within ASTM D2000 a typical requirement for natural rubber would be a maximum volume change of 10%. It is not apparent why the values would show so much variation when using APP, from around 5 to 48% volume swell, but is likely to be a result of both the poor dispersion and the ability of APP to absorb water.

The bonding is reduced as a result of thin rubber tearing at the rubber to cover interface, most likely as a result of reduced tear strength from the poor dispersion. The addition of APP or the other FR additives does not affect the MDR properties in a significant manner, indicating that this additive does not modify the material viscosity or vulcanisation chemistry.

The formulations based on APP have reduced physical properties, most likely an effect of the poor dispersion obtained. If grades of these additives can be obtained with improved polymer compatibility, for example by the use of surface treatments or smaller particle size, then acceptable physical properties are likely to result.

4.1.2.2 TGA results

TGA runs were carried out at a heating rate of 10°C per minute and a gas flow rate of 25 ml/minute.

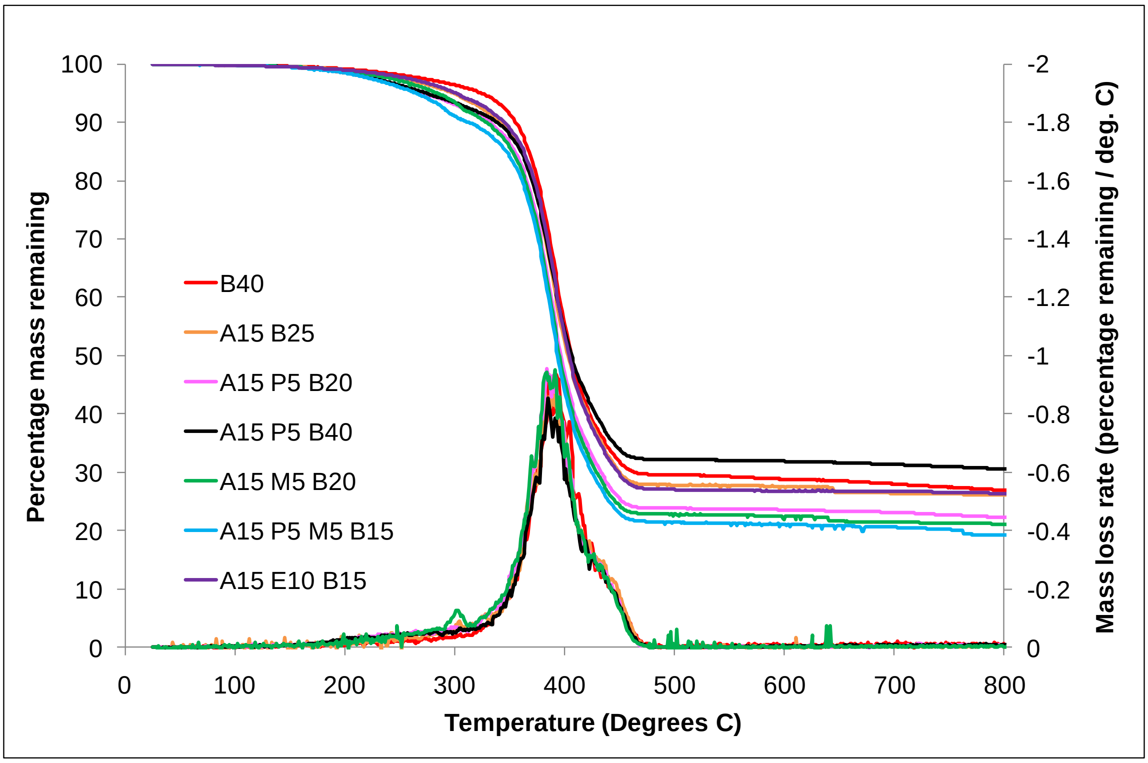


Figure 53 TGA and DTG curves for APP formulations in nitrogen

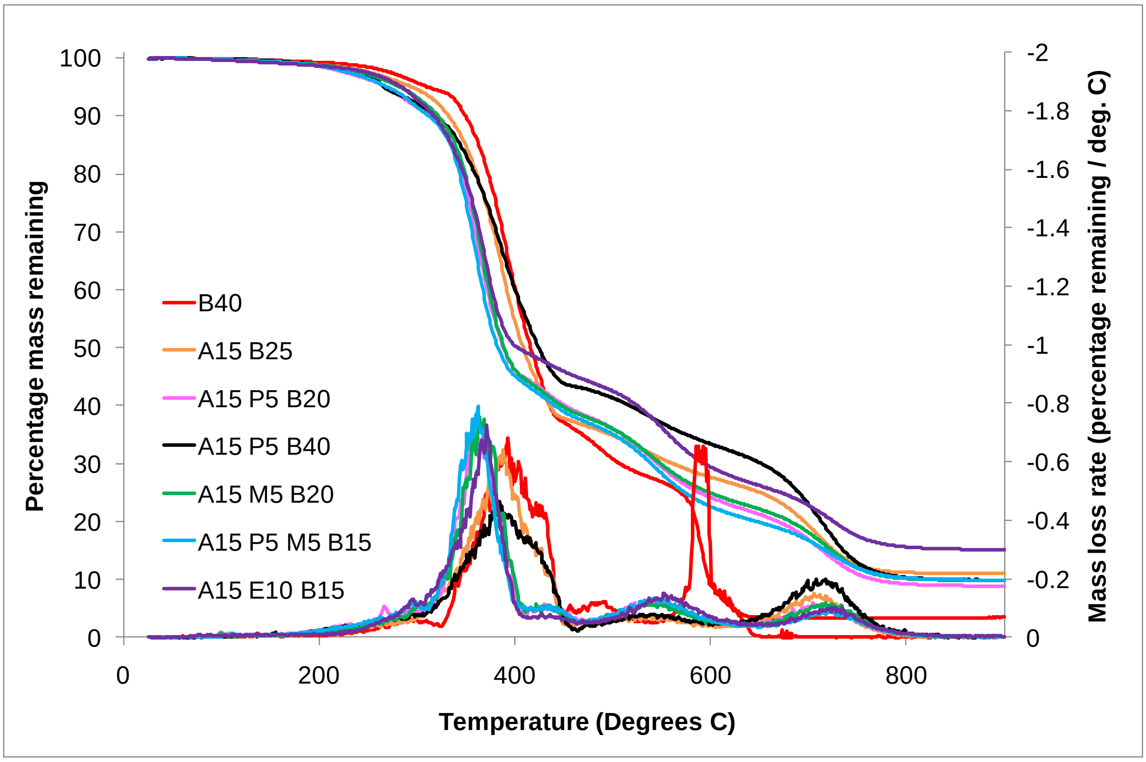


Figure 54 TGA and DTG curves for APP formulations in air

Formulation code	B40	A15 B25	A15 P5 B20	A15 P5 B40	A15 M5 B20	A15 P5 M5 B15	A15 E10 B15
Nitrogen	393	388	386	385	391	388	392
Air	393	388	358	384	363	362	371

Table 45 Maximum polymer DTG value °C for APP formulations

The addition of APP (Figure 53 and Table 45) gives initially reduced thermal stability, with a reduced temperature to the onset of significant mass loss. B40 remains stable to around 250°C, but the use of APP leads to mass loss initiating at around 200°C, lower than manufacturer's data for the grade of APP, indicating stability to over 270°C. The least stable combination is A15 P5 M5 B15, considered within literature the most useful mixture for an effective intumescent FR system. Considering the DTG profiles for the polymer, the use of APP systems has not greatly affected the shape of the curve, including the maximum DTG and temperature. This indicates that under nitrogen there is little chemical interaction between the phosphorus and the decomposing polymer products, so it does not contribute to the development of any char structure. In air APP causes a reduction in the peak DTG value for IR but generates some temporary char with an increased residue between 400 and 500°C. The decomposition of carbon black is modified, with the peak mass loss moved from 600°C for B40 to 700°C formulations using APP.

4.1.2.3 Burning behaviour

Small scale flammability tests

Formulation code	Units	B40	A15 B25	A15 P5 B20	A15 P5 B40	A15 M5 B20	A15 P5 M5 B15	A15 E10 B15
LOI	% oxygen	19.3	19.7	19.4	20.3	20.2	20.1	21.6
Mean burning rate	mm/min	40	31	34	32	32	32	20
ISO 1210 method A	rating	FH-4-40	FH-3-31	FH-3-34	FH-3-32	FH-3-32	FH-3-32	FH-3-20

Table 46 LOI and horizontal burning values for APP formulations

In Table 46 the LOI shows some modest increases in the oxygen index values. Adding just APP has little benefit, as does APP and pentaerythritol (PER). Comparing A15 P5 B20 with A15 M5 B20, adding APP with melamine confers more benefit than pentaerythritol. Adding the often recommended combination of APP, PER and melamine does not give any increased benefit than APP and melamine. APP with expandable graphite (EG) gives the greatest benefit of the systems tested, suggesting an additive benefit.

The horizontal burning rate is moderately reduced in comparison with the unmodified B40, but no materials achieved self extinguishing properties. APP with or without other additives all gave a similar reduced rate of linear burning, except for the addition of EG which is enhanced.

Cone calorimetry

Property	Units	B40	A15 B25	A15 P5 B20	A15 P5 B40	A15 M5 B20	A15 P5 M5 B15	A15 E10 B15
Time to ignition	Secs	19	21	17	18	18	13	22
Flameout	Secs	453	340	456	369	527	478	489
Total Heat evolved	MJ/m^2	146	139	147	135	139	143	141
Total smoke released	m^2/m^2	6272	6069	6024	5050	5614	5211	4770
HRR average	kW/m^2	337	319	346	412	278	310	304
HRR peak	kW/m^2	569	777	853	1251	681	829	595
HRR peak at time	Secs	173	203	184	175	205	232	218
Mass remaining	%	28.8	22.6	19.9	19.3	21.1	18.5	26.4
MARHE	kW/m^2	406	445	497	526	398	373	331

Table 47 Summary of average cone calorimeter values APP

A summary of cone calorimeter values is given in Table 47, and mean heat release curves are plotted in Figure 55.

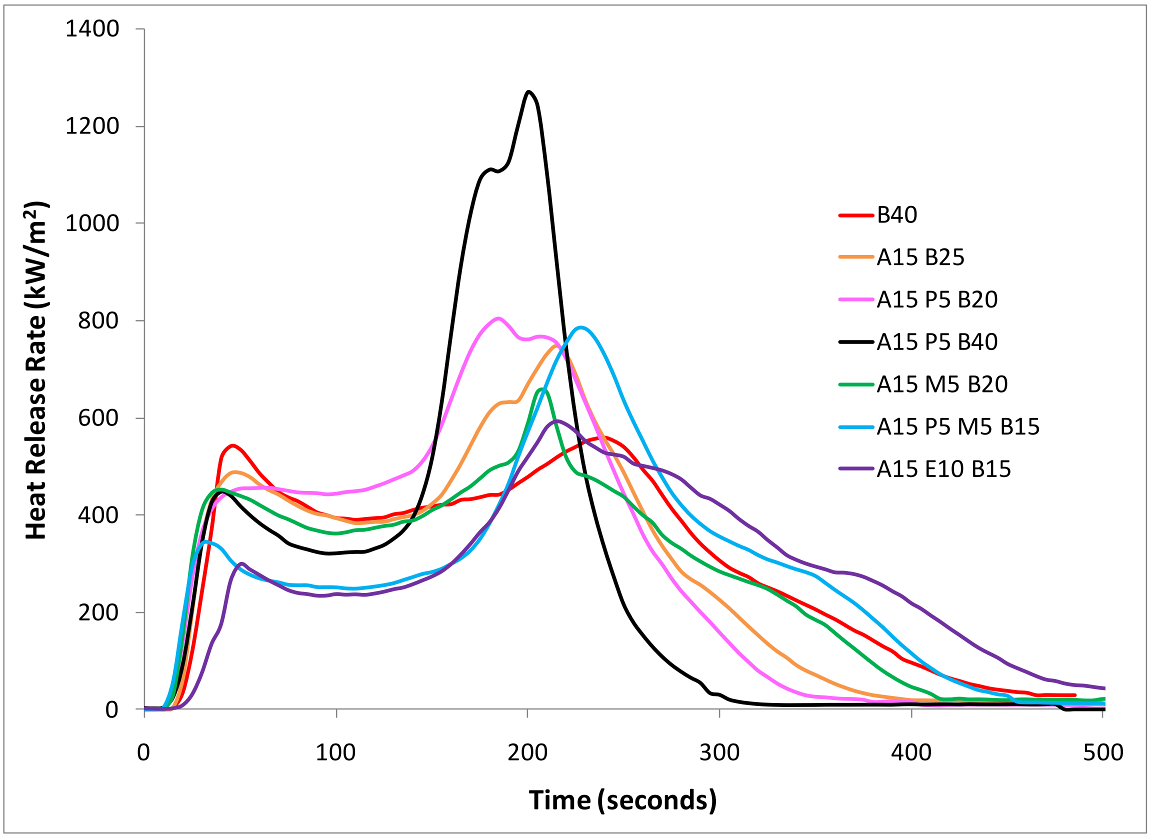


Figure 55 Heat release rate from cone calorimeter for APP formulations

Heat release rate (Figure 55) shows a significant influence of APP and other additives. Compared to B40, the use of APP in A15 B25 gave no benefit in burning, and led to a higher peak heat release rate. The higher carbon black loading in A15 B40 gave a high second peak, which was the result of significant sample swelling, a product of the combined intumescence of the APP and carbon black. When PER is added with APP in A15 P5 B20 the HRR is higher than for B40, and the use of melamine with APP in A15 M5 B20 shows little difference to B40. When APP, PER and melamine are used in A15 P5 M5 B15 the initial HRR is reduced, but attains a higher peak HRR. The addition of expandable graphite and APP in A15 E10 B15 gives the slowest development of burning and a similar second peak to B40, so giving the best overall performance.

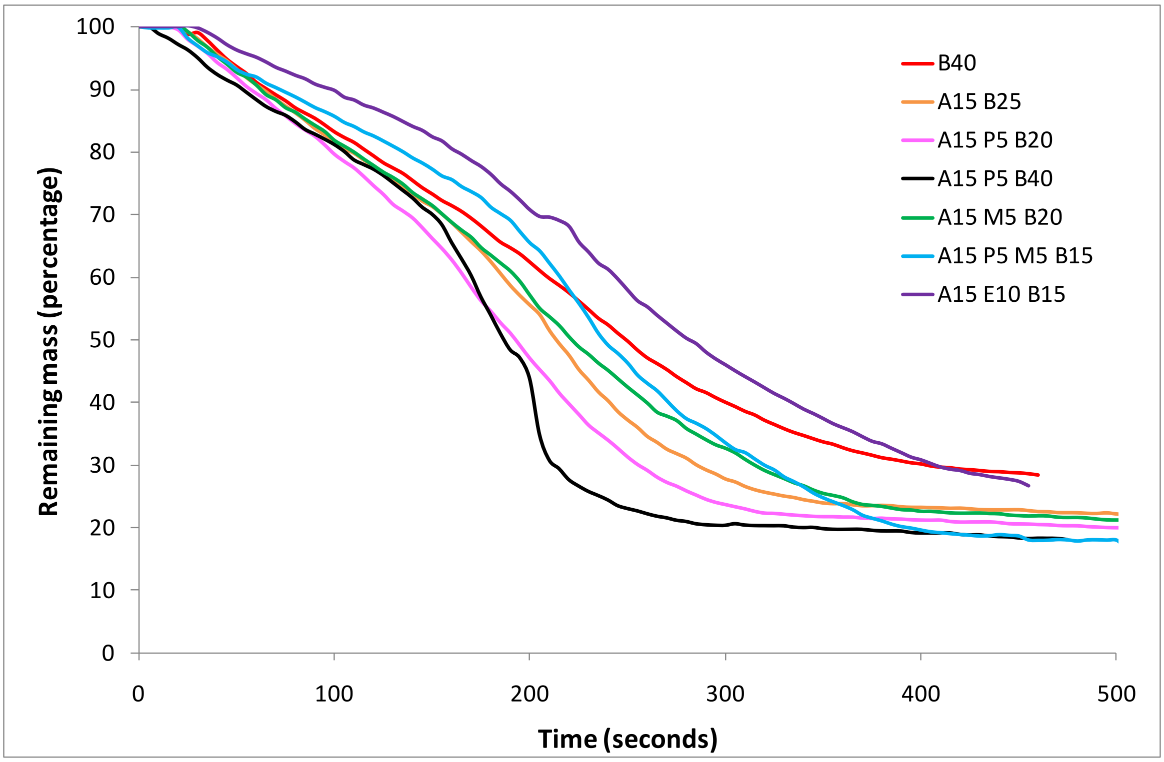


Figure 56 Residual mass from cone calorimeter for APP formulations

The effect of burning on mass loss is shown in Figure 56, with the lowest rate of mass loss in A15 E10 B15. This can be contrasted with the rapid mass loss of A15 B40 at around 200 seconds following excessive intumescence. At around 200 seconds there are several uneven elements in the mean mass loss curve, the result of significant mass loss at varying times for each of the three runs.

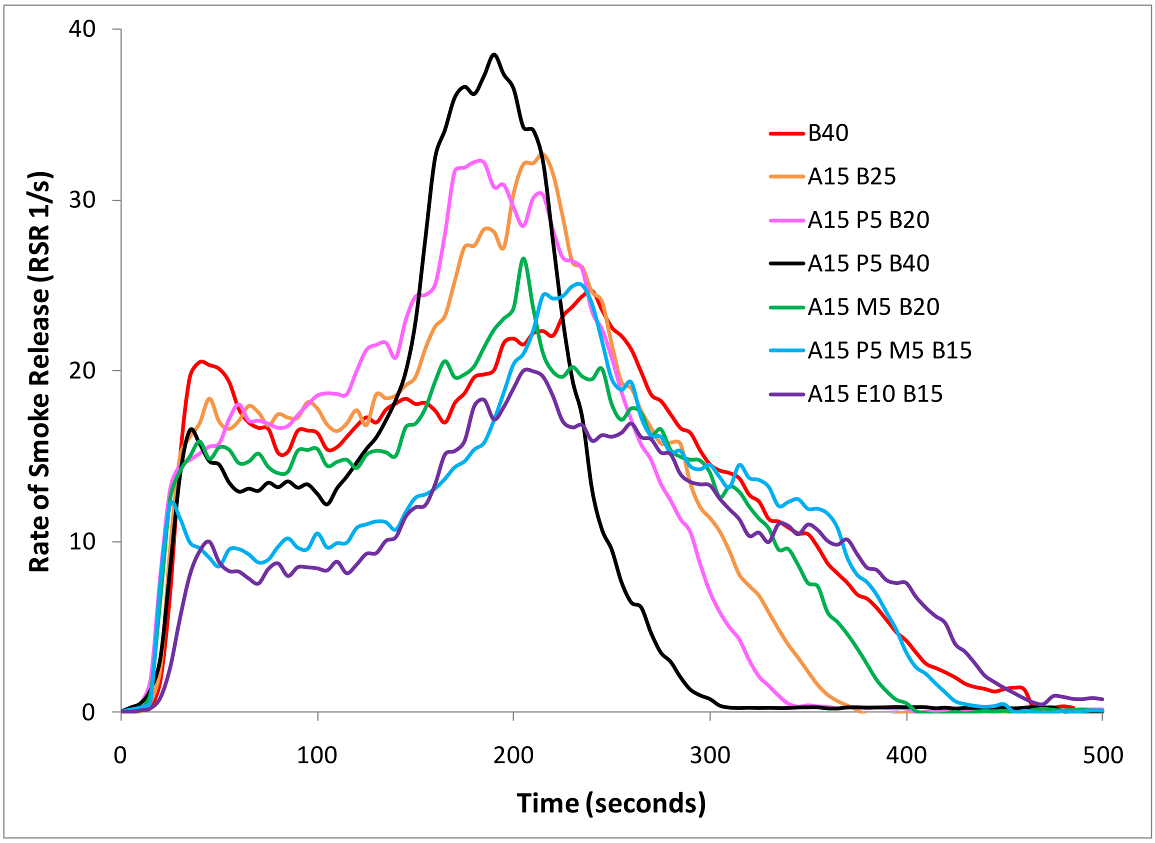


Figure 57 Mean Rate of Smoke Release for APP formulations

The use formulations A15 P5 M5 B15 and A15 E10 B15 show the lowest smoke yield (Figure 57) in common with the heat release, suggesting than any suppression of burning by APP or EG does not lead to any increase in smoke generation.

4.1.3 Summary

The use of APP led to a significant reduction in many of the desirable physical properties, such as dispersion, compression set and water absorption. TGA in air indicated that the use of APP reduced the initial thermal stability of the compounds with mass loss occurring at lower temperatures, but led to some temporary char development and an increased temperature of oxidation for the carbon black. The horizontal burning rate is moderately reduced in comparison with the unmodified compound, but no materials achieved self-extinguishing properties. The use of APP with PER and melamine gave a small increase in LOI, from 19.3 to 20.1% O_2. In the early stages of burning within the cone calorimeter, the use of APP/PER/MEL produced a significant reduction in peak HRR, but a second peak was more pronounced in the FR compounds with a significantly higher peak HRR measured. This second peak was attributed to a significant level of intumescence which develops after around 2 minutes in the cone calorimeter, increasing the surface area of polymer available for combustion dramatically. This effect was most pronounced in A15 P5 B40 where the

APP was added to the formulation without any substitution for carbon black, leading to a lower level of polymer, indicating that the carbon black made a significant contribution to the intumescent process. The combination of APP and a higher loading of carbon black have yielded an excessive level of intumescence which has opened the material plaque up to create a large surface area, allowing rapid burning and a subsequent high rate of heat release.

APP based systems do not show sufficient promise to merit further investigation. The best APP based system (excluding that with expandable graphite) used the classic APP/PER/MEL combination which imparted lower heat release over the first three minutes, but gave very modest improvements in LOI and horizontal burning. In addition the reduction in physical properties was unacceptable, particularly the increased water absorption and reduced tear strength, although these aspects may be improved by careful selection of FR particle size and possible encapsulation.

4.2 Fire retardancy of expandable graphite

4.2.1 Introduction

Rubber compounds were prepared and characterised using expandable graphite (EG) at various levels.

4.2.2 Experimental section

4.2.2.1 Materials

In Table 48, formulations from 0 to 20pphr EG, the percentage polymer remains the same, with the carbon black filler removed in proportion to the fire retardant added. This maintains an equal fuel load to provide an even comparison of burning behaviour. One exception to this is E10 B40, produced to evaluate the carbon black level independently of EG level. In addition, E10 T3 utilises triethyl phosphate plasticiser (TEP) with expandable graphite. In A15 E10 B15, APP is combined with EG to consider any synergistic effects as already compared to APP.

Ingredient (values in pphr)	B40	E5 B35	E10 B30	E20 B20	E10 B40	E10 T3 B27	A15 E10 B15
Base formulation B0	116.6	116.6	116.6	116.6	116.6	116.6	116.6
carbon black N550	40	35	30	20	40	27	15
ammonium polyphosphate							15
expandable graphite		5	10	20	10	10	10
triethyl phosphate (TEP)						3	
Total	156.6	156.6	156.6	156.6	166.6	156.6	156.6

Table 48 Polyisoprene formulations with expandable graphite

4.2.3 Results

4.2.3.1 Physical properties

Formulation code	Units	B40	E5 B35	E10 B30	E20 B20	E10 B40	E10 T3 B27	A15 E10 B15
Hardness	IRHD	54	56	56	53	60	52	52
Specific Gravity		1.08	1.08	1.08	1.09	1.11	1.08	1.09
Tensile Strength	MPa	24.9	20.6	22.0	17.0	20.7	19.8	18.3
Elongation at Break	%	465	403	433	458	417	448	513
Trouser tear	KN/m	12.6	6.9	4.8	3.8	6.1	6.7	4.9
Crescent tear	N/2mm	206	170	105	93	151	93	78
Aged 70h at 70°C								
Change in tensile strength	%	0.0	7.8	-1.7	11.3	-14.7	-20.6	-10.4
Change in E@B	%	-14.2	0.2	-0.9	-8.3	0.0	-14.7	-15.2
Change in hardness	IRHD	+3	+2	+6	+2	-2	+2	+4
Comp. Set 22hrs at 70°C	%	4.9	8.9	10.0	10.5	9.1	7.8	14.4
Yerzley properties								
Static modulus (SM)	MPa	0.66	0.71	0.72	0.64	0.86	0.64	0.62
Dynamic modulus (DM)	MPa	0.91	1.06	0.95	0.82	1.25	0.88	1.16
DM/SM Ratio		1.38	1.49	1.32	1.28	1.45	1.38	1.87
Resilience	%	78.6	74.3	79.4	84	69.8	77	84.3
Creep	%	4.09	4.02	4.04	3.59	4.43	4.56	3.17
70h at 100°C Volume Change water	%	+0.42	+2.66	+4.58	+5.31	+3.98	+4.37	+44
Adhesion tensile test	MPa	11.5	8.3	5.6	3.6	6.2	5.1	3.8
Dispersion indices								
X value (filler)		7.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Y value (agglomerates)		9.8	4.3	<0.5	<0.5	1.9	2.2	<0.5
E rating		7	1	1	1	1	1	1
Moving Die Rheometer								
Minimum torque (ML)	lb-in	0.64	0.76	0.78	0.69	0.99	0.6	0.7
Maximum Torque (MH)	lb-in	10.67	10.81	10.46	8.97	11.75	9.26	9.14
Time to Scorch (ts2)	min	4.01	4.16	3.97	4.64	3.86	4.3	5.07
Time to 90% cure (t90)	min	9.69	9.78	8.75	9.47	8.85	9.09	10.29
Peak rate of cure (Rh)	lb-in/min	1.86	2.05	2.24	1.82	2.4	1.82	1.72

Table 49 Physical properties for expandable graphite formulations

Comparing B40, E5 B35, E10 B30 and E20 B20 (Table 49) hardness is not greatly affected, so EG must increase modulus in a broadly similar manner to carbon black. In E10 T3 B27 the hardness is lower, an effect of the TEP acting as a plasticiser.

The tensile strength and elongation at break are slightly reduced for formulations with up to 10 pphr EG, but reduces more when the EG is added at 20 pphr. Tear strength was also considered, and all values fell with the introduction of EG, likely to be problematic for engineering components.

The effect of hot air ageing on tensile properties and hardness shows that the addition of EG has led to a minor but acceptable reduction of tensile and elongation properties, and hardness change. The presence of TEP led to a higher drop of physical strength. For the EG filled materials compression set increased to around double that of B40, detrimental to long term service.

The DM/SM ratio was similar for EG loadings compared to carbon black only, apart from A15 E10 B15, which had a significantly higher response. The use of EG led to fluctuation in the resilience, which follows no obvious pattern. There was some change of increase in the volume in water through the use of EG. This may be due to the low affinity of polymer to EG leading to water being absorbed within the EG flakes. In A15 E10 B15 the effect of boiling water was high, leading to a 44% increase in volume, due to the presence of APP, which has a high level of water solubility.

At 5 pphr the bond strength is reduced moderately, but is still acceptable. At 10 pphr the bonding levels only just acceptable, depending on application. At above 10 pphr and in conjunction with APP the level of bonding is inadequate. All of the mixes using EG had an E rating of 1, which would be considered an unacceptable level of dispersion. The addition of EG does not affect the MDR properties in a significant manner, indicating that this additive does not modify the material viscosity or vulcanisation chemistry.

4.2.3.2 TGA results

TGA Runs were carried out at a heating rate of 10°C per minute and a gas flow rate of 25 ml/minute.

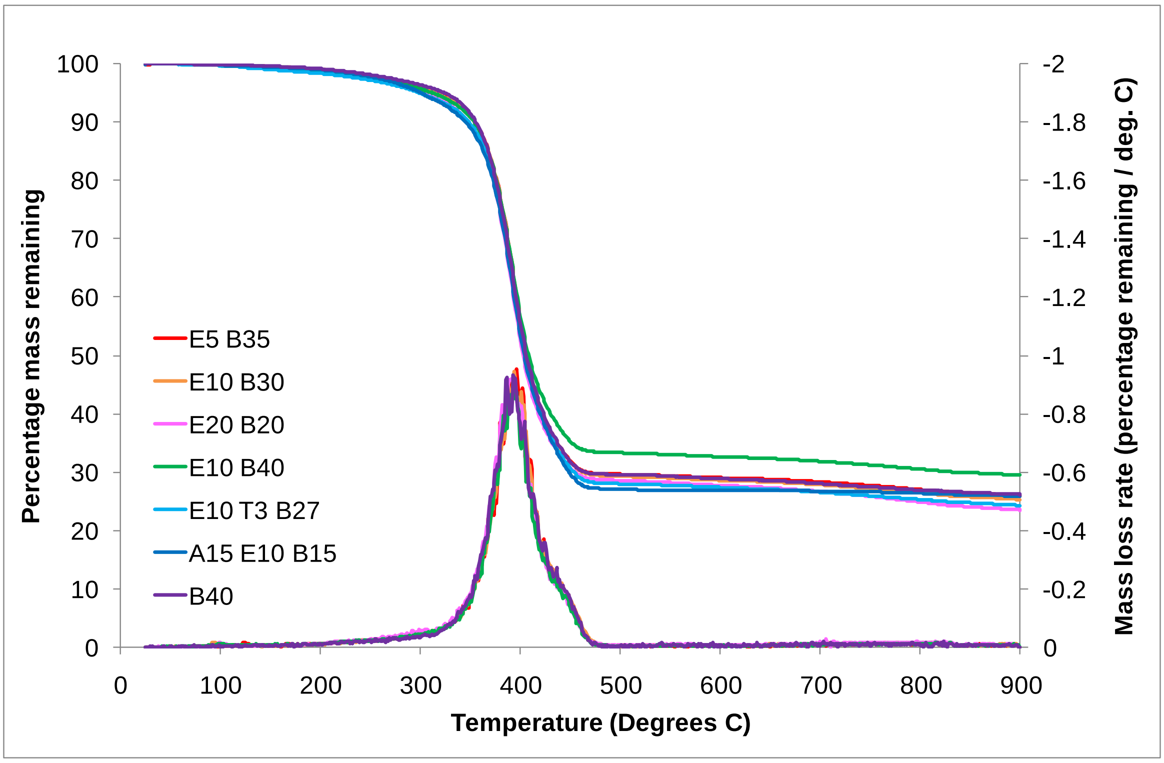


Figure 58 TGA and DTG curves for expandable graphite formulations in nitrogen

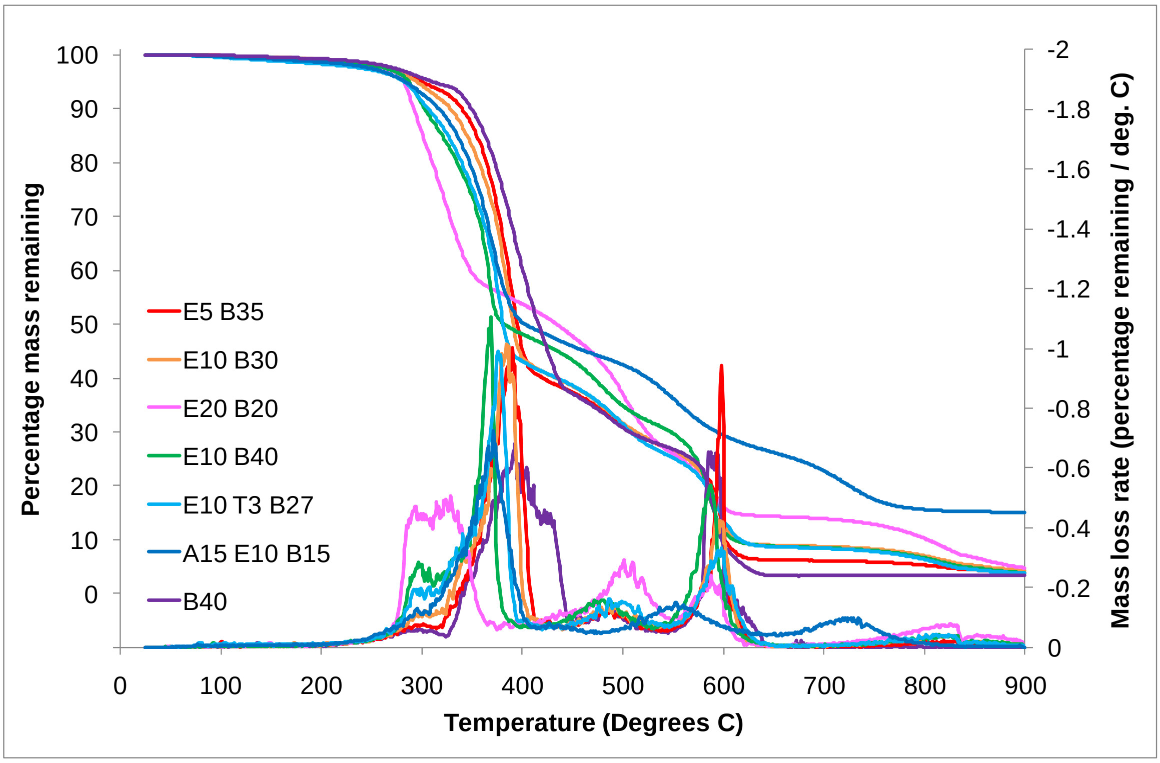


Figure 59 TGA and DTG curves for expandable graphite formulations in air

Formulation code	B40	E5 B35	E10 B30	E20 B20	E10 B40	E10 T3 B27	A15 E10 B15
Nitrogen	393	396	394	391	393	393	392
Air	393	390	384	326	367	376	371

Table 50 Maximum polymer DTG value °C for expandable graphite formulations

Figure 58 plots the TGA / DTG in nitrogen, and the only significant mass loss is for the polymer decomposition, which is unaffected by the presence of EG, TEP or APP. This is confirmed in Table 50, where the temperature of maximum DTG value remains within the range of 391 - 396°C. The remaining mass percentage is similar, indicating that EG does not lose significant mass under nitrogen when compounded. EG expands when heated but this does not appear to lead to any increase in degradation of the polymer.

In air the TGA / DTG (Figure 59) data show that the EG compounds commence mass loss at an earlier temperature. This can be seen more clearly in Table 51, where the temperature for 90% mass loss is lowered at increasing levels of EG. The increase in mass loss may be associated with EG expansion, causing a greater rate of oxidation in the decomposition of the polymer.

Percentage mass remaining	B40	E5 B35	E10 B30	E20 B20	E10 B40	E10 T3 B27	A15 E10 B15
98	226	208	214	204	205	148	173
95	297	290	288	280	282	274	274
90	346	336	325	291	300	302	313

Table 51 Temperature at percentage mass for expandable graphite formulations in air

In contrast to the reduced temperature for commencement of mass loss, the presence of EG at 20pphr in E20 B20 appears to promote the development of some temporary char structure between 350 and 500°C. By 500°C this mass is lost, and the carbon black is oxidised rapidly at around 600°C for all of the formulations. After this stage some of the EG appears to remain intact until around 750-850°C, at which point it is finally oxidised.

4.2.3.3 Burning behaviour

Small scale flammability tests

Formulation code	Units	B40	E5 B35	E10 B30	E20 B20	E10 B40	E10 T3 B27	A15 E10 B15
LOI	% O_2	19.3	19.7	20.1	22.2	20.8	21	21.6
Mean burning rate	mm/min	40	23	23	20	22	22	20
ISO1210 method A	rating	FH-4-40	FH-3-23	FH-3-23	FH-3-20	FH-3-22	FH-3-22	FH-3-20

Table 52 LOI and horizontal burning values for expandable graphite formulations

In Table 52 the LOI values are moderately improved by the addition of EG in place of carbon black, with the highest increase associated with the highest loading of EG. In E10 B40 the carbon black level was kept the same as B40, with EG added instead of substituted. In this case the LOI was higher than for E10 B30 indicating that increases in filler loading will still have some benefit in the presence of EG. Comparing E10 T3 B27 with E10 B30, a moderate improvement of almost 1% is noted which is most likely to be due to the presence of 3 parts of triethyl phosphate (TEP). Whether this effect is purely additive or synergistic cannot be determined from this work due to a lack of evaluation of TEP without EG. In A15 E10 B15 the effect of including APP with EG was considered. The effect of a total of 25 pphr FR was less than of 20 pphr EG, indicating that for LOI the combination was less effective than EG.

The average horizontal burning rate and final rating for the samples show that the test formulations out-perform the control compound B40 by yielding a reduced rate of burning, but none are sufficient to self-extinguish. The level of EG and the addition of either TEP or APP had little effect on the horizontal burning rate.

Cone calorimetry

Property	Units	B40	E5 B35	E10 B30	E20 B20	E10 B40	E10 T3 B27	A15 E10 B15
Time to ignition	secs	19	19	20	24	23	20	22
Time to flameout	secs	453	469	459	479	470	462	489
Total Heat Evolved	MJ/m^2	146	141	141	144	139	141	141
Total smoke released	m^2/m^2	6272	5184	4335	3829	4471	4518	4770
HRR average	KW/m^2	337	313	323	321	302	318	304
HRR peak	KW/m^2	569	631	718	796	630	637	595
HRR peak at time	secs	173	222	210	210	217	217	218
Mass remaining	%	29	29	25	19	29	26	26
MARHE	KW/m^2	406	361	355	353	340	340	331
Residue height	mm	20	35	40	45	55	50	45

Table 53 Mean cone calorimeter values for expandable graphite formulations

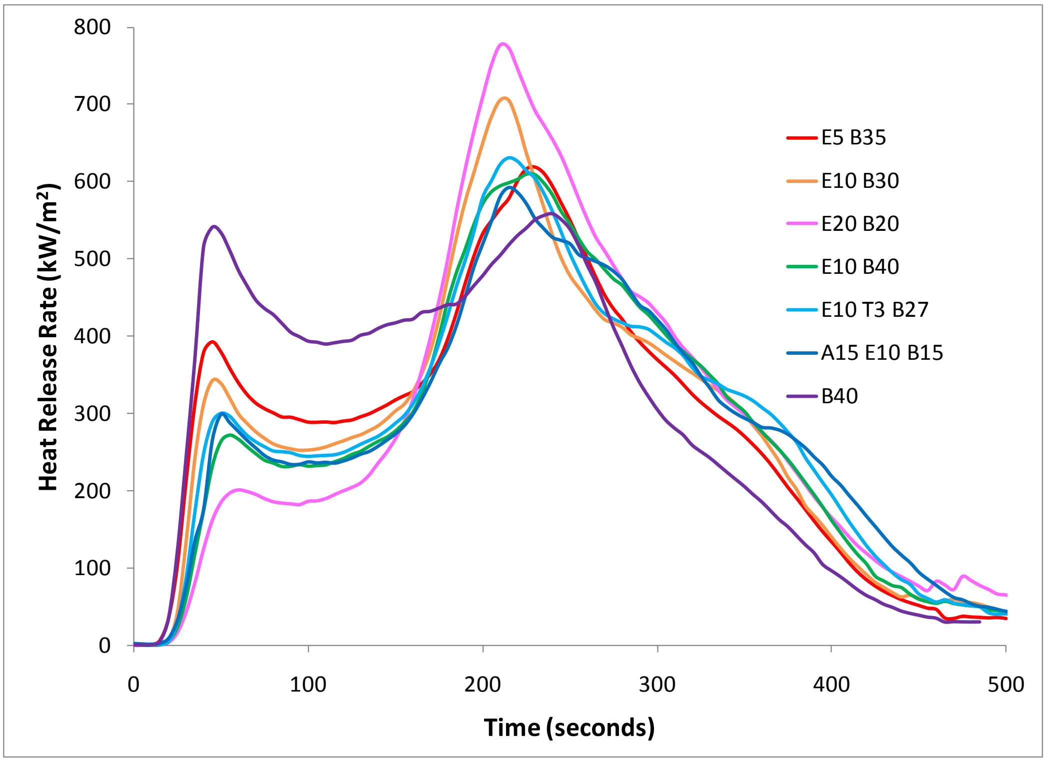


Figure 60 Heat release rate from cone for expandable graphite formulations

Considering the heat release curves in Figure 60, all of the formulations containing EG produce a lower level of heat release for approximately the first three minutes of test. The reduction in HRR is broadly increased in ranking order with the level of EG added, with the highest reduction in the first HRR peak for E20 B20. On observation in the first phase of burning in the cone, the surface was seen to swell and intumesce to a moderate degree. At around three minutes however, the whole sample was seen to dramatically increase in volume, especially for the more highly EG filled samples. In E20 B20 the sample was observed to increase in height so much as to enter the cone volume. The higher level of carbon black in E10 B40 also led to high levels of intumescence. The use of TEP gave no benefit in addition to EG.

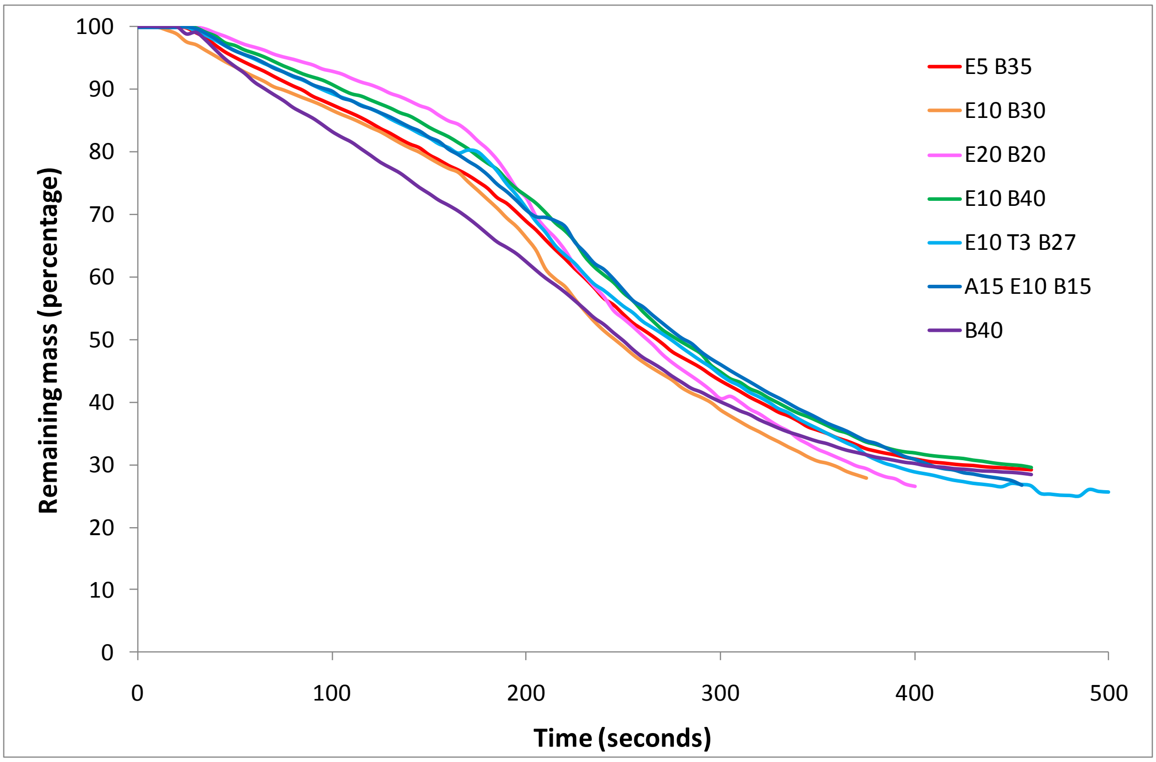


Figure 61 Residual mass from cone calorimeter for expandable graphite formulations

The rate of mass loss (Figure 61) is reduced by the use of EG in the first 200 seconds for all formulations, with E20 B20 having the highest reduction, in keeping with the heat release rates.

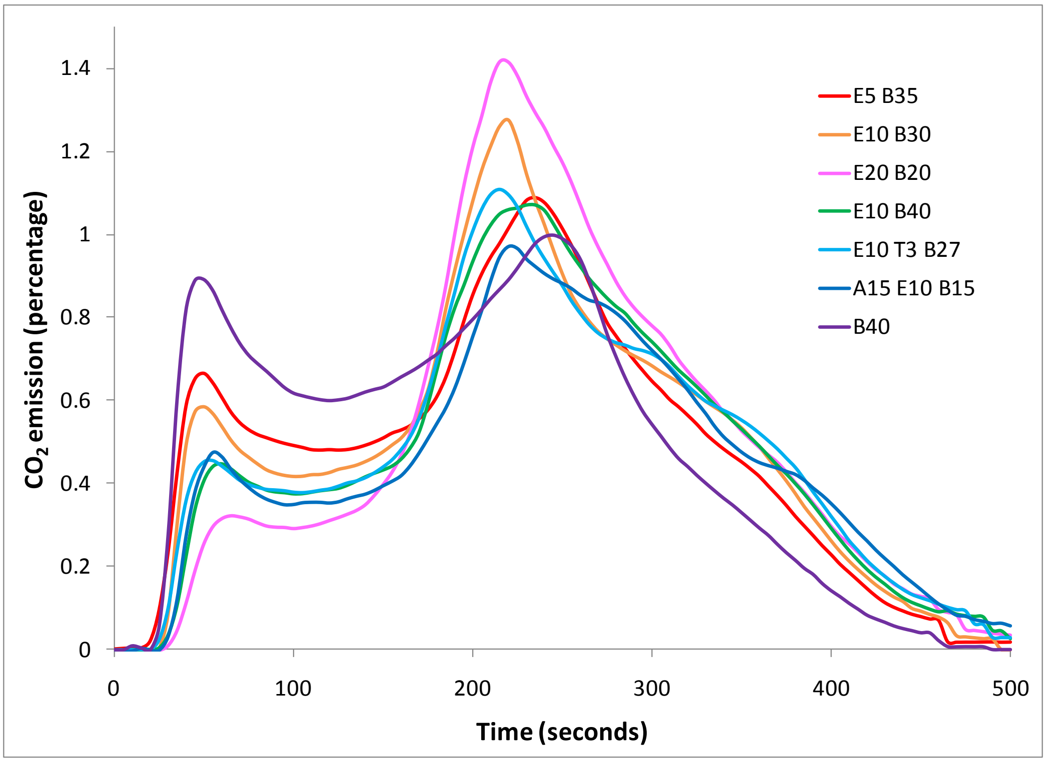


Figure 62 CO_2 emissions from cone for expandable graphite formulations

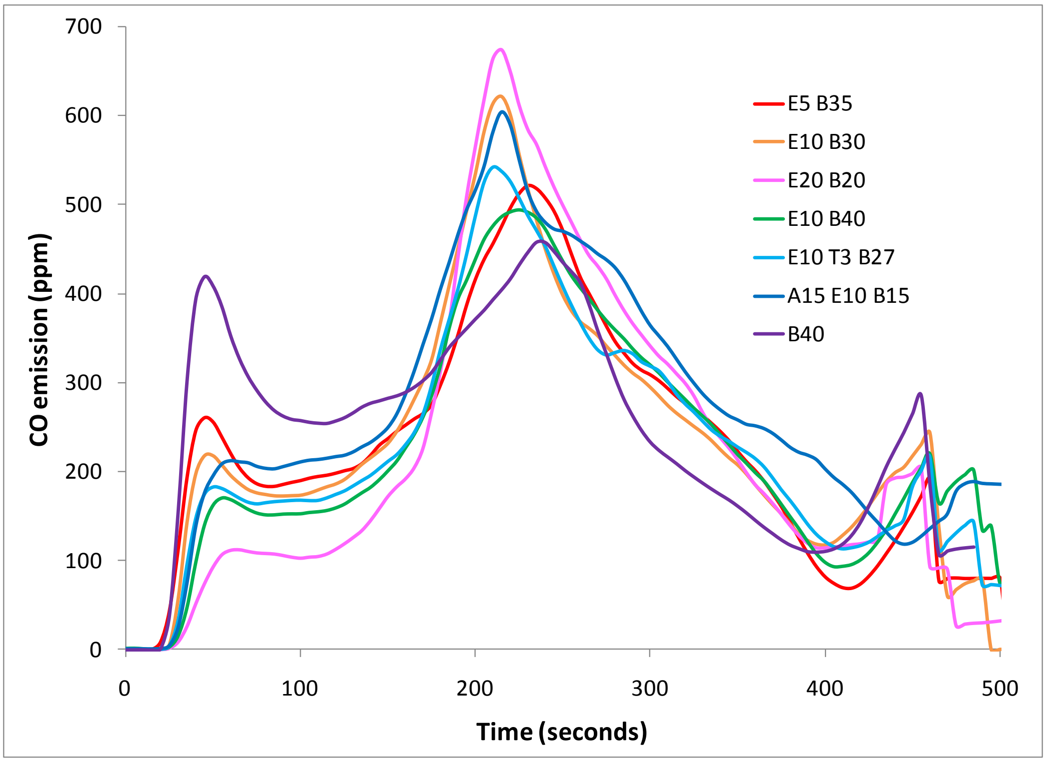


Figure 63 CO emissions from cone for expandable graphite formulations

CO_2 (Figure 62) and CO emissions (Figure 63) follow heat release closely, with the use of EG usefully suppressing the toxicant CO in the first 200 seconds of burning. The second peaks mirror the increased burning rate for the higher additions of EG. As the phosphorus containing plasticiser TEP might be expected to act in the gas phase as a flame quencher (like a halogen), it is significant that there is no change in the CO_2 / CO ratio for E10 T3 B27, explaining the lack of improved fire retardance from this additive in the cone calorimeter.

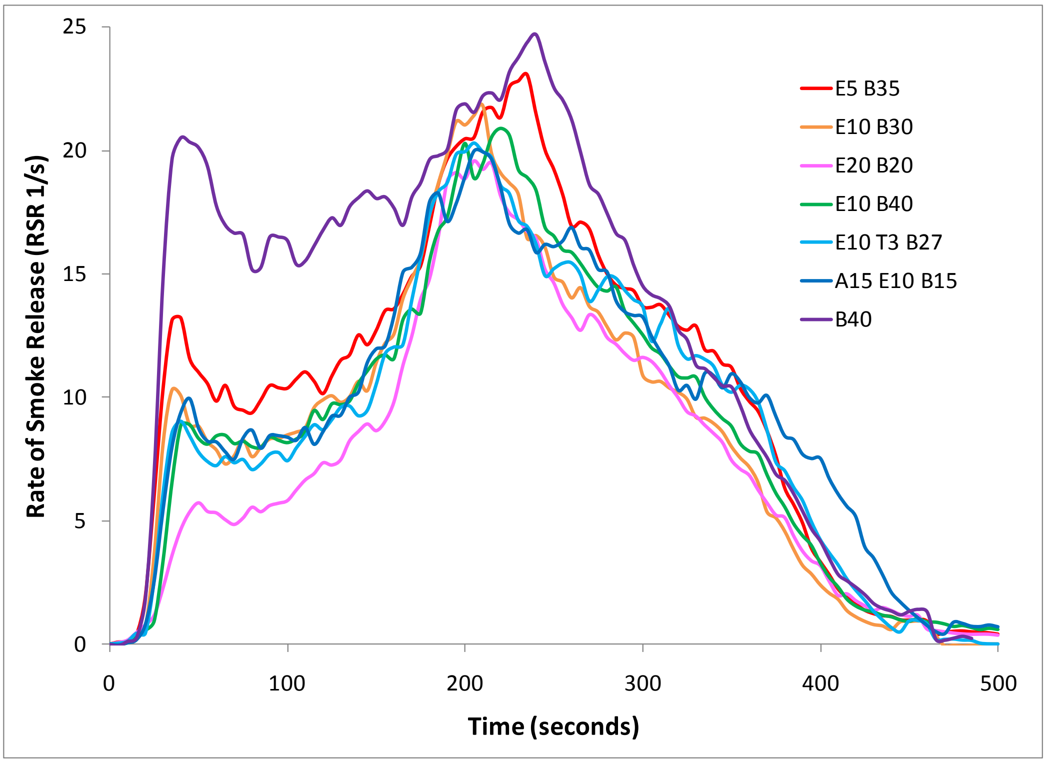


Figure 64 Mean Rate of Smoke Release for expandable graphite formulations

The rate of smoke production is significantly reduced by the use of EG in the first 200 seconds, and remains below B40 at the second burning peak. This shows that increasing levels of EG substituted for carbon black can suppress smoke yields. The use of TEP did not affect the smoke yield, confirming the lack of fire retardant action.

4.2.4 Summary

Formulations were produced using EG at varying levels and in combination with TEP or APP. The large particle size of EG led to poor dispersion with a reduction in physical properties. At 5pphr addition of EG, the material physical properties remain acceptable for use within bonded articles for anti-vibration usage. At 10 pphr EG and over a severe reduction in physical properties were recorded which would limit the application of such compounds within industrial engineering products, but may be satisfactory in many less demanding areas. When subjected to TGA, little effect is seen in a nitrogen environment of EG loading. In air, however, increasing loadings of EG led to reduced thermal stability between 300 and 350°C, but some increased temporary residue between 400 and 500°C.

The use of EG gives a small improvement in LOI and a reduction in the rate of horizontal burning, but does not yield any self-extinguishing behaviour. In the cone calorimeter, EG confers a significant benefit in the first 3 minutes of heating, where a surface char develops reducing peak heat release, smoke, CO, CO_2 and mass loss rate. In a second stage however, a high level of intumescence develops which opens up the sample and increases the burning rate with a higher peak HRR than for the unmodified carbon black filled compound. Whilst the char structure is very thick, which has the potential for good barrier properties to the flow of heat and gas, at higher loadings it is friable with cracks and gaps. The highest reduction of heat release in the first peak is for the highest level of EG (20pphr), but has the largest increase in HRR at the second peak. A more useful reduction of HRR is afforded by the lowest level of EG at 5pphr. In this case a useful reduction in HRR is given in the initial stages of burning without a large increase at the second peak.

To make further improvements in fire retardancy using EG will require the addition of other fire retardants which can function additively.

4.3 Fire retardancy of hydrated fillers

4.3.1 Introduction

The literature indicates the widespread use of aluminium hydroxide in polyisoprene for non-halogenated systems, but little evidence of other hydrated fillers in use. A basic study comparing some common endothermic fillers is therefore desirable. The effects of hydrated fillers and additives in a polyisoprene rubber compound were investigated, with the following specific objectives:

1 Compare aluminium hydroxide (ATH), Ultracarb (a blend of huntite of hydromagnesite), magnesium hydroxide (MH) and calcium carbonate with an unmodified rubber compound.

2 Compare a blend of ATH and MH with ATH and MH alone

3 Determine the effects of ATH and MH at a lower level of incorporation

Calcium carbonate was included as a simple filler to provide a compound with an equal fire load but no endothermic filler decomposition at a temperature likely to benefit polyisoprene.

4.3.2 Experimental section

4.3.2.1 Materials

The benchmark carbon black filled formulation B20 in Table 38 is formulated based on a formulation within a standard text on rubber compound formulations. This formulation is used as a base for modified compounds in Table 54. The formulations are coded to aid the reader as to the level and type of additive employed. The letter indicates the materials used, A100 for example, indicating aluminium hydroxide at 100 pphr.

Ingredient (values in pphr)	A50	A100	C100	M50	M100	A50 M50	UC12 100	UC15 100
B20 base formulation	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6
aluminium hydroxide	50	100				50		
calcium carbonate			100					
magnesium hydroxide				50	100	50		
UltraCarb 1291 (60% huntite)							100	
UltraCarb LH15C (40% huntite)								100
Total	186.6	236.6	236.6	186.6	236.6	236.6	236.6	236.6

Table 54 Polyisoprene formulations with additions of hydrated fillers

4.3.3 Results

4.3.3.1 Physical properties

Formulation code		B20	A50	A100	C100	M50	M100	A50 M50	UC12 100	UC15 100
Hardness	IRHD	47	54	60	58	52	58	56	54	55
Specific Gravity		1.02	1.21	1.35	1.39	1.20	1.34	1.35	1.36	1.34
Tensile Strength	MPa	25.2	17.6	12.7	11.5	14.6	12.3	21.6	15.0	13.8
Elongation at Break	%	560	433	461	458	404	509	457	500	480
Trouser tear	KN/m	4.7	2.7	4.5	2.1	5.7	7.0	3.6	2.7	2.5
Crescent tear	N/2mm	66.5	53.3	55.9	28.4	50.0	61.2	57.7	66.4	47.7
Aged 70h @ 70°C										
Change in tensile strength	%	-7	-17	3	5	-1	0	-8	2	1
Change in E@B	%	-17	2	-15	-5	18	-13	14	-2	-6
Change in hardness	IRHD	1	1	1	2	0	2	2	5	2
Comp. Set 22hrs 70°C	%	6.4	9.9	17.5	18.6	12.0	22.5	8.7	18.5	12.7
Yerzley properties										
Static modulus (SM)	MPa	0.52	0.69	0.84	0.85	0.64	0.69	0.73	0.57	0.61
Dynamic modulus (DM)	MPa	0.61	0.80	1.14	1.03	0.84	1.11	1.01	0.98	0.92
DM/SM Ratio		1.17	1.17	1.35	1.21	1.32	1.62	1.38	1.71	1.51
Resilience	%	80	76	69	71	71	61	65	60	62
Creep	%	1.85	2.65	4.50	3.84	3.81	5.16	4.82	4.95	4.18
70h @ 100°C Volume Change water	%	1.3	2.1	2.4	1.6	1.9	1.7	4.3	2.4	1.5
X value (filler dispersion)		6.7	6.9	6.9	<0.5	7	7.5	7.4	5.3	5.6
Y value (agglomerate count)		9.5	9.8	9.8	2.2	9.8	9.9	9.9	9.3	9.4
Dispersion rating		E7	E7	E7	E1	E7	E7	E7	E5	E6
Moving Die Rheometer (MDR)										
Minimum torque (ML)	lb-in	0.68	0.67	0.7	0.67	0.7	0.74	0.8	0.63	0.58
Maximum Torque (MH)	lb-in	8.55	10.3	11.9	13.1	8.71	9.5	10.2	8.38	9
Time to Scorch (ts2)	min	4.75	4.54	4.42	4.2	3.33	1.89	2.51	3.65	4.14
Time to 90% cure (t90)	min	10.1	10.1	10.3	9.9	10.9	11.5	11.1	8.5	9.1
Peak rate of cure (Rh)	lb-in/min	1.46	1.84	2.12	2.58	1.14	2.49	1.54	1.5	1.69

Table 55 Physical properties for hydrated filler formulations

Hardness (Table 55) is increased by addition of the fillers used, and at 100 pphr filler, the formulations using the UltraCarb materials give the lowest increase in hardness at 7-8 IRHD. Both ATH and MH give a higher increase in hardness, at 11-13 IRHD. A50 and M50 give lower hardnesses, in proportion with the lower addition level. An asset to a fire retardant is to have a low effect on hardness, so the use of the UltraCarb materials shows a benefit over ATH and MH.

The formulations with 100pphr filler all have similarly increased SG values, beneficial for fire retardance, since this creates a higher product mass and therefore heat-sink. The tensile strength and elongation at break for the modified compounds is significantly reduced, in most cases at around 50% of formulation B20. This level of physical strength using ATH has been previously reported [62] as an acknowledged drawback and considered by Fernando [9], who suggests that ATH imparts poor physical properties due to a lack of reinforcement and a lack of interaction between filler and polymer. Surface treated grades may therefore address this reduction in properties. In most of the FR formulations the tear strength is less adversely affected except for formulation C100 where crescent tear drops by over 50%. Hot air aged physical properties are all at acceptable levels, so these fillers are not promoting degradation at lower temperatures.

Yerzley static modulus increases broadly in line with hardness as expected. The reduction in polymer increases the DM/SM ratio, broadly increasing with filler loading, but varying by filler type. Damping increases at a higher level for MH than ATH. The use of UltraCarb also increases the DM/SM ratio, with the highest damping for formulation UC12 100 with the huntite/hydromagnesite ratio of 60/40. These increases in damping are broadly reflected in reduced resilience. Compression set significantly rises with filler loading, with 100pphr typically giving values of over 15% set. A50 M50 is an exception to this with a compression set value of 8.7%, which does not agree with the overall increases, requiring further investigation.

Dispersion values indicate that all of the fillers with the exception of calcium carbonate in C100 are well dispersed. The MDR tests demonstrate that the addition of these fillers have affected the rheological data at the higher loadings. ATH and MH separately impart an increased rate of cure, but when blended in A50 M50 have less effect.

In summary, acceptable physical properties are retained in A50 and M50 with the lower filler addition. Of the higher filler additions, A50 M50 retains acceptable properties, with high tensile strength and low compression set. The remaining formulations could be acceptable in a less demanding application, but would need product specific evaluation.

4.3.3.2 TGA results

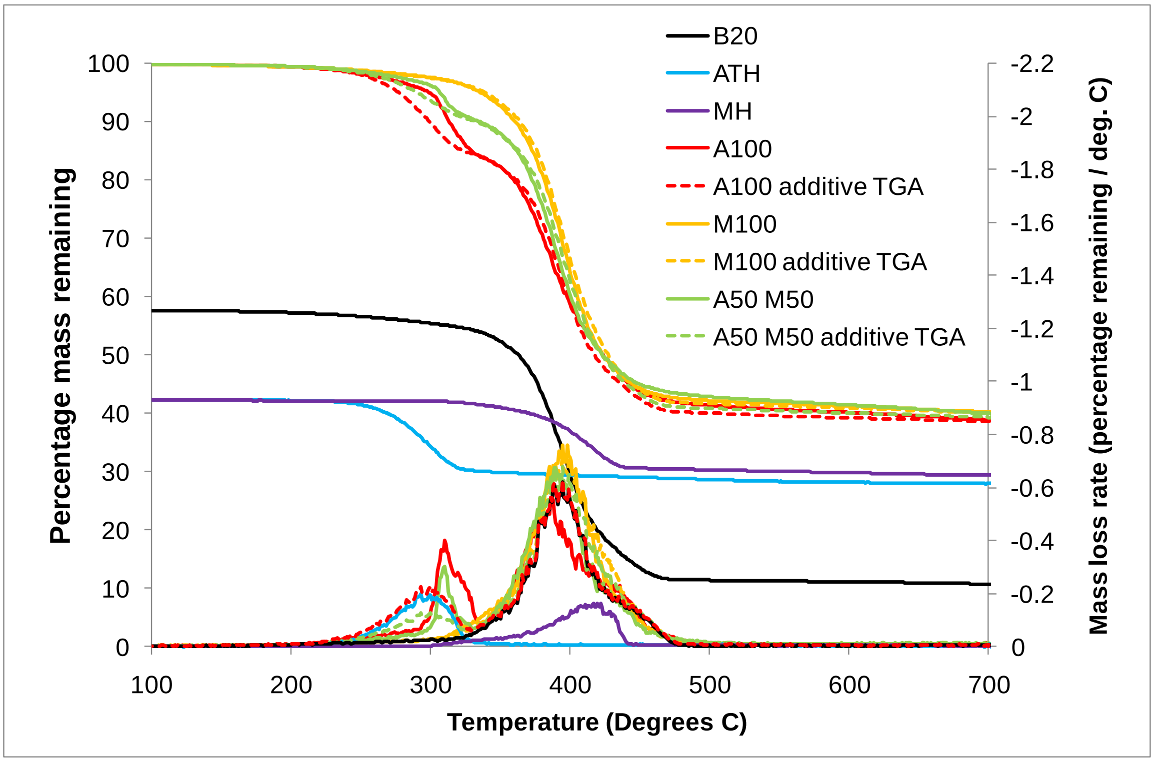


Figure 65 TGA and DTG curves actual and additive for ATH / MH formulations in nitrogen

B20 provides a base line of un-modified rubber compound (Figure 65). In A100, the presence of aluminium hydroxide causes a sharp mass loss peak at 310°C; whereas magnesium hydroxide loses mass in M100 at a similar temperature to the peak decomposition temperature for polyisoprene (typically around 391°C). The reduced level of material addition in A50 and M50 had little effect on the peak mass loss temperature (Table 56), with the level of mass loss was in proportion to the percentage incorporated (TGA curve omitted). In A50 M50 there is a simple combined effect of the two additives, with a similar level of mass remaining above 500°C for 100 pphr of either additive. For all of the formulations, there is little effect on the polymer decomposition stage in terms of rate once the percentage of polymer is considered, indicating that the fillers are not affecting the decomposition reactions in this atmosphere. A further consideration was made of formulations A100, M100 and A50 M50, with the construction of additive TGA plots. ATH is more resistant to decomposition within the rubber compound than as an additive alone, which indicates that ATH can be used safely for high-temperature cross-linking processes such as continuous vulcanisation (up to 240°C for short periods).

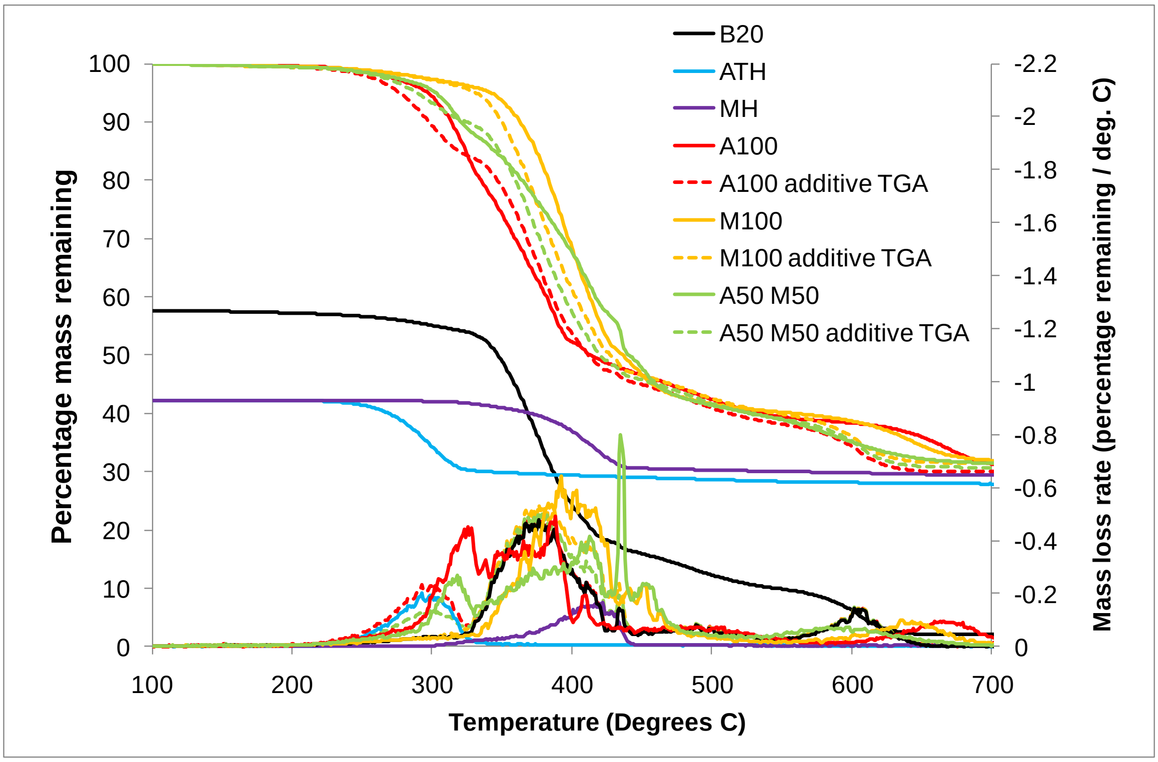


Figure 66 TGA and DTG curves actual and additive for ATH / MH formulations in air

In air, however, significant variation occurs between the actual and constructed TGA curves (Figure 66). Both A100 and M100 are slower to commence mass loss than indicated by the additive curves, indicating that both the ATH and MH initial decomposition is slowed within the rubber compound. In addition, the mass loss of carbon black is at around 60°C higher in the ATH and MH fire retarded rubber compounds than by additive TGA – but not for A50 M50, which indicates some interaction of the blend. The most interesting aspect, however, is the much slower rate of mass loss from A50 M50 between 350 and 430°C, than predicted by the additive TGA. This suggests a synergistic benefit from the combination of ATH and MH, and this increased thermal stability would indicate reduced flammability.

Formulation code	B20	C100	A100	M100	A50	M50	A50 M50	UC12 100	UC15 100
Nitrogen (°C)	391	393	387	398	393	396	389	392	394
Air (°C)	376	364	388	392	349	409	400	398	414

Table 56 Peak polymer decomposition temperatures for hydrated filler formulations

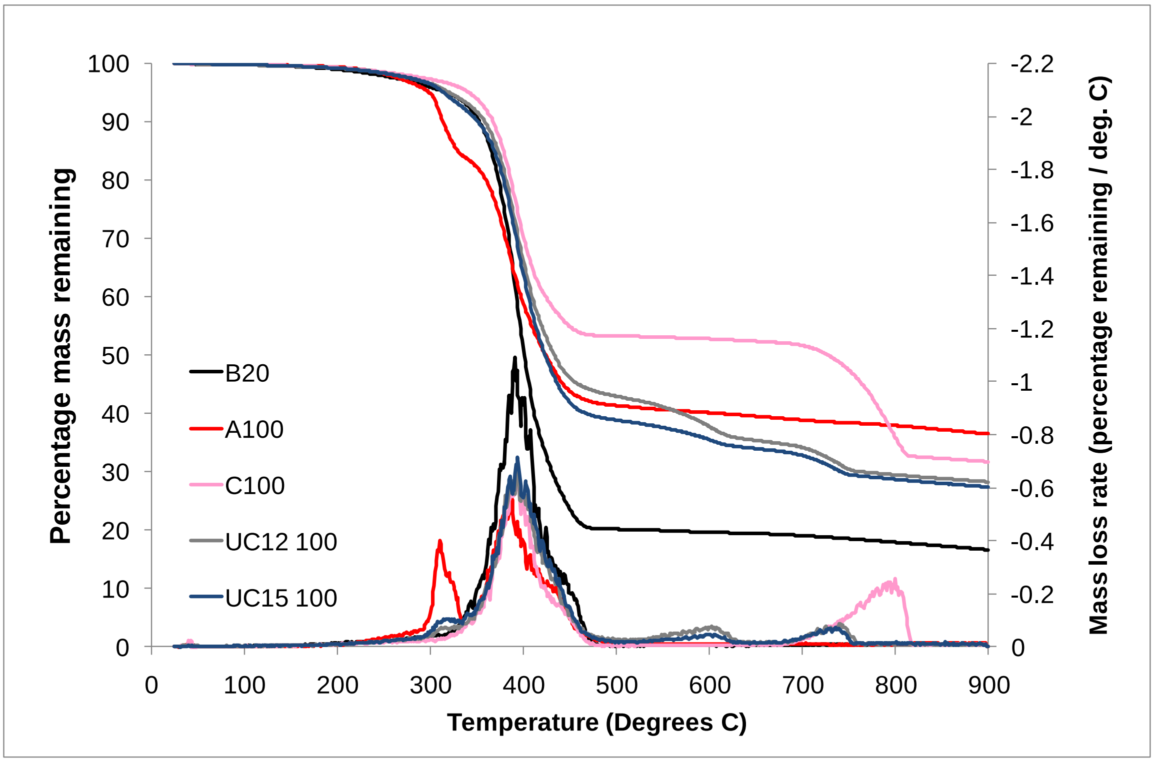


Figure 67 TGA and DTG curves for selected hydrated filler formulations in nitrogen

C100 has the highest filler stability with no decomposition noted in nitrogen until around 680°C (Figure 67), with a peak loss rate at 792°C, associated with the decomposition of calcium carbonate to calcium oxide with the loss of CO_2. The lack of endothermic decomposition either before or during the thermal decomposition of the polymer would indicate that the only fire retarding benefit from calcium carbonate may be as a barrier to gas and heat, and as a diluent of the polymer. The Ultracarb blends of huntite and hydromagnesite can be compared to A100, with an insignificant mass loss at around 310°C, and a significant mass loss at 400°C, coinciding with the polymer decomposition in a similar manner to M100. In addition, two further mass loss events peak place at 600°C and 730°C. The first two events can be attributed to the decomposition of hydromagnesite, and the latter two with huntite (Figure 11).

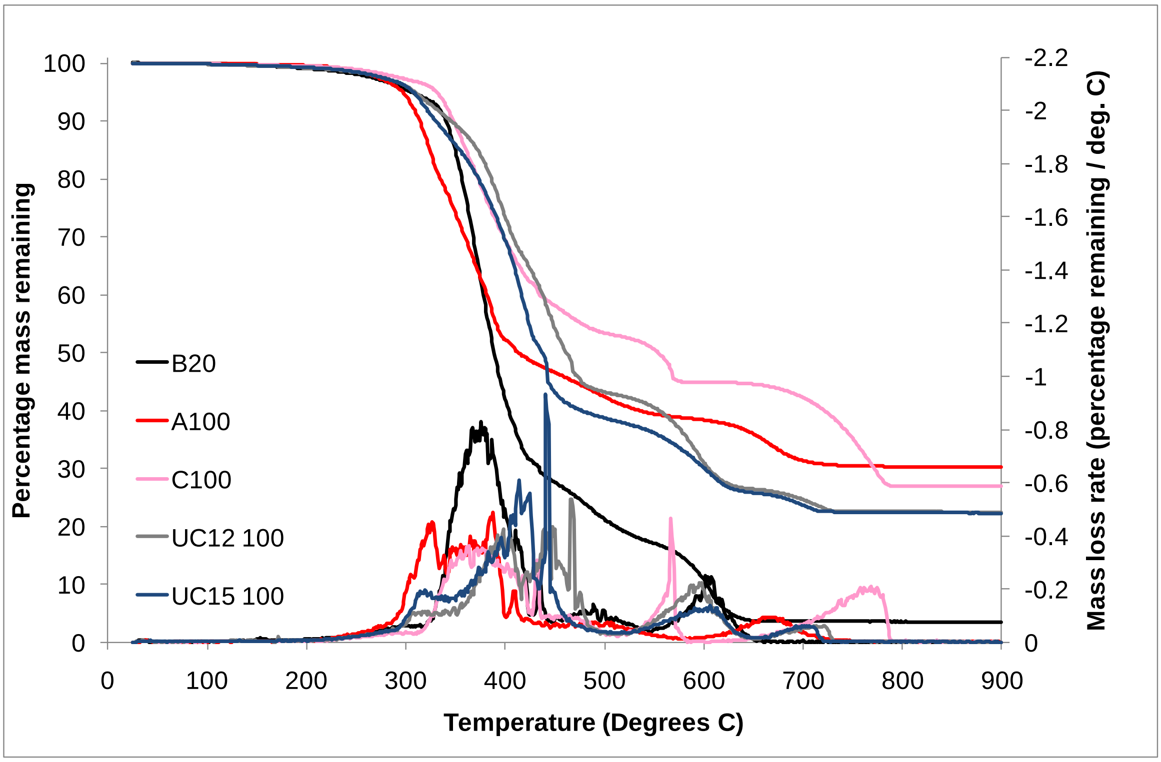


Figure 68 TGA and DTG curves for selected hydrated filler formulations in air

In air (Figure 68) the use of calcium carbonate slows the rate of mass loss from polymer decomposition, indicating some stabilising function. The carbon black mass loss, however, takes place at around 40°C lower.

Comparing the Ultracarb blends, the lower proportion of hydromagnesite in UC12 100 increases the thermal stability of the compound, and both grades have no effect upon the carbon black mass loss. The main mass loss occurs after the polyisoprene, which may be somewhat late to slow decomposition, suggesting less benefit to retarding burning behaviour by endothermic cooling than ATH or MH.

4.3.3.3 Burning behaviour

Small scale flammability tests

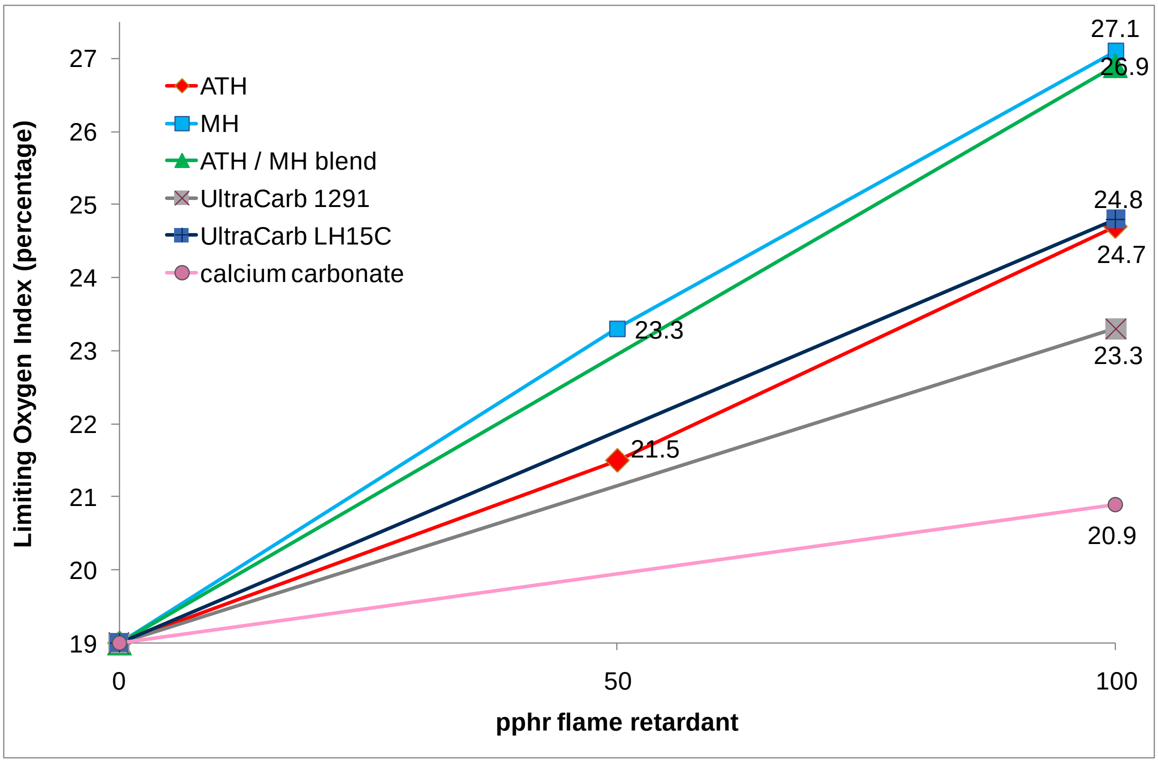


Figure 69 Contribution to LOI for hydrated filler formulations

The dilution of B20 with calcium carbonate in C100 increases the LOI to 20.9% (Figure 69). To remove the effect of dilution this value can be used for comparison with the fire retarded formulations at 100pphr. Considering the use of ATH, A50 gave a modest improvement to 21.5%, but A100 yielded 24.7%, higher than by Ismawi [62] who obtained 23.8% for 100pphr of ATH. This difference is most likely to be because A100 also had 20pphr of carbon black, which will reduce the percentage polymer. The use of magnesium hydroxide resulted in higher LOI values in comparison with equivalent ATH formulations, and suggests a linear relationship between LOI and filler loading. An equal blend of ATH and MH, A50 M50, with an LOI value of 26.9%, is very close to the value for M100. This showed that a blend shows interesting behaviour and may merit further investigation, since whilst MH gave the highest LOI, ATH is significantly lower in cost and has less effect on the material properties. UC12 100 and UC15 100, blends of huntite and hydromagnesite, gave LOI lower or equal to ATH. UC15 100, with a blend of 40% huntite and 60% hydromagnesite was the most effective material.

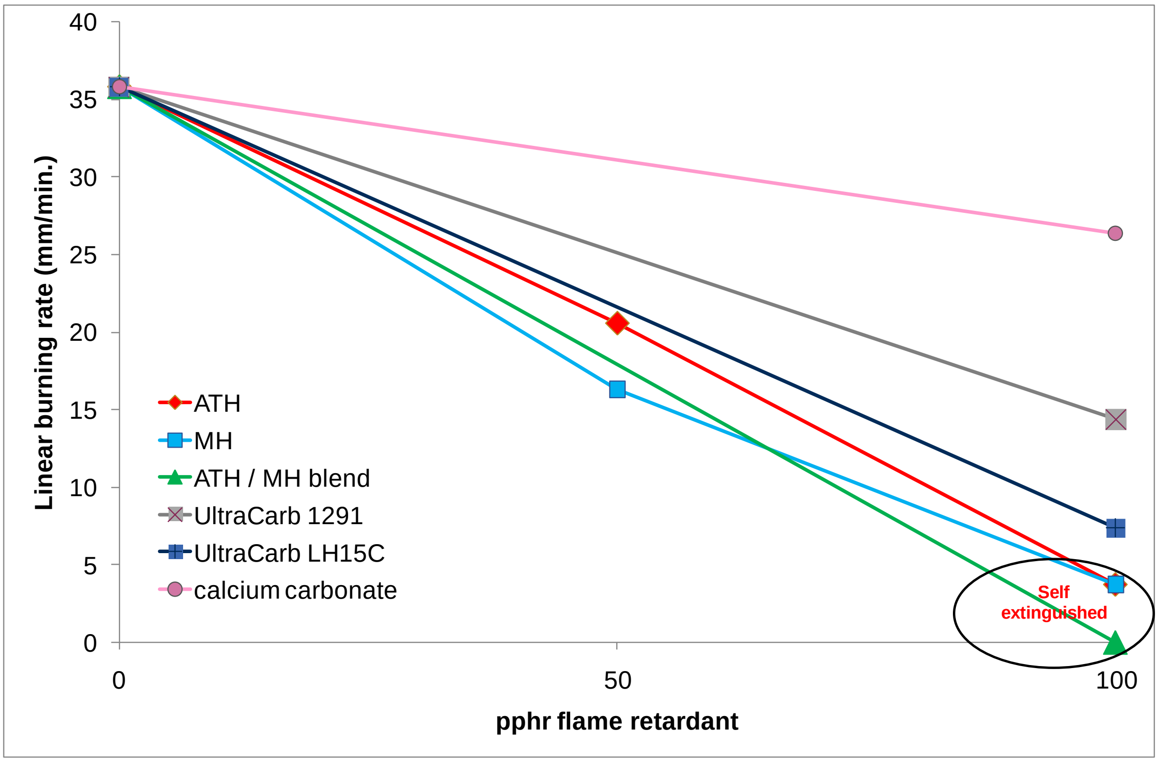


Figure 70 Contribution to horizontal burning rate for hydrated filler formulations

The average horizontal burning rate (Figure 70) starts with B20 giving the highest rate of linear burning at 36mm/minute. The use of 100pphr calcium carbonate gave little improvement in linear burning. The use of 50pphr MH is an improvement with a reduction to 16mm/minute. Considering 100pphr of ATH and MH performance is similarly improved for both with self extinguishing behaviour with a rating of FH2 and a low rate of burning. As with LOI, a blend of ATH and MH in formulation A50 M50 gave an improvement in flammability, with the lowest rate of burning. This was not achieved with either A100 or M100, so would appear to demonstrate a synergism between these hydrated fillers. The use of blends of huntite / hydromagnesite in UC12 100 and UC15 100 gave worse performance than for A100 or M100, with no self-extinguishment recorded.

Cone calorimetry

Property	Units	B20	A50	A100	C100	M50	M100	A50 M50	UC12 100	UC15 100
Time to ignition	secs	21	25	39	31	29	39	38	28	31
Flameout	secs	660	954	1136	883	1026	1131	**1226**	1055	1021
Total Heat Evolved	MJ/m^2	183	147	124	139	139	125	**114**	137	127
Total smoke released	m^2/m^2	12165	5578	**4004**	6869	5826	5216	4444	4528	4502
HRR average	KW/m^2	286	157	114	164	139	115	**96**	134	129
HRR peak	KW/m^2	537	348	237	326	333	204	**192**	263	238
HRR peak at time	secs	263	318	86	306	**383**	82	322	217	337
Mass remaining	%	20	36	46	**54**	37	47	51	39	40
MARHE	KW/m^2	392	232	154	225	184	144	**120**	178	162

Table 57 Summary of mean cone calorimeter values for hydrated filler formulations

In Table 57 the ‘best’ value determined for each property is highlighted. These are summary values however, and cannot be viewed alone without consideration of the whole process observed, particularly with the release of heat and smoke with respect to time. One measure from this table includes time to ignition, for which the use of aluminium hydroxide gave almost doubling compared to the unmodified B20 formulation. The use of hydrated fillers is generally reported as giving a useful reduction in smoke output, and in this case the formulation A100 gave the lowest smoke yield, at around 30% of the formulation B20. Overall the best performer was formulation A50 M50, with a high smoke reduction, the lowest peak and average heat release rate and the lowest MARHE value, an important classification for evaluation to EN45545 part 2.

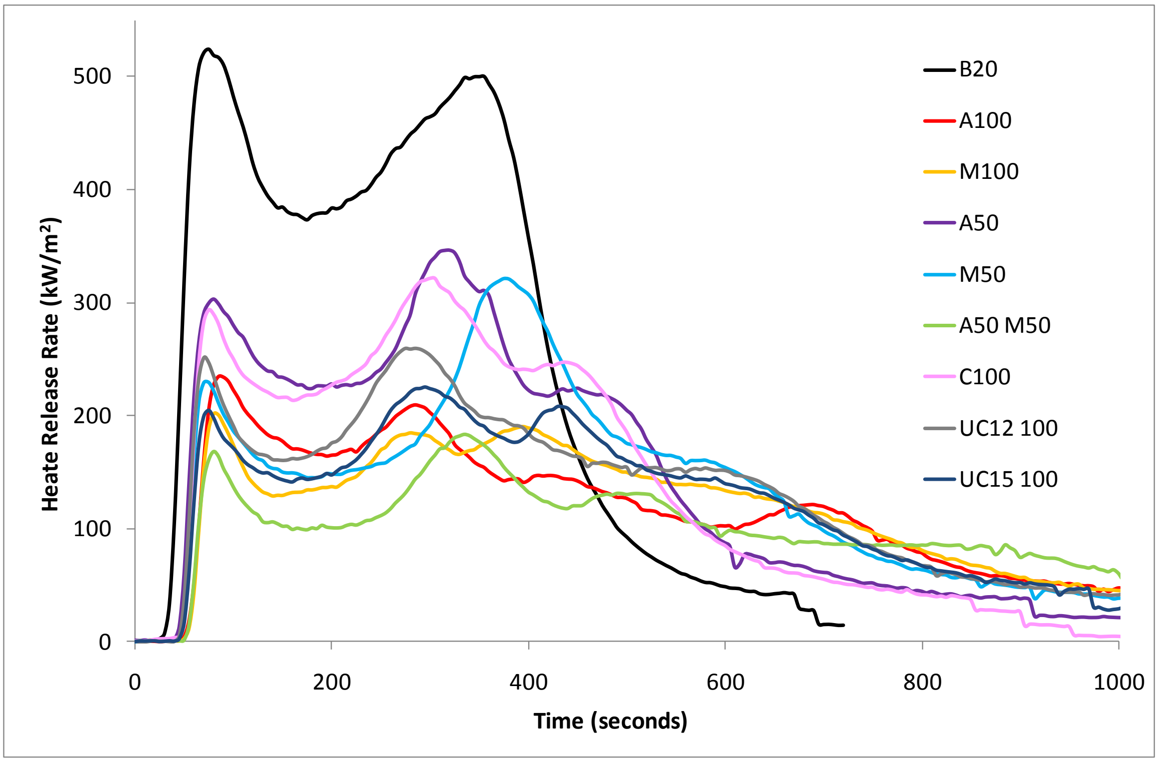


Figure 71 Heat release rate from cone for hydrated filler formulations

In Figure 71 all of the modified formulations have significantly a reduced HRR compared to B20. The highest modified compound heat release rate is for A50, with C100 following a very similar profile, so ATH can be proposed twice as effective as calcium carbonate for reducing heat release. Magnesium hydroxide at 50pphr is much more effective than ATH with a lower initial peak, but gave a final high peak later on at 400 seconds. At 100 pphr addition, MH is again more effective than ATH, but the difference is much less apparent. Considering the UltraCarb materials, UC12 100 (1290) and UC15 100 (LH15C) behaved overall in a similar manner to ATH, but with higher second peak HRR values. UC15 100 gave the lowest HRR of the two blends. The best performing formulation for heat release was A50 M50 with the lowest first and second peaks, and the lowest peak value of around 175kW/m^2, around 1/3 that of B20 formulation. The rate of mass loss (Figure 72) also demonstrates that A50 M50 has the best performance with the highest percentage mass over at any given point, noticeably better than any other hydrated filler. It is also of interest that M50 performs comparably to ATH and UltraCarb at 100 phr for the first 300 seconds.

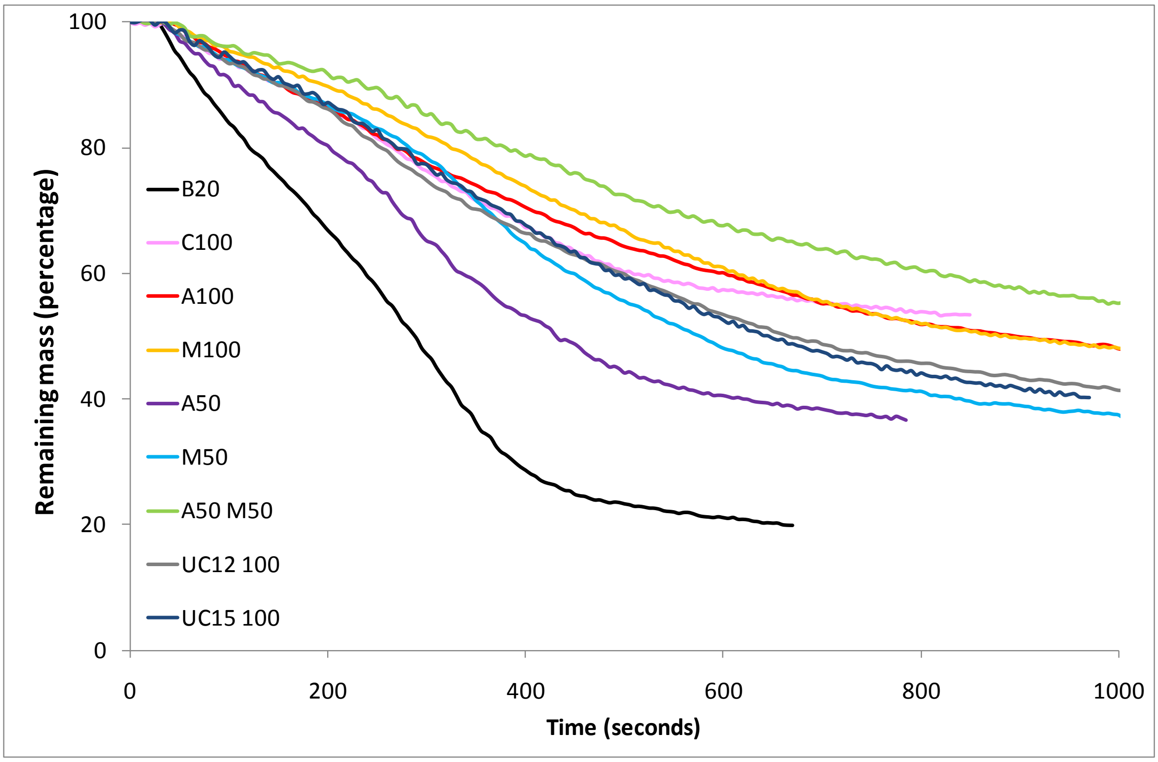


Figure 72 Residual mass from cone calorimeter for hydrated filler formulations

CO_2 and CO emissions (not included) are comparable in terms of rank by formulation and all of the hydrated fillers show reduced production compared to B20. The pattern of CO_2 / CO gas production is roughly similar to HRR, so the use of hydrated fillers has not increased levels of toxic fume. In a real fire scenario, with reduced ventilation however, this situation cannot be guaranteed.

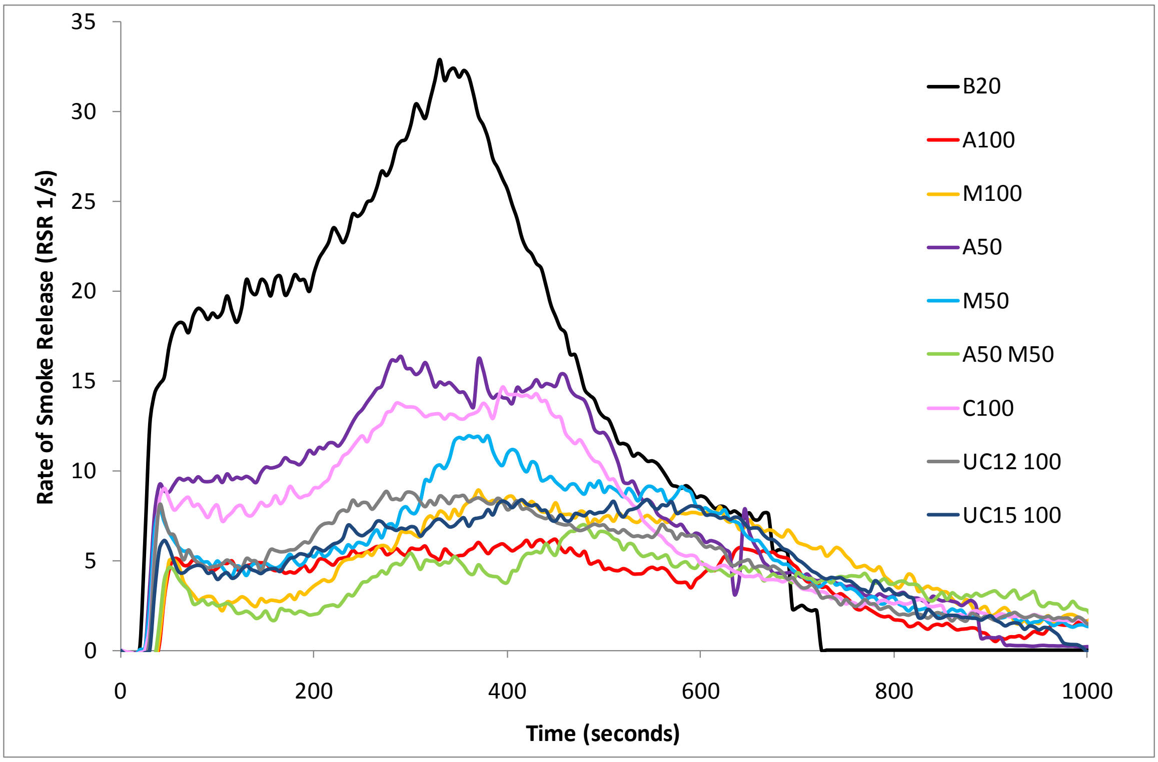


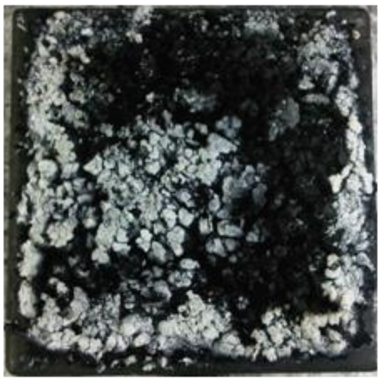
Figure 73 Mean Rate of Smoke Release for hydrated filler formulations

Considering Figure 73, there are some different patterns of smoke release than for heat release. B20 for instance releases less smoke at the first HRR peak and then builds steadily to the final peak coincident with the second HRR peak. The addition of hydrated fillers has significantly reduced smoke production, with A50 M50 yielding the lowest rate of smoke production mostly throughout the run. M50 significantly out-performs A50 and C100 throughout, and is comparable to ATH and UltraCarb for the first 300 seconds.

Observations of cone samples

The residue from A50 was extremely friable with small residual particles and carbon black and ATH residue.

Figure 74 A50 residue

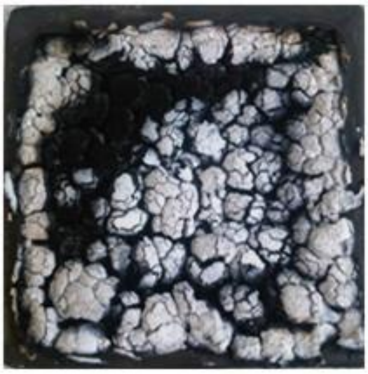


M50 had a noticeably more defined residue with some evidence of more clumped material.

Figure 75 M50 residue

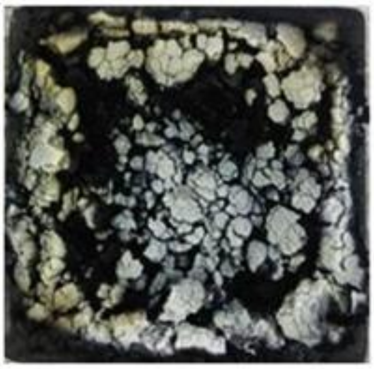
A100 shows increased evidence of a char formation, but it is weak and friable.

Figure 76 A100 residue



M100 has a noticeably stronger and complete residue, although still not continuous.

Figure 77 M100 residue

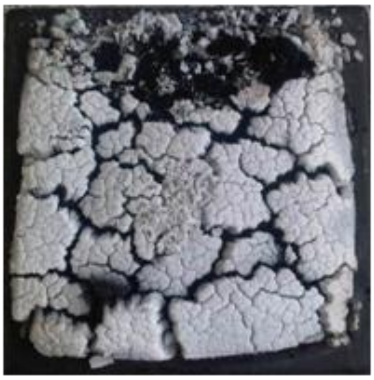


A50 M50 has a residue in appearance in-between A100 and M100, with some regions of well clumped residue, but patchy and inconsistent across the sample.

Figure 78 A50 M50 residue

The use of calcium carbonate leads to an almost continuous and rigid residue structure, broken by long cracks along areas of weakness.

Figure 79 C100 residue



UC12 100 leaves a residue stronger and more intact than ATH or MH, but with more cracks than C100.

Figure 80 UC12 100 residue

UC15 100 leaves a similar appearance residue to UC12 100, more intact than ATH and MH.

Figure 81 UC15 100 residue

4.3.4 Discussion

In TGA tests under nitrogen, the use of hydrated fillers did not indicate any direct protection of the polymer from thermal decomposition, and in the case of ATH led to a reduced temperature of mass loss from the decomposition of the filler commencing at around 240°C. In air, however, the combination of ATH and MH in A50 M50 resulted in a slower rate of polymer mass loss than predicted by additive TGA, indicating a synergistic effect.

The burning behaviour led to the widest differences observed of the varying fillers employed. To eliminate the dilution of polymer by filler as a factor, comparisons can be made to the more thermally stable calcium carbonate. Until 650°C this material will function as inert filler, so can be used as a benchmark to look for the added benefit of endothermic decomposition from ATH, MH and the huntite/hydromagnesite UltraCarb materials.

In the small scale flammability tests M100 attained the highest LOI value of 27.1%, significantly better than C100 at 20.9%. MH was also significantly better than A100, UC12 100 and UC15 100, which were between 23-25%. At a lower loading of 50 pphr, M50 was significantly better than A50. The blend of ATH and MH in A50 M50 also yielded a high LOI of 26.9%, and also attained the only rating of FH-1 on the horizontal burning test.

On the cone calorimeter A50 M50 was somewhat better overall than A100 and M100, indicating some synergistic behaviour between the two systems. The heat release curve demonstrates the most even burning behaviour with the least dramatic peaks, which led to the lowest MARHE value. The resultant low rate of mass loss confirms this improvement in burning, along with low CO, CO_2 and smoke yields. Some consideration is necessary to explain this enhanced performance compared to ATH, MH and UltraCarb. Re-considering the thermal decomposition in comparison to the polymer decomposition is therefore necessary. The polymer decomposition will take place in a low oxygen environment once burning commences, so we should consider the TGA in nitrogen (Figure 65). In A100 there is a significant mass loss from water between around 280 and 340°C, which is likely to provide a sacrificial protection to the polymer by removing heat so slowing the rate of decomposition. The usefulness of the ATH may be therefore exhausted at a lower temperature than ideal for the polymer. MH on the other hand decomposes at around the same temperature at the polyisoprene, so will protect the polymer once it is decomposing, but not before, so may be considered a little late for optimum protection. It may therefore be proposed that a blend of ATH and MH can better protect a polyisoprene rubber compound. The ATH cools the material, so delaying decomposition, and the MH releases water during the decomposition process so reducing the rate of fuel production for subsequent burning within and reducing the flame temperature. This wider operating range from using a combination of fire retardants is therefore proposed as the reason for the success of this system.

Examining the char residue, this suggests physical effects from the presence of hydrated fillers. The control material C100 has the most continuous residue remaining, so a barrier property cannot be the most important factor to protection, since C100 was the worst performing additive. For the same level of addition however, A100 had the least continuous residue, and yielded lower heat release than the Ultracarb materials. This indicates that the endothermic decomposition has a more significant bearing on the heat release. The residue from the ATH/MH blend A50 M50 is more intact than for A100, so this may have led to the improvement in cone calorimeter values above a simple substitution of magnesium hydroxide.

4.3.5 **Summary**

To restate the objectives for this section:

1 Compare aluminium hydroxide (ATH), Huntite/Hydromagnesite, magnesium hydroxide (MH) and calcium carbonate with an unmodified rubber compound.

2 Compare a blend of ATH and MH with ATH and MH alone

3 Determine the effects of ATH and MH at a lower level of incorporation

These objectives were met, with an improved understanding gained of the effect of a range of hydrated fillers in a polyisoprene rubber compound not available in the literature for the combination of physical properties, TGA data, flammability and burning behaviour.

These formulations were evaluated for physical, thermal and burning properties. The use of increasing levels of filler led to a significant reduction in physical strength, but some of the formulations retained sufficient properties to remain useful in many industrial applications, such as bonded rubber buffers. The use of hydrated fillers has led to significantly improved burning behaviour even at just 50pphr (27%) loading of magnesium hydroxide.

Interestingly, at 100 pphr (42%) loading of an equal mixture of aluminium hydroxide and magnesium hydroxide, (A50 M50) a dramatic improvement is noted in all aspects of burning behaviour, smoke, CO, and CO_2 emissions. It would be desirable however to either further reduce burning or allow a reduction in the percentage filler for the same performance. The use of small additions of other additives in hydrated filler will be considered next for this task.

4.4 Hydrated Fillers and Synergists as Fire Retardants

4.4.1.1 Introduction

The effects of hydrated fillers and additives in a polyisoprene rubber compound were investigated, with the following objectives:

1 Evaluate the effect of zinc hydroxystannate (ZHS) as a proposed synergist in ATH and MH, both as an additive and a coating onto the filler. ZHS has been promoted as reducing the LOI and smoke emissions when used in natural rubber [139] as an additive with ATH.

2 Evaluate zinc borate (ZB) with ATH. ZB, commonly used as a smoke suppressant [141] in other polymers, is evaluated.

3 Investigate the effect of expandable graphite (EG) when used in conjunction with ATH. EG was evaluated in section 4.2, and gave improvements at low levels of addition.

4 Consider the effect of red phosphorus (RP) when used in conjunction with ATH. Whilst RP is considered to promote char formation in the condensed phase within oxygen containing polymers, phosphorus can also function as a free-radical trap in the gas phase as an alternative to halogenated fire retardants.

4.4.2 Experimental section

4.4.2.1 Materials

Table 58 and Table 59 contain formulations using ATH and MH, using B20 compound (Table 38). In each formulation the total phr remains the same, with any other additives subtracting from the hydrated filler pphr loading. The formulations are coded to aid the reader as to the level and type of additive employed. Formulations A100 and M100 are the benchmark formulations for any comparison.

Ingredient (values in pphr)	A100	A90 ZHS10	ZAH100	A90 ZB10	A80 ZB10 ZHS10	A90 RP10	A95 EG5
B20 base formulation	136.6	136.6	136.6	136.6	136.6	136.6	136.6
aluminium hydroxide	100	90		90	80	90	95
zinc borate				10	10		
zinc hydroxystannate (ZHS)		10			10		
aluminium hydroxide coated with ZHS			100				
red phosphorus 50% on castor oil						10	
expandable graphite							5
Total	236.6	236.6	236.6	236.6	236.6	236.6	236.6

Table 58 Polyisoprene formulations with ATH and synergists

Ingredient (values in pphr)	M100	M90 ZHS10	ZMH 100
B20 base formulation	136.6	136.6	136.6
magnesium hydroxide	100	90	
zinc hydroxystannate (ZHS)		10	
magnesium hydroxide coated with ZHS			100
Total	236.6	236.6	236.6

Table 59 Polyisoprene formulations with MH and ZHS

4.4.3 **Results**

4.4.3.1 Physical properties

Formulation code		A100	A90 ZHS10	ZAH 100	A90 ZB10	A80 ZB10 ZHS10	A90 RP10	A95 EG5
Hardness	IRHD	60	57	58	61	59	51	60
Specific Gravity		1.35	1.37	1.40	1.36	1.36	1.33	1.35
Tensile Strength	MPa	12.7	10.8	14.9	13.4	12.2	14.1	12.4
Elongation at Break	%	461	277	424	404	433	510	390
Trouser tear	KN/m	4.5	3.0	6.4	3.4	2.1	3.6	4.2
Crescent tear	N/2mm	55.9	42.6	53.3	37.0	48.1	46.6	38.5
Aged 70h @ 70°C								
Change in tensile strength	%	3	23	-19	-8	6	*	6
Change in E@B	%	-15	64	5	16	1	*	27
Change in hardness	IRHD	1	2	3	2	5	2	-1
Comp. Set 22hrs 70°C	%	17.5	15.0	14.2	15.2	17.8	13.7	14.1
Yerzley properties								
Static modulus (SM)	MPa	0.84	0.77	0.81	0.90	0.87	0.59	0.92
Dynamic modulus (DM)	MPa	1.14	1.13	1.19	1.23	1.16	0.92	1.25
DM/SM Ratio		1.35	1.47	1.48	1.36	1.34	1.55	1.36
Resilience	%	69	67	65	70	71	61	68
Creep	%	4.50	3.42	4.57	4.57	3.81	2.65	4.15
70h @ 100°C water Volume Change	%	2.4	4.9	14.1	14.8	21.2	1.1	3.0
Dispersion rating		E7	E7	E7	E7	E7	E6	E3
Moving Die Rheometer								
Minimum torque (ML)	lb-in	0.7	0.48	0.41	0.76	0.46	0.48	0.89
Maximum Torque (MH)	lb-in	11.9	11.5	11.8	12.6	11.5	10.3	12.1
Time to Scorch (ts2)	min	4.42	4.48	3.36	4.64	4.59	4.93	4.21
Time to 90% cure (t90)	min	10.3	10.5	7.2	10.2	9.7	9.9	9.7
Peak rate of cure (Rh)	lb-in/min	2.12	2.08	4.04	2.55	2.63	2.15	2.28

Table 60 Physical properties for ATH / synergist formulations

* Test result not possible due to slipping samples from surface bloom

Considering additives for ATH (Table 60) there are few effects apart from some notable exceptions. A90 ZHS has inconsistent tensile properties resulting in a low elongation, but the values are more normal after heat ageing. This possibly indicates problems with the ZHS/filler dispersion, which may also result in lower tear strength. A90 RP10 presented a problem with the heat ageing test, because an oily bloom came to the surface which made the samples very slippery so could not be tested for tensile properties. This may have been the result of the presence the castor oil carrier. The presence of expandable graphite has caused the dispersion values to drop as would be expected for the large particle size material. The use of ZHS and zinc borate has led to an increase in the level of water absorbed into the compound.

Formulation code		M100	M90 ZHS10	ZMH100
Hardness	IRHD	58	57	61
Specific Gravity		1.34	1.36	1.36
Tensile Strength	MPa	12.3	15.2	15.2
Elongation at Break	%	509	439	405
Trouser tear	KN/m	7.0	4.3	6.1
Crescent tear	N/2mm	61.2	41.8	59.6
Aged 70h @ 70°C				
Change in tensile strength	%	0	-6	-12
Change in E@B	%	-13	22	7
Change in hardness	IRHD	2	1	0
Compression Set 22hrs at 70C	%	22.5	13.1	9.8
Yerzley properties				
Static modulus (SM)	MPa	0.69	0.79	0.86
Dynamic modulus (DM)	MPa	1.11	1.08	1.23
DM/SM Ratio		1.62	1.37	1.42
Resilience	%	61	67	66
Creep	%	5.16	2.18	4.11
70h @ 100°C Volume Change water	%	1.7	3.8	9.8
Dispersion rating		E7	E7	E7
Moving Die Rheometer (MDR)				
Minimum torque (ML)	lb-in	0.74	0.67	0.5
Maximum Torque (MH)	lb-in	9.5	9.84	12.53
Time to Scorch (ts2)	min	1.89	1.8	2.85
Time to 90% cure (t90)	min	11.5	11.18	9.49
Peak rate of cure (Rh)	lb-in/min	2.49	2.67	2.26

Table 61 Physical properties for MH / ZHS formulations

The effect of ZHS on the physical properties in MH filled formulations (Table 61) is not exceptional, the main change being the increased water absorption for the MH coated with ZHS (ZAH100). This effect was also observed with ATH coated with ZHS, (ZMH100).

4.4.3.2 TGA results

TGA runs were carried out at a heating rate of 10°C per minute and a gas flow rate of 25 ml/minute.

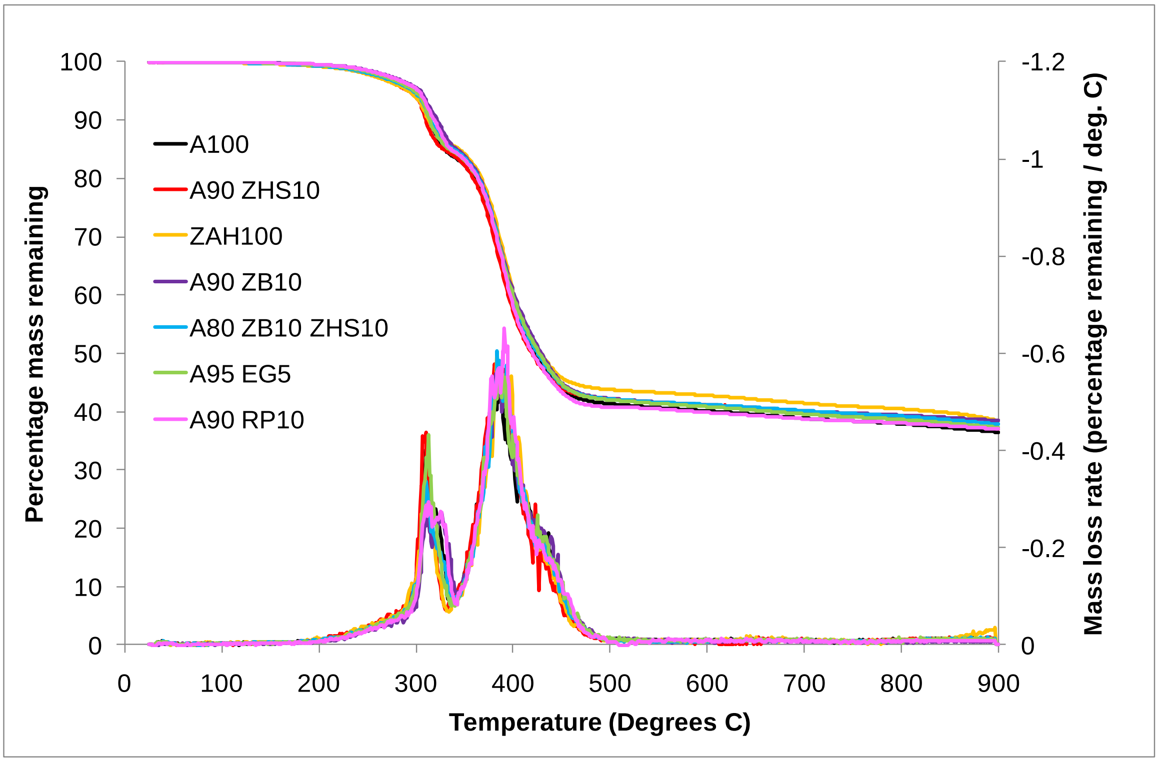


Figure 82 TGA and DTG curves for ATH / synergist formulations in nitrogen

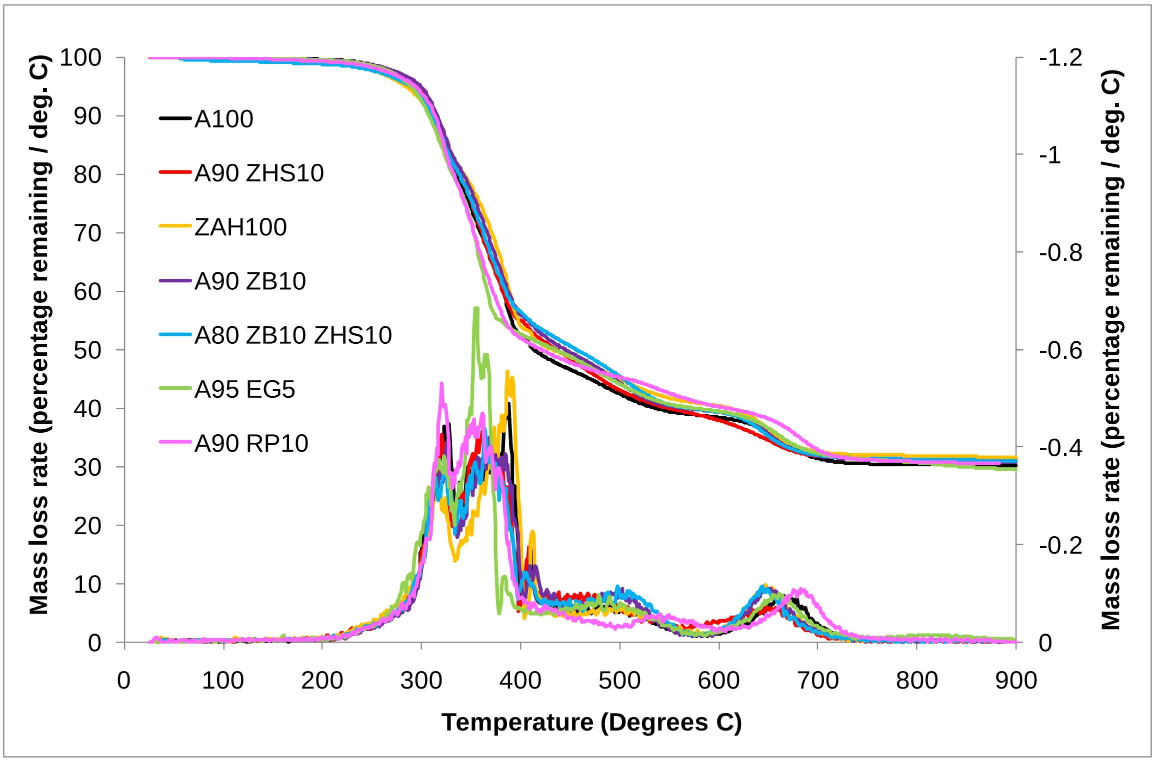


Figure 83 TGA and DTG curves for ATH / synergist formulations in air

The addition of ZHS and ZB had no discernable effect on the decomposition stages of either ATH or polyisoprene. Figure 82 plots the TGA/DTG in nitrogen and Figure 83 the

TGA/DTG in air. The mass loss rates in nitrogen and air showed little effect with the addition of both zinc borate and zinc hydroxystannate, indicating that these additives have little influence chemically on the thermal decomposition of the polymer or filler.

The use of red phosphorus and expandable graphite (EG) also showed no significant effect in nitrogen. In air EG tended to increase the rate of mass loss between around 350 and 380°C, which causes the rubber compound to swell rapidly when upon heating. This does not cause mass loss of the polymer directly, but in an expanded state the 10mg sample within the TGA will have a much larger surface area, so will be exposed to oxygen at a higher rate. This will lead to a more rapid rate of oxidation and therefore faster mass loss. Red phosphorus caused some minor effects upon the decomposition of polyisoprene in air. Since phosphorus is used in other (usually oxygen containing) polymers to promote char, it was of interest to look for this effect in polyisoprene. There are some small clues to chemical modification by the red phosphorus; notably that in air the mass loss commences more rapidly at around 350°C, and that the residual mass remains higher between 500 and 600°C. Also it can be seen that the carbon black loss, which typically peaks at around 650°C for the other formulations, peaks somewhat later for A90 RP10. This increased stability points toward an increased char yield which may confer some benefit during burning to reduce fuel availability.

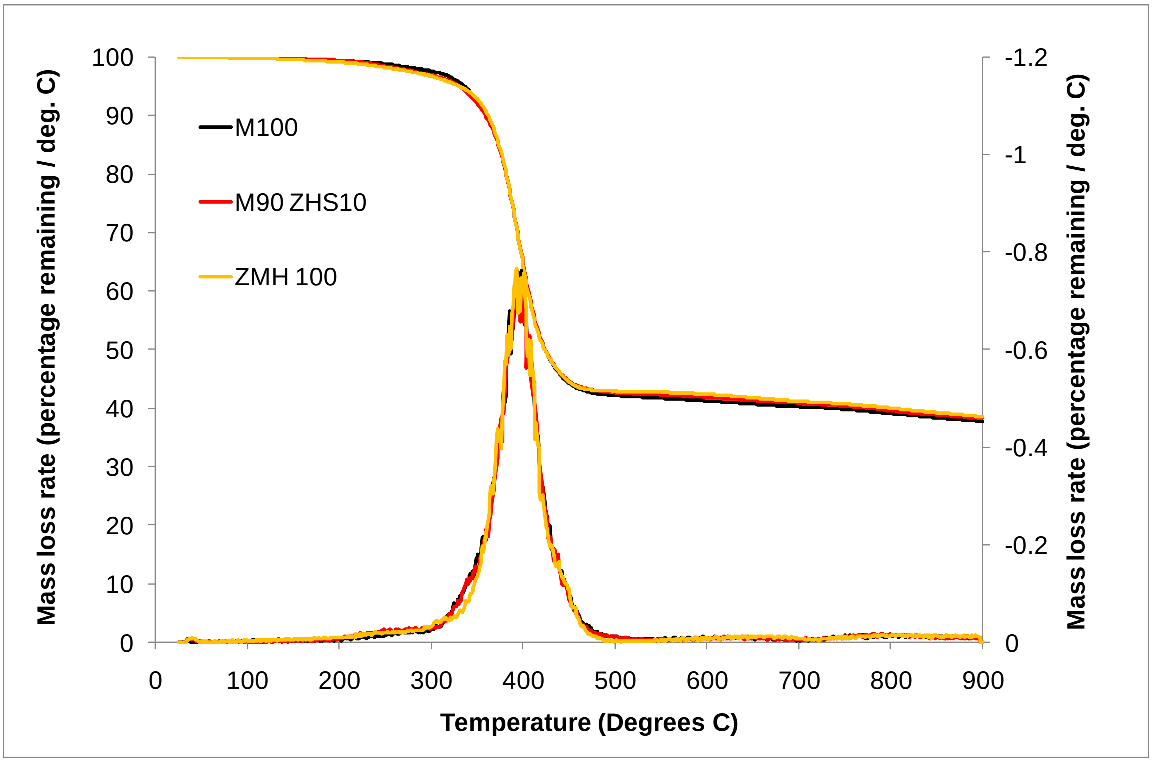


Figure 84 TGA and DTG curves for MH / ZHS formulations in nitrogen

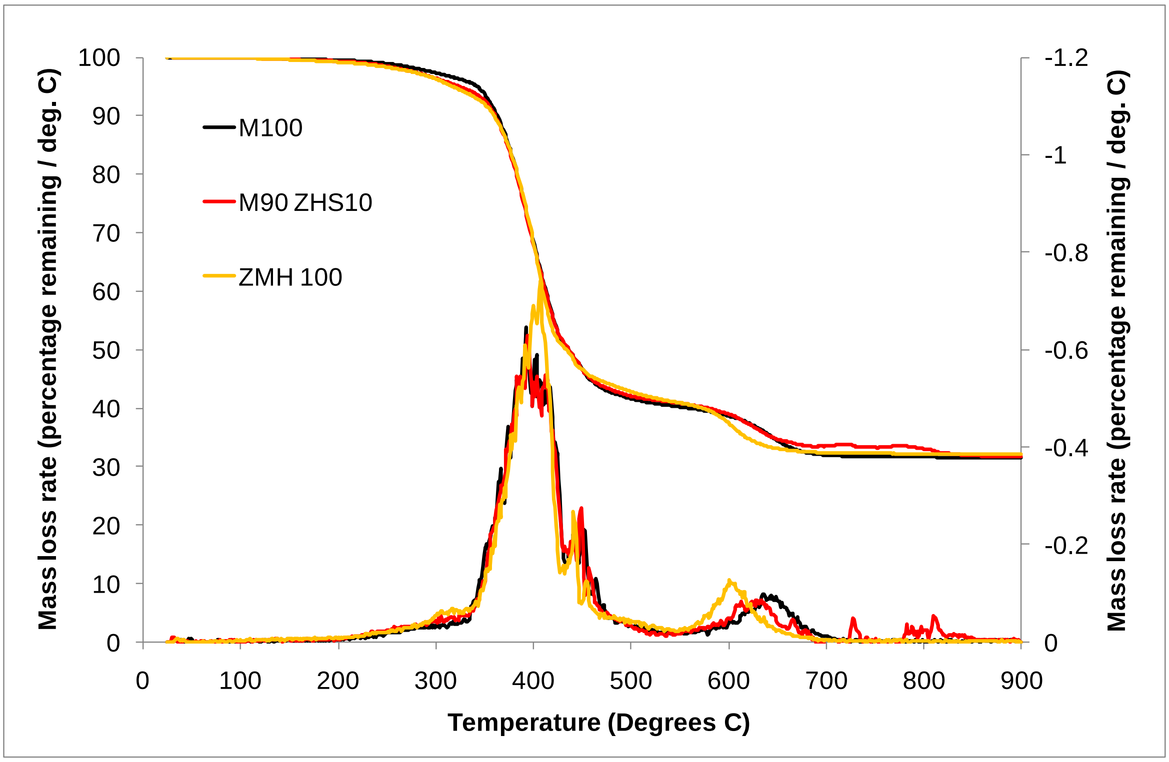


Figure 85 TGA and DTG curves for MH / ZHS formulations in air

The use of ZHS in magnesium hydroxide had little effect on the mass loss of rubber compounds in nitrogen (Figure 84). In air (Figure 85) there was a small increase in the onset of mass loss at around 300°C.

4.4.3.3 Burning behaviour

Small scale flammability tests

Formulation code	LOI %	Avg. burning. rate mm/min	Self extinguishing	ISO 1210 method A Rating
A100	24.7	4	Y	FH-2-11 mm
A90 ZHS10	24.5	6	N	FH-3 6 mm/min
ZAH100	24.5	6	N	FH-3 6 mm/min
A90 ZB10	25.1	8	N	FH-3 8 mm/min
A80 ZB10 ZHS10	24.2	10	N	FH-3 10 mm/min
A90 RP10	24.9	3	Y	FH-2-6mm
A95 EG5	28.2	4	Y	FH-2-10mm
M100	27.1	4	Y	FH-2-24 mm
M90 ZHS10	28.7	4	Y	FH-2-6mm
ZMH100	28	0	Y	FH-1

Table 62 LOI and horizontal burning rate values for ATH, MH and synergists

The use of zinc hydroxystannate in A90 ZHS10 and ZAH100 led to a small drop in LOI (Table 62), indicating that ZHS imparted no benefit as a partial replacement of ATH. In A90 ZB10 the use of zinc borate gave a modest improvement in LOI compared to A100, but a combination of ZHS and ZB with ATH in A80 ZB10 ZHS10 gave a lower LOI value than A100 or A90 ZB10. In A90 RP10, the effect of red phosphorus was found to give no benefit to LOI. A96 EG5, with 5 pphr of expandable graphite gave a useful increase in LOI value to 28%, an improvement of 3.3% over A100.

The use of magnesium hydroxide resulted in higher LOI values in comparison with equivalent ATH formulations. Interestingly in magnesium hydroxide, the use of ZHS whether as an additive in M90 ZHS10 or as a coating in ZMH100 gave an increase in LOI values measured. M90 ZHS10 gave an LOI of 28.7%, which was the highest value obtained overall.

The use of zinc hydroxystannate in A90 ZHS10 and ZAH100 led to an FH3 rating, with no self extinguishment, but with a low rate of horizontal burning. ZHS therefore conferred no benefit. In A90 ZB10 the use of zinc borate also and a combination of ZHS and ZB with ATH in A80 ZB10 ZHS10 conferred no benefit, with none of these material self-extinguishing. It appears that the reduction of the ATH loading simply increases flammability with these formulations. In both A90 RP10 and A95 EG5 the addition of either red phosphorus or expandable graphite was found to give equal performance to A100, with FH2 self-extinguishment noted.

The use of ZHS with MH improved the self-extinguishing properties with the highest rating for ZMH100.

Cone calorimetry (carried out at 50 kW m^{-2} radiant heat)

Property	Units	A100	A90 ZHS10	ZAH 100	A90 ZB10	A80 ZB10 ZHS10	A90 RP10	A95 EG5
Time to ignition	secs	39	37	33	37	35	36	40
Flameout	secs	1136	1120	1166	1029	1196	997	1037
Total Heat Evolved	MJ/m^2	124	120	123	120	132	111	105
Total smoke released	m^2/m^2	4004	4327	4649	4728	5544	5318	3579
HRR average	KW/m^2	114	111	109	122	114	116	106
HRR peak	KW/m^2	237	213	229	216	221	246	231
HRR peak at time	secs	86	150	80	85	83	290	323
Mass remaining	%	46	49	45	49	44	43	49
MARHE	KW/m^2	154	147	142	148	153	162	142

Table 63 Summary of mean cone calorimeter values for ATH / synergist formulations

Property	Units	M100	M90 ZHS10	ZMH100
Time to ignition	secs	39	36	39
Flameout	secs	1131	1097	1035
Total Heat Evolved	MJ/m^2	125	142	122
Total smoke released	m^2/m^2	5216	5645	7112
HRR average	KW/m^2	115	134	122
HRR peak	KW/m^2	204	279	286
HRR peak at time	secs	82	453	410
Mass remaining	%	47	48	44
MARHE	KW/m^2	144	162	162

Table 64 Summary of mean cone calorimeter values for MH / ZHS formulations

In Table 63 the most desirable value determined for each property is highlighted in bold for ATH with synergists. Formulation A95 EG5 has good fire retarding performance, with the longest time to ignition, lowest total heat evolved, the lowest MARHE value and the lowest total smoke emitted. The use of zinc hydroxystannate gave a minor reduction in peak and average heat release but an increase in smoke produced.

Table 64 compares magnesium hydroxide in M100 with zinc hydroxystannate modified versions. The use of ZHS has not conferred any improvement in burning behaviour.

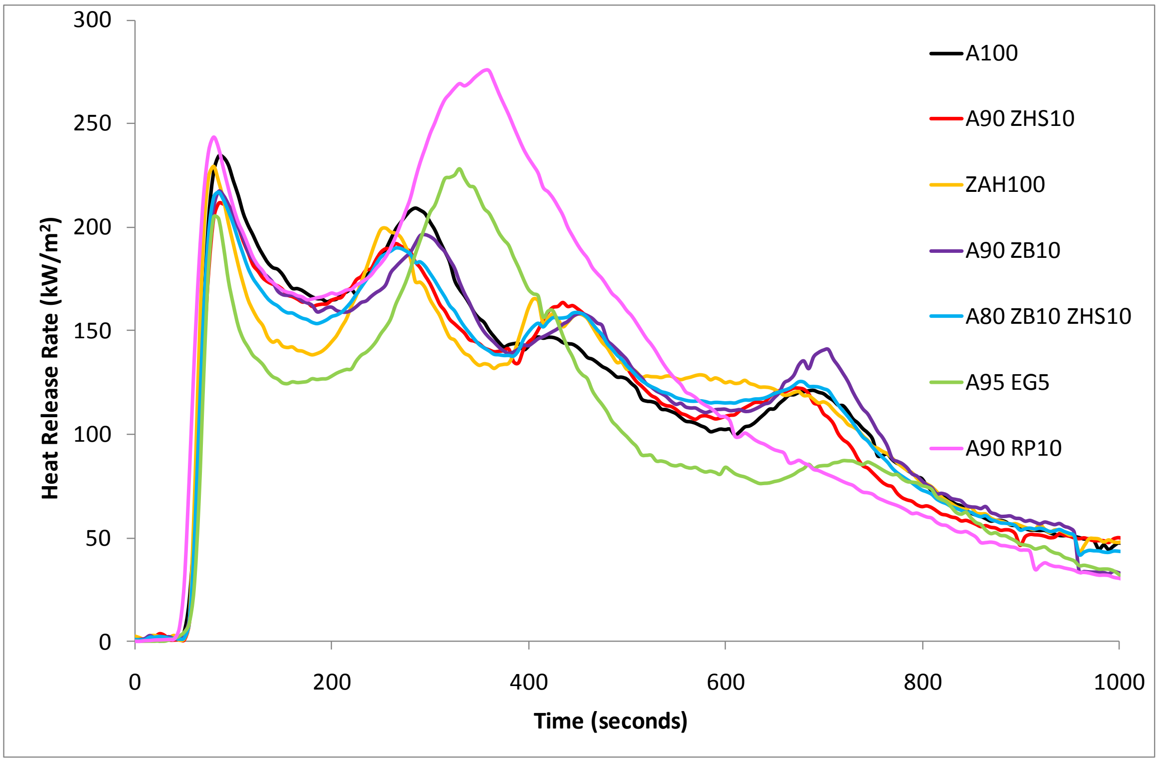


Figure 86 Heat release rate from cone for ATH / synergist formulations

In Figure 86, A100 is plotted in black as a benchmark to evaluate all modifications. All have equal total pphr to make a fair comparison. Considering the use of zinc hydroxystannate, A90 ZHS10 was comparable to A100. The coated version ZAH100 however showed a good reduction in heat release between the first and second peaks which remained similar to A100. The use of zinc borate gave a very minor reduction in peak HRR. Using ZHS and ZB together in A80 ZB10 ZHS10 also gave a modest reduction in peak HRR. The use of expandable graphite gave a useful reduction in the initial peak HRR and a very significant reduction of HRR between the two peaks between 100 and 200 seconds, but gave a higher second peak value than A100. The use of red phosphorus led to similar burning to A100 initially, but with a significantly higher second peak.

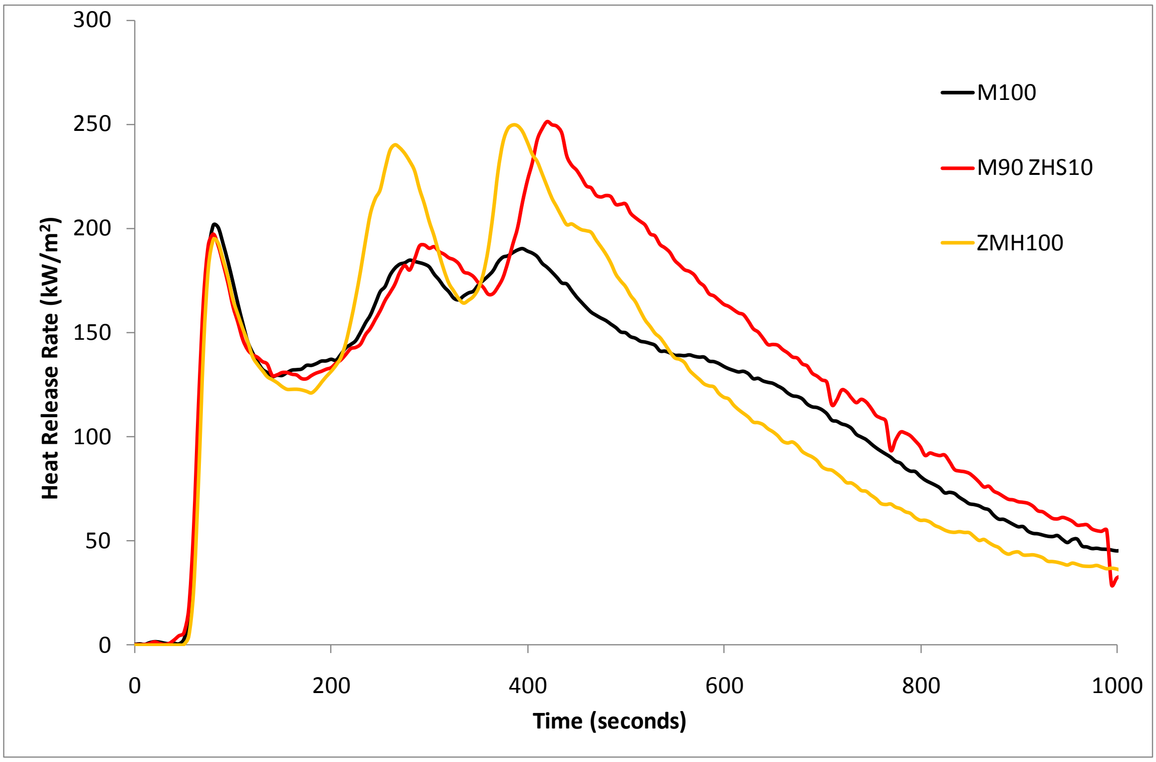


Figure 87 Heat release rate from cone for MH / ZHS formulations

In Figure 87 using 100 pphr MH is used as a benchmark, the use of ZHS in both formulations M90 ZHS10 and ZMH100 lead to higher values of HRR from the second HRR peak onwards. From observation of test this can be related to higher rates of intumescence developed from the use of ZHS. This led to a less stable char barrier, which broke down more readily under the sustained burning within the cone to increase the rate of polymer decomposition deeper in the sample depth.

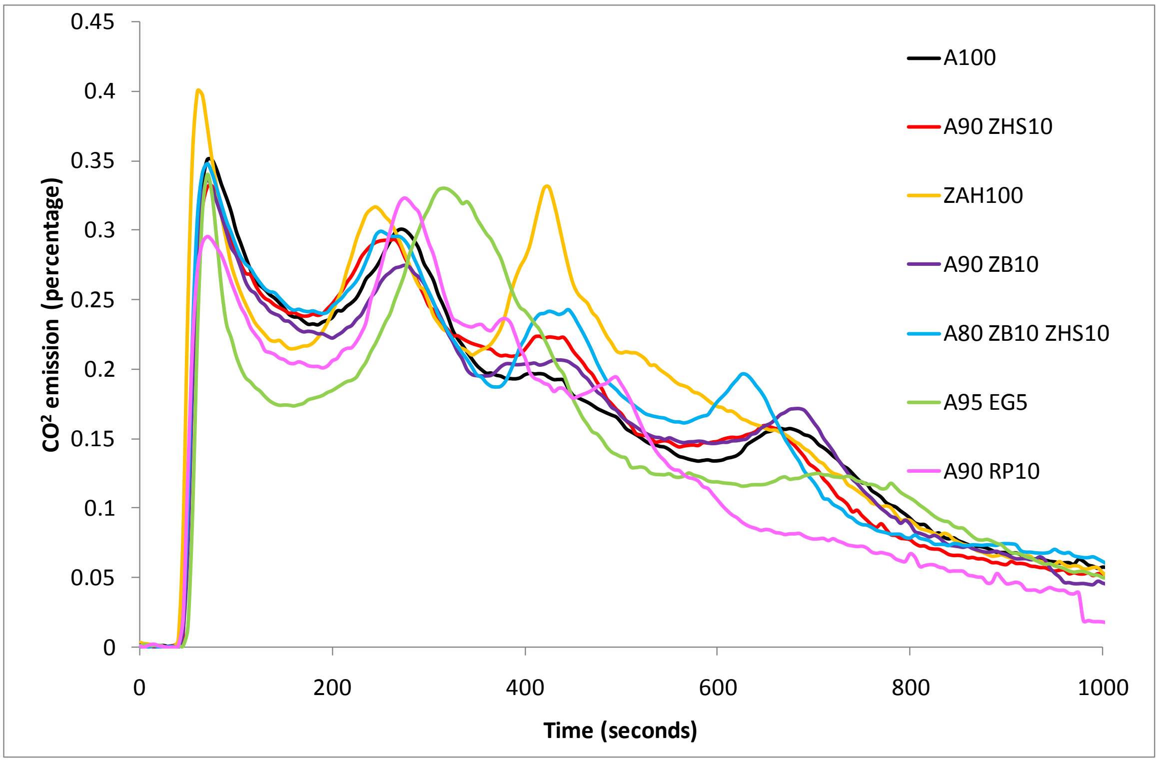


Figure 88 CO_2 mean % emission from cone for ATH / synergist formulations

CO_2 emissions for ATH formulations (Figure 88) are reduced with the addition of 5pphr EG, but are otherwise broadly similar for the first 300 seconds.

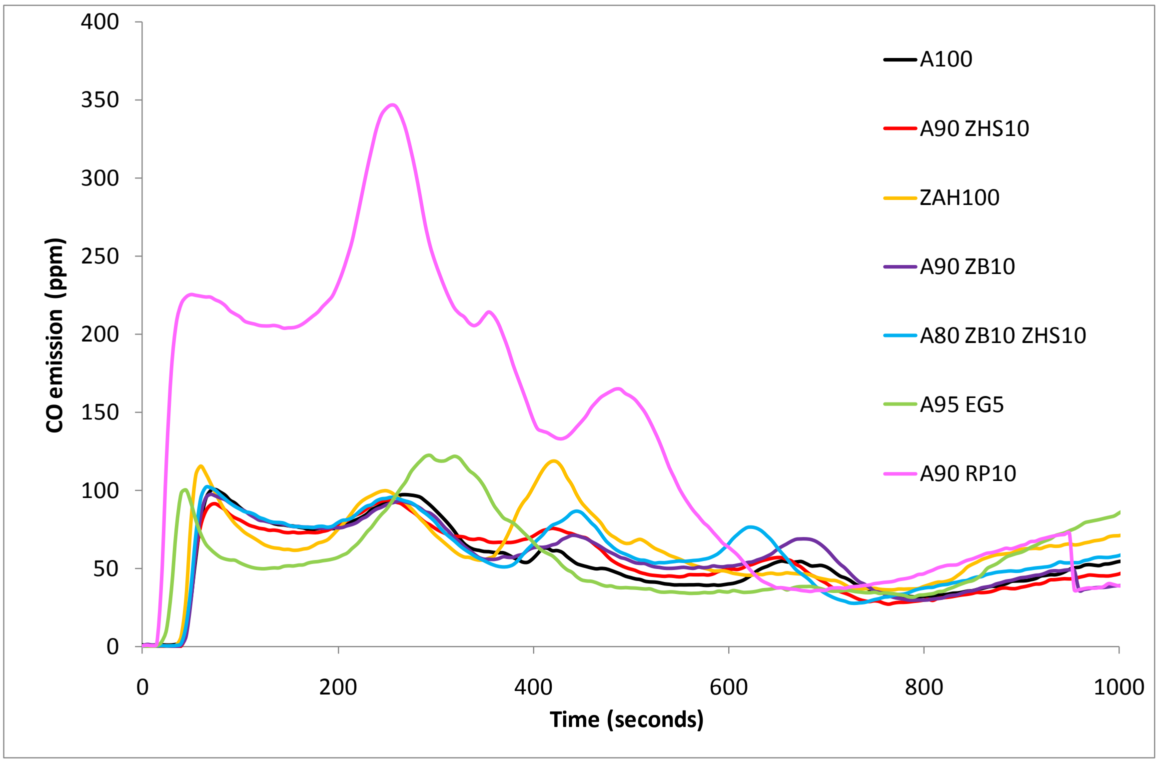


Figure 89 mean CO ppm from cone for ATH / synergist formulations

CO production (Figure 89) is generally produced in line with the values seen in CO_2 and HRR, indicating no change in the decomposition processes. A clear exception to this is A90 RP10, where it appears that the addition of red phosphorus has promoted the production of CO. This could be attributed to gas phase flame inhibition by the phosphoric acid generated weak-radical reactions. A95 EG5 gives a good initial reduction in CO, followed by higher levels than A100 at the second peak of HRR. The use of ZHS and zinc borate had relatively little effect.

CO_2 and CO emissions (not plotted) for ZHS modified MH formulations closely follow the pattern of heat release, indicating that the use of ZHS has no effect in the gas phase.

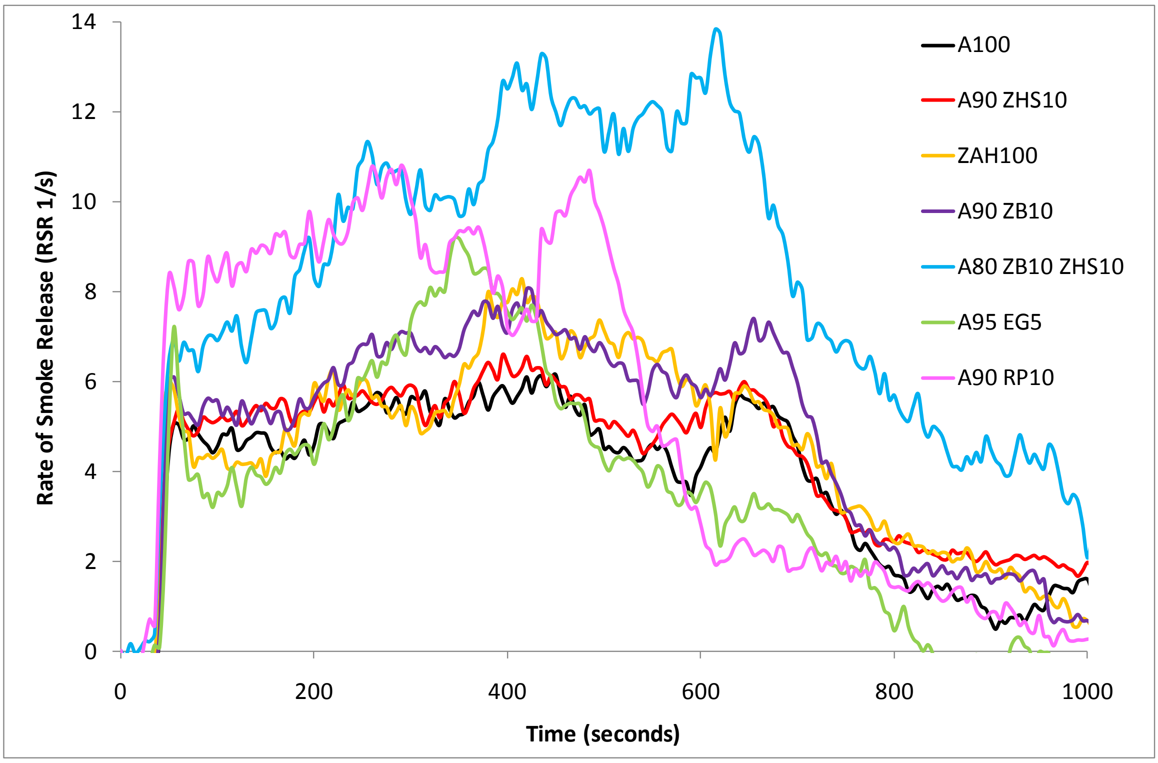


Figure 90 Mean rate of smoke release from cone for ATH / synergist formulations

In Figure 90, no modifications gave improved smoke values, and are generally higher. The only exception to this is A95 EG5, for which the total smoke yield is the lowest recorded in Table 63. The use of red phosphorus led to a much higher rate of smoke emission, as does A80 ZB10 ZHS10. Zinc borate is generally promoted for use a smoke suppressant, but in this case was found not to give any benefit.

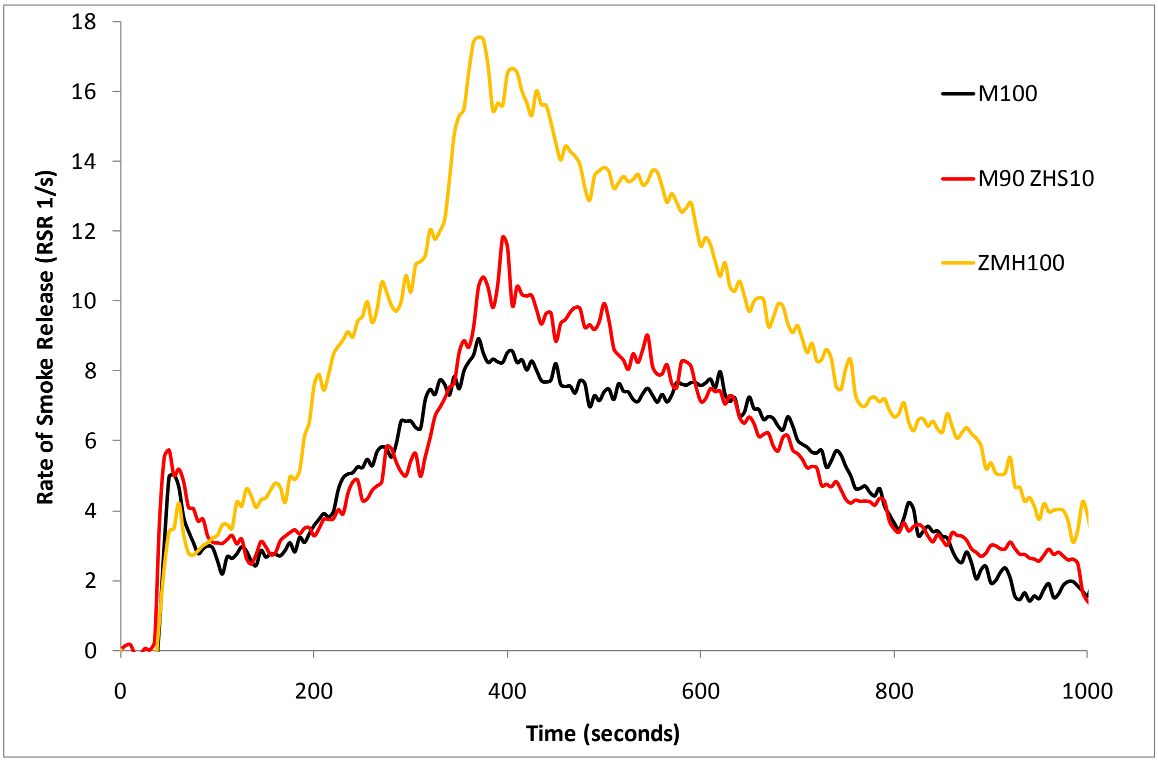


Figure 91 Mean rate of smoke release from cone for MH / ZHS formulations

Figure 91 shows that the use of zinc hydroxystannate gave similar or higher smoke yields, and shows that magnesium hydroxide is overall less effective than aluminium hydroxide at smoke suppression. In the initial burning stages (up to 3 minutes), the reduced burning rate from MH did produce lower smoke release than ATH formulations.

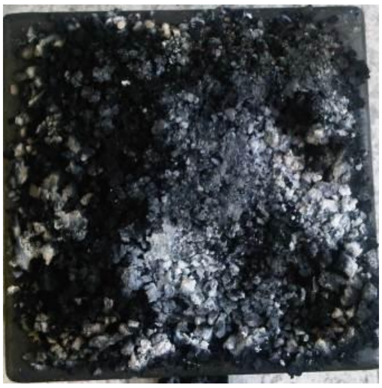
Observations of cone samples

A100 shows evidence of a residue, but it is weak and friable

Figure 92 A100 residue

A90 ZHS10 has a very loose residue with little agglomeration

Figure 93 A90 ZHS10 residue



ZAH100 has a fine powdery residue, much weaker than A100

Figure 94 ZAH100 residue

A90 ZB10 has a residue similar to A100, agglomerated in places but very friable

Figure 95 A90 ZB10 residue

A80 ZB10 ZHS10 has a residue similar to A100, agglomerated in places but very friable

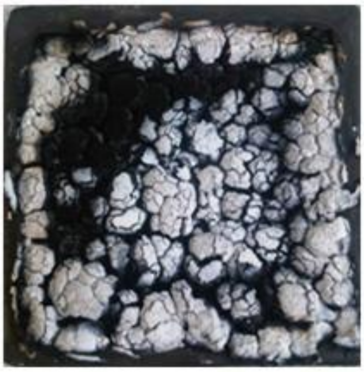
Figure 96 A80 ZB10 ZHS10 residue

A95 EG5 left an expanded and powdery residue around 25mm in height

Figure 97 A95 EG5 residue

The use of red phosphorus led to a bound residue structure within the remaining residue

Figure 98 A90 RP10 residue



M100 has a noticeably stronger and complete residue than A100, although not continuous.

Figure 99 M100 residue

Compared to M100, the use of ZHS had reduced the residue strength, becoming more friable

Figure 100 M90 ZHS10

The use of ZHS coated onto MH in ZAH100 give a more powdery residue than M100

Figure 101 ZAH100 residue

4.4.4 Discussion

Zinc hydroxystannate

Zinc hydroxystannate had no effect on the micro-scale thermal decomposition of MH/ATH or polyisoprene as measured by TGA. In small scale flammability tests the use of ZHS in ATH made little difference to the LOI, and reduced the ability to self extinguish in the horizontal burn test. In the cone calorimeter the peak heat release was reduced by around 10% with an addition of ZHS, but increased smoke yield. With MH the results are more apparent, with a good increase in LOI and horizontal burning, but worse behaviour in the cone.

The results with zinc hydroxystannate are disappointing, since the product is promoted to work with ATH to reduce burning behaviour in polymers, including natural rubber, as reviewed in section 1.10.12. ITRI reported an improvement in LOI by 1.8% and a reduction in smoke yield when added at 2.5% with 50% ATH [138]. The formulation used by ITRI based on natural rubber is similar in many respects to the polyisoprene formulation A100 and A90 ZHS 10, except that the use of ZHS was additive and did not remove ATH. A second difference is the level of additives used with 50% ATH equal to 161pphr and 2.5% ZHS is equal to 8pphr.

In the work by Ismawi [62] a natural rubber compound with 100pphr ATH gave an LOI of 23.8%, comparable to the 24.7% for A100. ZHS was substituted for ATH with a total pphr of 140, and only gave a marginal improvement in LOI, from 26.2 for all ATH to 26.6% LOI for 10pphr ZHS, 130pphr ATH. When the ZHS was increased to 15 pphr however, the LOI dropped slightly, indicating that the optimum value had been exceeded. It may be that ZHS may have worked in A100 but at a different pphr, possibly lower. In the formulations based upon magnesium hydroxide, the use of ZHS improved the measured LOI and horizontal burning appreciably. No literature could be found for the use of this combination in polyisoprene, but the use of ATH and MH coated with ZHS is considered by Cusack [174] in other polymers such as EVA, and is reported to improve the efficiency of any synergism to yield lower heat release in the cone calorimeter. In this study, the use of ZHS, whether additive or coated onto ATH or MH, did not significantly improve the burning performance in the cone calorimeter. In ATH, a very small improvement was noted in peak heat release, and in MH heat release actually increased significantly. This can be attributed to increased intumescence which caused the sample to crackle and spit during burning. It seems that the presence of ZHS caused production of increased volatile species upon heating, or that it may have initially prevented the release of volatiles which then escaped more rapidly later on. To consider what is happening with ZHS it is necessary to consider the possible mechanism of fire retardance. In halogenated systems, it is asserted that ZHS can increase the efficiency of the halogen radical traps in the gas phase rather like antimony III oxide and in addition works in the condensed phase to increase char yield [138]. In non-halogenated systems there are less firm conclusions about the mechanism of improvement. It is generally asserted that ZHS promotes increased char in non-halogenated polymers, and some evidence is presented for AEM (ethylene acrylic elastomer) compounds of an increase of char residue at 600°C from 1.3% with ATH only to 4% with 2.5% ZHS incorporated[139]. Assuming that the thermal decomposition of ATH is equal then this residue has to come from the polymer. AEM contains oxygen and has some char potential, so it is feasible that ZHS has improved the rate of conversion to some thermally resistant carbon structure. Polyisoprene however has no char forming tendency so it seems less likely that ZHS could promote charring. In the TGA data there is no change in the thermal decomposition behaviour of the compounds with the addition of ZHS, so any benefit such as noted with ATH in the cone must be related to physical effects. Once ATH decomposes from around 200°C onwards to become Al_2O_3, this residue has the potential to form a barrier to absorb heat and insulate the underlying polymer from decomposition, but from cone calorimetry this residue does not agglomerate into any significant structure. If ZHS could bind the Al_2O_3 together then a benefit would be conferred in radiant heat forced burning tests like the cone, but may not have much benefit on a thin sample such as for LOI or ISO 1210/UL94 type tests. Examination of char residues after cone calorimetry showed that the use of ZHS tended to equally reduce agglomeration of the aluminium or magnesium oxide residues. It would have been useful to evaluate ZHS at different loading levels, since 10pphr may have been an unsuitable level. It seemed to initiate excessive expansion when used with magnesium hydroxide, but not with aluminium hydroxide.

Zinc borate

Zinc borate was evaluated in conjunction with ATH in A90 ZB10 and with ATH and ZHS in A80 ZB10 ZHS10. Zinc borate is promoted for use as a smoke and afterglow suppressant in ATH filled compounds such as EVA. It is said to provide this benefit by acting as a sintering aid to bind the metal hydroxide filler, which can act as an insulating layer to the remaining polymer [141]. In this study zinc borate had little effect on small scale flammability, and whilst yielded a small reduction in peak heat release rate in the cone, caused an increase in smoke yield. When used with ZHS the smoke increase was 38%, so was either antagonistic in effect or merely ineffective compared to ATH.

Expandable graphite

Expandable graphite (EG) was added at 5pphr with ATH in A95 EG5 and achieved a successful enhancement in fire retardance compared to 100pphr ATH. The LOI value was increased by 3.5% to exceed the performance of 100pphr MH. In the cone calorimeter A95 EG5 showed the longest time to ignition at 40 seconds, an 11% reduction in smoke yield and the lowest average HRR. EG is reported to work in the condensed phase by expanding the surface into a high volume fluffy residue able to provide a barrier to heat and gas transfer. In this case the expansion of EG caused the heat release to drop rapidly (Figure 88). A second peak in heat release arises when the cone heat penetrates through the sample causing a more significant overall expansion of the sample as recorded in Figure 102.

Figure 102 Cone calorimeter sample showing the expansion of A95 EG5

There are some problems to be noted in the testing of intumescent samples, as outlined by Schartel and Hull [100]. The sample expands into the cone area so increasing the heat flux onto some the expanded part of the sample. The second heat release rate peak may resultantly be artificially higher due to the increasing imposed heat flux. A solution proposed is to contain the intumescence using a metal grid, but this would be much less realistic of a fire scenario so is considered imperfect. Another option is to have the sample mounted further away from the cone heater, or to drive the sample holder down to provide an equal cone to sample height. None of these options are ideal. In a real fire the radiant source is further away, and planar, not conical, so some artefacts from cone calorimetry are inevitable. During the high expansion the smoke output is rather high, but the overall smoke yield is lower for A95 EG5.

Red phosphorus

In A90 RP10 red phosphorus (RP) bound 50% in oil was evaluated, so was present at 5pphr. This material was added somewhat speculatively with polyisoprene and ATH to see if any fire retardant synergism would be discovered. Phosphorus and phosphorus containing compounds are typically used as fire retardants in char producing polymers which may be characterised as containing halogens or oxygen. Polyisoprene incurs very little char yield (less than 1% normally), so may not have been expected to provide much fire retardance in the condensed phase. It is possible however that phosphorus can function in the gas phase if it is converted into phosphoric acid which can act as a free radical trap. Some differences in the thermal decomposition in air were measured in TGA, with some evidence of charring behaviour with a higher residue between 500 and 600°C and an increase to the thermal stability of the carbon black. This potential increase in char did not improve burning properties however, with similar LOI and horizontal burning to A100, and worse behaviour in the cone calorimeter. For these studies A90 RP10 had the highest peak heat release rate with a large second peak value. Average HRR was around the same as for A100, but the burning was over a shorter period, resulting in a higher MARHE value. The remaining mass was the lowest on test indicating no substantial char generation. Whilst CO_2 generation was similar to A100, CO emission was increased by around 2.5X (Figure 89), indicating two possibilities. The first is that phosphorus has converted some polymer to a carbon char structure, which then smoulders in the condensed phase so generating CO. The possibility is that the phosphorus has generated phosphoric acid, which working in the gas phase is acting as a weak radical so reducing combustion efficiency and preventing the full combustion of CO generated in the flame. Smoke generation was also very high for A90 RP10, often an indication of inefficient combustion. Higher smoke levels are typically seen in halogenated polymers under forced burning conditions, chloroprene being an example for rubber compounds. Peacock [94] found that chloroprene being used in seals for rail-cars generated non-compliant high levels of smoke in the NBS smoke chamber [42], for instance. Considering the cone sample residue, the red phosphorus had some effect creating some grey/white bound structure with the aluminium oxide. Castrovinci [125] considered antagonism between ATH and APP in SBR rubber compound, and concluded that the basic gas from ATH reduces the acidity of acidic gases from APP decomposition, and that together aluminium phosphate is generated on the surface which is a less effective surface barrier. These effects are thought to reduce the efficiency of APP for fire retardance. Possibly some similar activity is taking place when using RP with ATH.

4.4.5 Summary

Restating the objectives of this section:

1 Evaluate the effect of zinc hydroxystannate (ZHS) as a proposed synergist in ATH and MH, both as an additive and a coating onto the filler

2 Evaluate zinc borate (ZB) with ATH

3 Investigate the effect of expandable graphite (EG) when used in conjunction with ATH

4 Consider the effect of red phosphorus (RP) when used in conjunction with ATH

These objectives were met, with the most useful enhancement to fire retardancy in ATH contributed by the addition of expandable graphite.

In an ATH or MH filled compound, zinc hydroxystannate had no chemical effect on the thermal decomposition of either filler of polymer. The physical properties were mostly unaffected by the use of ZHS. Limited benefit was gained in burning behaviour by using ZHS, whether as an additive or as a coating, contrary to some reported benefits from the use of ZHS. In an MH filled compound, whilst ZHS improved the LOI value, it resulted in a significant increase in peak heat release on the cone calorimeter from an increased level of sample expansion, and lower residue strength.

The use of zinc borate with ATH in a polyisoprene rubber compound also did not give any benefit to burning behaviour and gave an increased smoke yield on the cone calorimeter, somewhat contrary to literature reports.

In an ATH filled rubber compound the addition of 5 pphr expandable graphite (EG) generated a high volume fluffy char when heated to decomposition. This provided a barrier to burning, gave a useful increase in LOI, and improved many of the burning properties on the cone calorimeter. This included a longer time to ignition, a reduction in smoke yield and a lower average heat release rate.

Red phosphorus created an increased char yield in IR during microscale thermal decomposition which improved LOI, but increased heat release, smoke and CO yield in the cone calorimeter, suggesting antagonism with the ATH filler.

4.5 Optimisation of Hydrated Fillers

4.5.1.1 Introduction

Following positive results from an equal blend of ATH and MH, reported in section 4.3, further mixtures were investigated. The following objectives are stated thus:

1 Repeat the evaluation of ATH, MH and an equal blend of ATH and MH to confirm if the positive effects were reproducible

2 Evaluate unequal blends of ATH and MH to look for an optimal level of fire retardancy and physical properties

4.5.2 Experimental section

4.5.2.1 Materials

Table 65 contain formulations using blends of ATH and MH, using B20 compound (Table 38), with the total pphr remaining equal.

Ingredient (values in pphr)	A100	A75 M25	A50 M50	A25 M75	M100
B20 base formulation	136.6	136.6	136.6	136.6	136.6
aluminium hydroxide	100	75	50	25	
Magnesium hydroxide		25	50	75	100
Total	236.6	236.6	236.6	236.6	236.6

Table 65 Polyisoprene formulations with blends of ATH and MH

4.5.3 Results

4.5.3.1 Physical properties

Formulation code		A100	A75 M25	A50 M50	A25 M75	M100
Hardness	IRHD	57	54	53	54	54
Specific Gravity		1.35	1.34	1.34	1.34	1.33
Tensile Strength	MPa	11.7	11.6	10.9	13.3	15.7
Elongation at Break	%	478	572	453	521	559
Trouser tear	kN/m	7.11	6.62	9.35	10.47	7.67
Crescent tear	N/2mm	102	101	111	112	108
Aged 70h @ 70°C						
Change in tensile strength	%	15	16	29	3	-15
Change in E@B	%	2	-10	19	2	-5
Yerzley properties						
Static modulus (SM)	MPa	0.80	0.68	0.62	0.67	0.67
Dynamic modulus (DM)	MPa	1.10	0.97	0.98	1.08	1.05
DM/SM Ratio		1.37	1.42	1.57	1.61	1.58
Resilience	%	68.0	65.2	61.2	61.8	56.0
Creep	%	3.1	4.4	4.0	5.7	5.1
Compression Set 22hrs at 70°C	%	14.6	8.3	8.6	12.5	12.7
Dispersion index	E rating	E6	E7	E7	E7	E7
Moving Die Rheometer (MDR)						
Minimum torque (ML)	lb-in	0.52	0.43	0.46	0.45	0.43
Maximum Torque (MH)	lb-in	11.58	10.65	9.24	9.45	9.26
Time to Scorch (ts2)	min	4.64	3.27	2.94	2.27	1.93
Time to 90% cure (t90)	min	10.4	10.7	12.3	11.9	12.2
Peak rate of cure (Rh)	lb-in/min	2.13	1.62	1.33	2.01	2.71

Table 66 Physical properties for ATH / MH blend formulations

Considering the physical properties, Table 66 shows little variation between fillers, but MH leads to slightly improved tensile strength and elongation at break indicating, suggesting some improved filler/polymer compatibility. For industrial use the tensile values are all somewhat inferior, so would require improvement for successful application. This may be improved by the use of improved mixing techniques, smaller particle size filler and/or surface coatings to improve polymer compatibility.

Filler ratio affects the dynamic properties measured, with MH increasing phase angle and reducing resilience. Physical creep over 60 minutes also increased with MH, but compression set is lowest for the blended fillers. The MDR test assesses processability, with time to onset of cure (scorch) considerably lower for higher loadings of magnesium hydroxide. It is not clear how the MH is reducing scorch time, whether chemical or physical. Since the MDR is less than 4mm thick, any change in thermal conductivity will be unlikely significantly change scorch time, so it is likely that MH is chemically increasing the time to onset of cross-linking.

4.5.3.2 TGA results

TGA runs were carried out at a heating rate of 10°C per minute and a gas flow rate of 25 ml/minute.

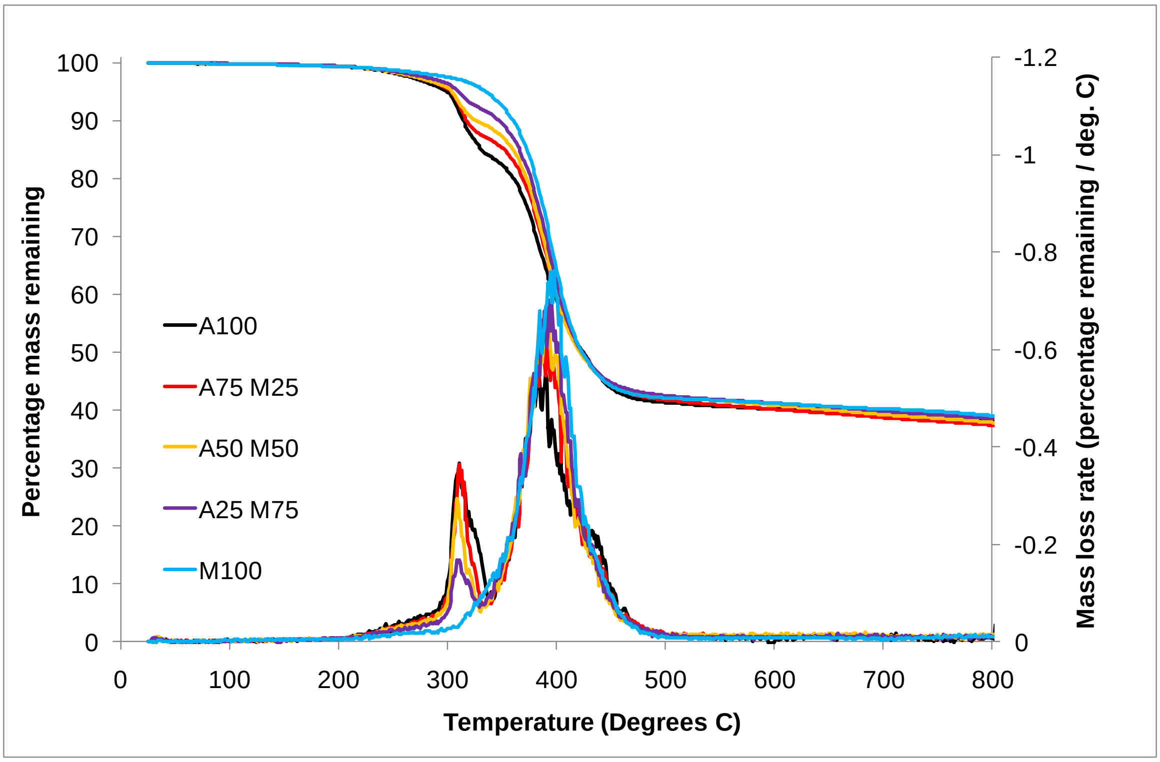


Figure 103 TGA and DTG curves for ATH / MH blend formulations in nitrogen

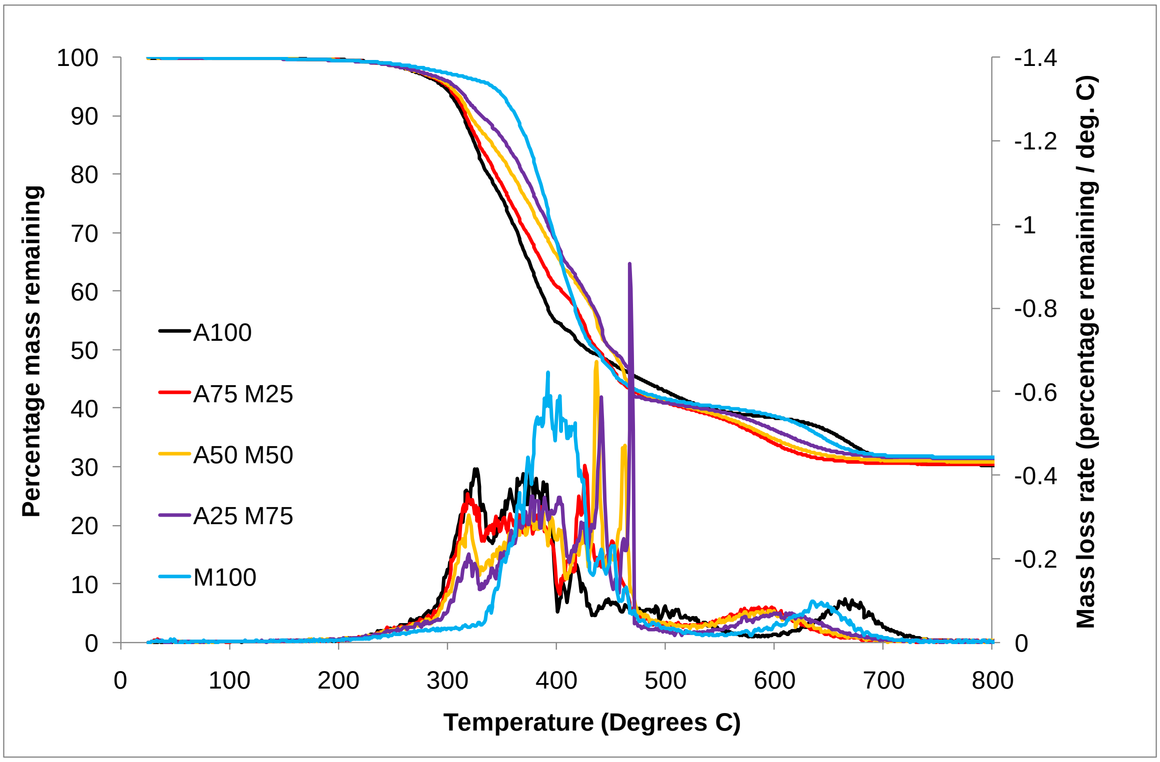


Figure 104 TGA and DTG curves for ATH / MH blend formulations in air

Figure 103 shows that the blend of ATH and MH gives two peaks of mass loss, the first for ATH at around 310°C, and the second peak combines the decomposition of MH and polyisoprene. In air (Figure 104) the decomposition stages are less distinct; with the peak mass loss rate of ATH around 10°C higher than in N_2 (Table 67) and the peak mass loss rate for the polymer and MH at a lower temperature than in N_2. The ratio of ATH to MH also affects the mass loss temperature for the carbon black, with the lowest stability of the carbon black for blends of ATH and MH. To compare the magnesium hydroxide mass loss to the polymer, values of mass loss for B20 (with no mineral filler) are included. This shows that the fillers have little direct effect on the polymer decomposition in air or nitrogen, but the filler residues reported as being Al_2O_3 and MgO (section 1.10.11) appear to have some role in affecting the oxidation of the carbon black. Some large DTG peaks are noted for the blends A50 M50 and A25 M75 at around 440 and 470°C which are not apparent for the other formulations, which may indicate the loss of some char structures developed.

Maximum DTG values (°C)	B20	A100	A75 M25	A50 M50	A25 M75	M100
ATH in nitrogen	-	311	311	309	311	-
MH/IR in nitrogen	391	383	388	389	389	395
ATH in air		325	319	320	319	-
MH/IR in air	376	376	385	377	377	392
Carbon black in air	602	662	579	586	601	633

Table 67 Peak DTG values for ATH / MH blend formulations

4.5.3.3 Burning behaviour

Small scale flammability tests

Formulation code	LOI %	Avg. burning. rate mm/min	Self extinguishing	ISO 1210 method A Rating
A100	24.5	6	Y	FH-2-49 mm
A75 M25	26.1	4	Y	FH-2-25 mm
A50 M50	26.7	6	Y	FH-2-43 mm
A25 M75	27.2	0	Y	FH-1
M100	25.8	7	Y	FH-2-42 mm

Table 68 LOI and horizontal burning rates values for ATH / MH blend formulations

The use of blends of magnesium hydroxide and aluminium hydroxide resulted in higher LOI values than ATH or MH alone showing a synergistic benefit, with the best performance for both tests from 25 pphr ATH and 75 pphr MH. This benefit is also seen in the horizontal burning test with classification FH-1 determined for A25 M75 only. The other formulations achieved equal ratings, and self extinguished.

Cone calorimetry

Property	Units	A100	A75 M25	A50 M50	A25 M75	M100
Time to ignition	secs	36	34	34	33	36
Flameout	secs	948	1088	1081	1037	1040
Total Heat Evolved	MJ m^{-2}	123	125	123	134	133
Total smoke released	m^2 m^{-2}	2700	2361	3045	3197	2800
HRR average	kW m^{-2}	142	122	118	135	133
HRR peak	kW m^{-2}	279	244	253	310	270
HRR peak at time	secs	263	283	303	423	294
Mass remaining	%	49.1	48.5	49.6	45.2	46.9
MARHE	kW m^{-2}	184	157	147	174	173

Table 69 Summary of mean cone calorimeter values for ATH / MH blend formulations

The best reported values for the cone calorimeter are highlighted in bold (Table 69), showing that whilst the most preferable results are not associated with a single formulation, the use of ATH/MH blends were more successful as fire retardants that ATH or MH alone. The heat release rate curves (Figure 105) show that A100 has the highest HRR values for the first 300 seconds, and M100 has the second highest peak in this period. All of the blends show reduced HRR peaks, with the lowest average HRR overall from A50 M50 (Table 69). A significant third peak is recorded for A25 M75, which occurred after the burning sample swelled significantly and the structure opened up, allowing a rapid release of fuel into the flame. Third HRR peaks were also noted for the other blends, but were much less severe. The lower rate of HRR for A50 M50 is also reflected in the MARHE value of 147 kW m^{-2}, which is somewhat lower than for A100 or M100.

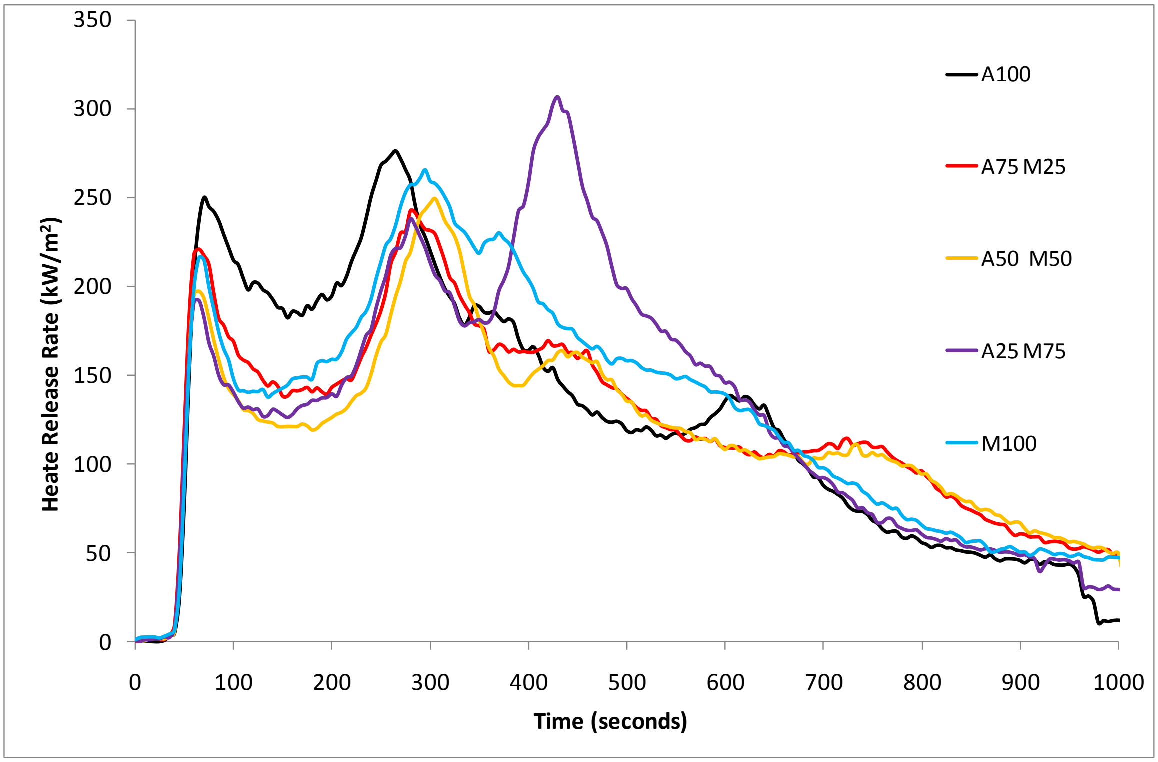


Figure 105 Heat release rate from cone for ATH / MH blend formulations

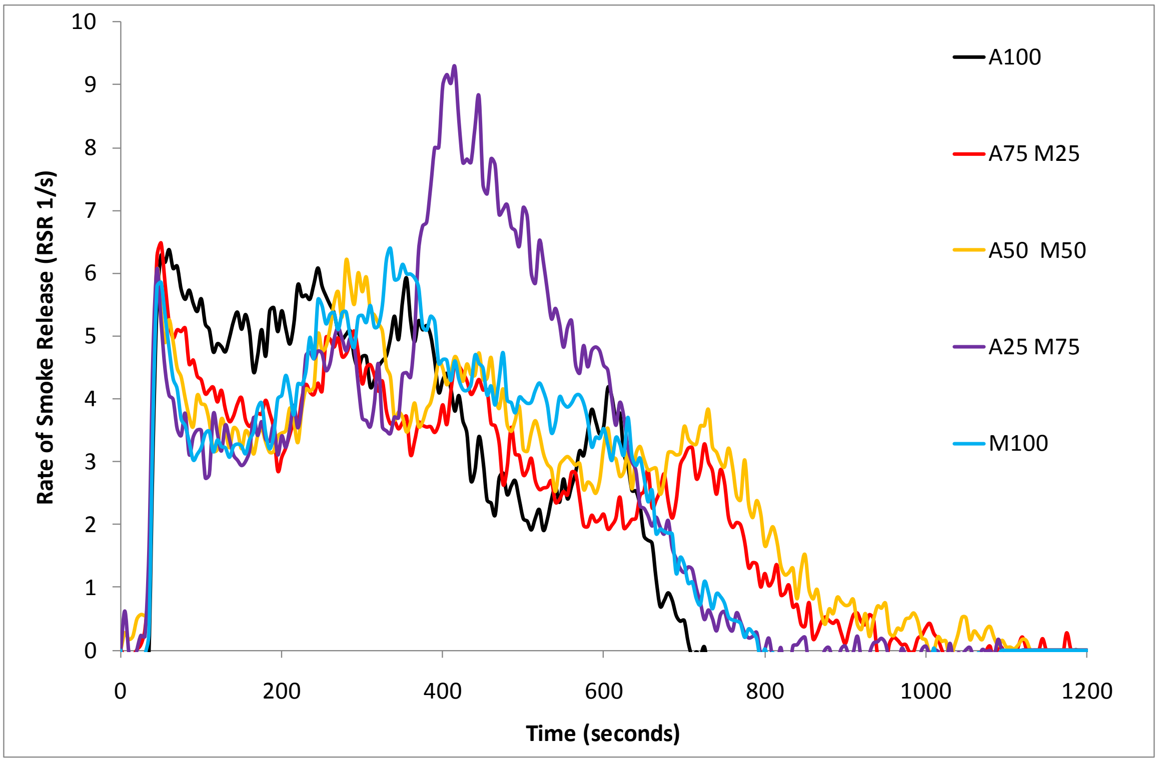


Figure 106 Mean rate of smoke release from cone for ATH / MH blend formulations

In the first 300 seconds, the rate of smoke release (RSR) is reduced compared to A100. Overall the lowest overall smoke yield is for A75 M25, at 12% lower than for A100, and 15% lower than M100. The other blends gave a higher smoke yield than A100 or M100 however, so any reduction in smoke yield may be tenuous. The smoke values reported are for the average of three runs per formulation, and some variation was noted which may be associated with the equipment. Comparing the smoke values with previous test of A100, M100 and A50 M50 (Table 57 and Figure 73), the values recorded for this run are lower for equal formulations. Problems with the laser for the cone calorimeter have been subsequently reported, but the unit was in calibration for the commencement of these runs, so it is unclear what caused this disparity. As a relative measure for these tests however, the use of ATH/MH blends were shown to reduce smoke yields in the early stage of burning.

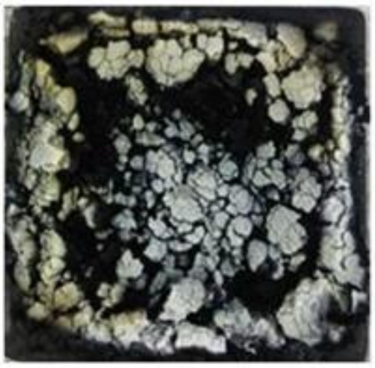
Observations of cone samples

A100 has a weak and friable residue

Figure 107 A100 residue

A75 M25 has more agglomerated lumps of residue

Figure 108 A75 M25 residue

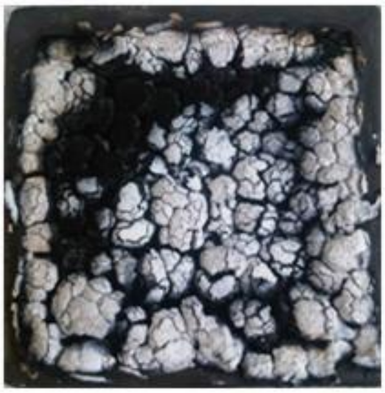


A50 M50 also has agglomerated lumps in the residue

Figure 109 A50 M50 residue

A25 M75 was heavily cracked but possessed more some moderate sized areas surface of smooth residue

Figure 110 A25 M75 residue



M100 has a similar structure to A25 M75, with smooth sections separated by deep cracks in the residue

Figure 111 M100 residue

The cone residues (Figure 107 to Figure 111) show that the variation in filler type affects the morphology of the remaining residue, which consists of approximately 72% combined Al_2O_3 and/or MgO, 22% carbon black and 6% ZnO. The apparent structure indicates that some of these residual materials can combine or sinter into a larger structure. This improved residue strength may be a contributing factor to the improved fire retardance reported.

4.5.4 Discussion

In section 4.3 an equal blend of 100 pphr ATH and MH (A50 M50) was found to have improved burning performance over either ATH or MH alone. In this section a wider range of blends were evaluated. Increasing levels of MH led to increased physical strength and elongation indicating an increased level polymer / filler interaction, which led to higher levels of dynamic stiffening and lower resilience. Increasing levels of MH also led to reduced processing safety as measured by time to scorch (ts2).

Increasing levels of MH leads to higher thermal stability as measured by TGA, attributable to reducing levels of ATH which decomposes at a peak of around 310°C in nitrogen.

In small scale flammability tests, limiting oxygen index was increased in blend formulations and in horizontal burning tests A25 M75 attained the highest rating of FH-1.

In the cone calorimeter the burning performance was improved for the blends compared to A100 or M100, but there was not one optimum blend for all measures, but the best range of properties were obtained between the blends A75 M25 and A50 M50. Figure 112 plots the key cone calorimeter heat release values along with LOI, with the most desirable values the lowest on the axis. Total smoke release is divided by 10 to enable comparison on the same scale.

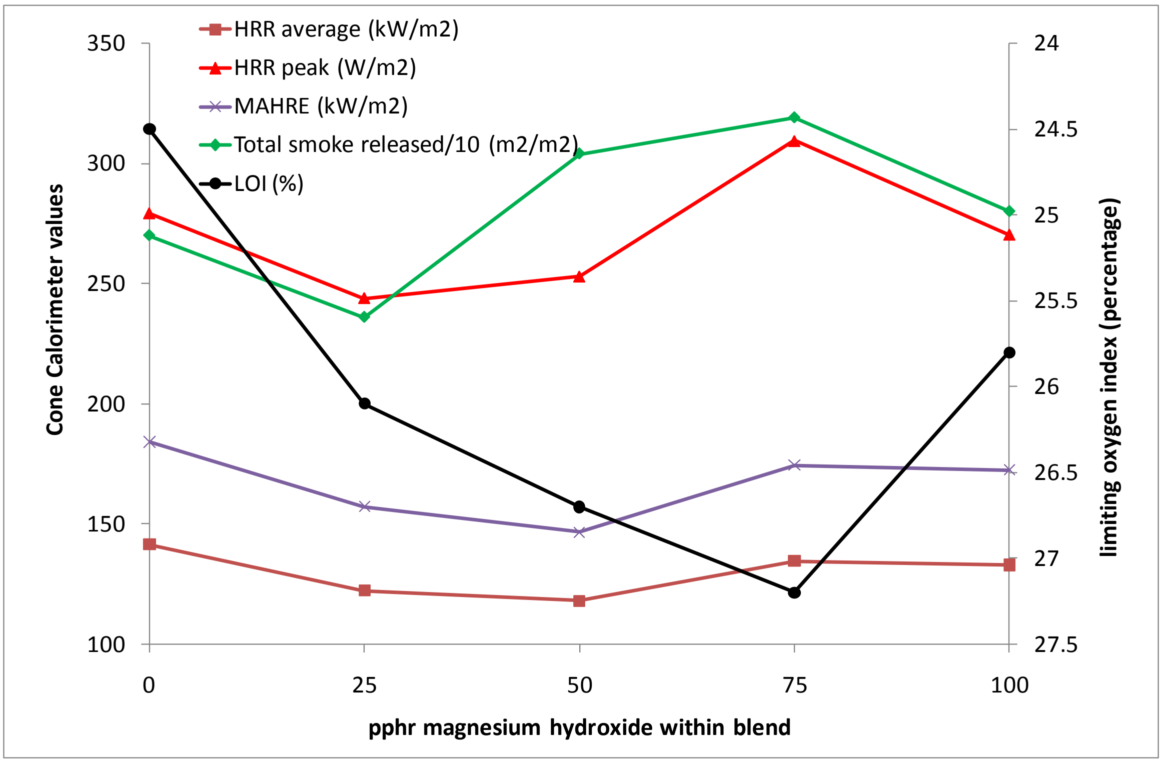


Figure 112 Comparison of burning values for ATH / MH blend formulations

Overall the use of a blend of ATH and MH clearly provide a benefit, but the blend percentage depends on the main requirement. For small scale flammability A25 M75 has the best properties, but in the cone the best values fall between A50 M50 and A75 M50.

It is proposed that the reason for this improved performance relates to a progressive action of cooling of the solid and gas phase from the mixture of endothermic decomposing fillers. Comparing the two fillers there is relatively little difference relating to the mode of action, apart from the effective temperature of action. Hull [132] compares the relative contributions of factors towards the fire retardancy of mineral filler fillers, including ATH and MH. Hull also points out that the analysis is very simplistic, but a useful tool for identifying more subtle effects. If any of the fire retardant behaviours predominated then it could be expected that one filler would out-perform the other, with an averaged response for a blend. The synergism of the blend must require, therefore, a combination of the properties. MH was noted to have a more substantial residue structure in the cone, so may provide a better barrier property. ATH however with a lower temperature of decomposition performs a role of delaying polymer decomposition, lacking in the MH with a higher temperature action. Both the endothermic effect of cooling and dilution, and the filler effect of residue contribute to the fire retardancy, and the ratio of these effects will vary according to the test. For a thicker sample in the cone calorimeter there is the possibility of a residue of burnt matter on the surface, providing a barrier to heat transfer to the lower layers, so slowing the rate of volatile production. In the LOI test, however, an intact residue will serve to absorb heat from the flame, but will provide a lesser barrier effect.

	Relative Contribution Fire Retardant Effects				T_{decomp}	ΔH_{decomp}
Additive	% Filler	Endotherm	% Residue	% Gas	/°C	/kJ g^{-1}
Aluminium hydroxide	9	55	13	23	180-200	1300
Magnesium hydroxide	19	56	9	15	300-320	1450

Table 70 Relative contributions of fire retardant effects from ATH and MH (Hull)

To compare the polymer decomposition with that of ATH and MH, TGA and DTG are plotted in Figure 113, with the peak temperatures of decomposition in Table 71. ATH completes decomposition prior to the commencement of significant mass loss for B20, whilst MH begins to decompose at a similar point to B20, with a peak DTG 23°C higher. A simple mixture of ATH and MH powder was also subjected to TGA, with the expectation that the mass loss curve would be a simple additive curve from the two additives. This was not the case, with the mass loss period shorter for each material (plotted as ATH MH mixture), than for the addition of the two curves (ATH MH additive TGA). It is not apparent why this occurs, but may suggest some interaction between the two additives. The TGA data indicates then that a blend of ATH and MH can serve to slow on the onset of polymer decomposition by cooling the material by the evolution of water, and the MH can either slow the decomposition process of the polymer directly by cooling through the evolution of water, or as part of a sacrificial layer above underlying polymer.

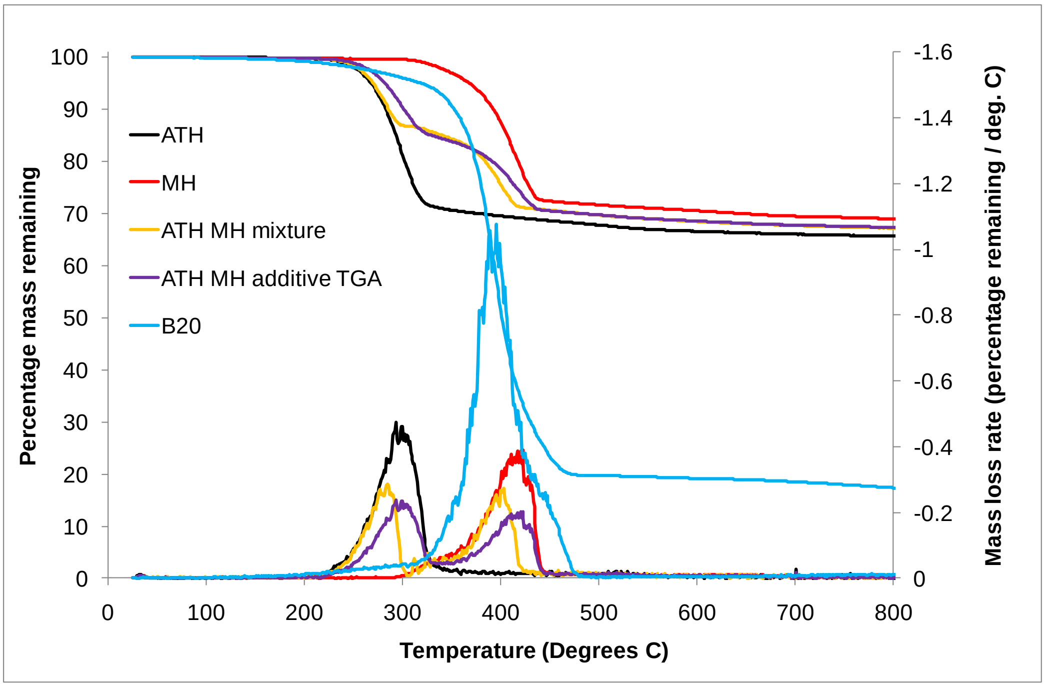


Figure 113 TGA and DTG curves actual and additive for ATH, MH and a mixture, in nitrogen

	ATH	MH	ATH/MH mixture	B20
Peak DTG °C	299	422	285, 395	391

Table 71 Peak DTG values for ATH, MH and a mixture in nitrogen

4.5.5 Summary

The restate the objectives set:

1 Repeat the evaluation of ATH, MH and an equal blend of ATH and MH to confirm if the positive effects were reproducible

2 Evaluate unequal blends of ATH and MH to look for an optimal level of fire retardancy and physical properties

The first objective was met, with A50 M50 again showing an overall improved performance over aluminium hydroxide or magnesium hydroxide as single additives. Considering further blends of ATH and MH, each blend has particular attributes, so there was no a single best blend. Within the cone calorimeter, however, the data suggest that a blend of between 25 to 50 phr magnesium hydroxide will result in the highest reduction in peak heat release, smoke emissions and the regulatory MARHE value.

CHAPTER 5. CONCLUSIONS AND FURTHER WORK

This research aimed to develop new fire retardant rubber formulations, surveying the existing knowledge base for fire retardant approaches for polyisoprene rubber, characterising unmodified compounds, formulating and studying fire retarded compounds, and optimising compounds for use within suspension and anti-vibration mounting systems. Materials have been prepared on a bench scale and their physical properties evaluated. Thermal decomposition has been studied using Thermogravimetric Analysis (TGA) in both air and nitrogen. Burning behaviour has been studied using a horizontal burning rate method, Limiting Oxygen Index (LOI) and the cone calorimeter.

In Chapter 1 (Introduction), existing literature provided the background understanding of the applications, structure, decomposition and burning behaviour of rubber, particularly polyisoprene. Methods of evaluation for thermal decomposition and flammability were considered, alongside the use of fire retardants in rubber.

In chapter 2 (Experimental Procedures) a specification was defined to identify fire retardants acceptable for use in polyisoprene rubber compounds, which eliminated the use of halogenated additives for reasons of environmental concern, toxicity and smoke yield. The remaining classes of fire retardants for evaluation were identified.

A model rubber compound based on synthetic polyisoprene was formulated and the additives discussed. Methods for the bench scale manufacture of rubber compounds and test pieces were described. The importance of TGA for the analysis of rubber compounds and additives, and particularly as a method of gaining insight into the types of information obtainable from microscale thermal decomposition was discussed. Burning tests used in this study were described: limiting oxygen index and horizontal burning flammability tests to evaluate the ease of extinction, and flame spread respectively; and cone calorimetry to assess burning behaviour particularly as it penetrated into the solid; by heat release rate, mass loss, smoke and CO/CO_2 emission in a developing fire. Cone calorimetry was considered the most suitable bench scale model of burning behaviour for large masses of rubber, because penetrative burning rather than flame spread is the major vector of fire growth as it does when large rubber springs etc, are burning.

In Chapter 3 (Results – Polyisoprene and Additives), rubber compounds were produced using typical additives without fire retardants, and evaluated by the methods described in Chapter 2. The aim of this section was to gain insight into the effect of commonly used additives on the physical properties, thermal decomposition and burning behaviour of rubber compounds, so as to enable the best approach to fire retarding rubber.

Polyisoprene and commonly used additives were subjected to TGA. The additives typically showed less thermal stability than polyisoprene with the exceptions of zinc oxide and carbon black. This suggests that a rubber compound with the addition of mineral oil will have reduced thermal stability, so is likely to have increased ignitability and flame spread. It also indicates that the addition of significant quantities of zinc oxide or carbon black will contribute to a more thermally resistant residue.

Basic rubber mixtures were prepared in order to better understand the interactions between polyisoprene and the additives zinc oxide, carbon black and silica filler using TGA. Zinc oxide had no measurable effect on the polymer decomposition, while silica reduced the thermal stability. When decomposed in air, increasing levels of carbon black reduced the rate of mass loss in the polymer, suggesting some interaction, possibly promoting the production of temporary char-like structures. The temperature of carbon black oxidation was reduced when incorporated into a rubber compound, compared to than when tested alone.

The effect of different cross-linking systems was studied. The addition of sulphur slightly reduced the peak decomposition temperature of the polymer as determined by TGA. TGA curves were constructed from the addition of additives and compared with actual data for a sulphur cross-linked compound. In nitrogen there was relatively little difference between the two curves, but when tested in air, the actual compound increased the thermal stability of the polymer by around 40°C. Values of LOI showed little variation with cross-linking systems. When burned in a cone calorimeter, sulphur without cross-linking increases the heat release, but when low levels of sulphur efficiently cross-link the polyisoprene chains, heat release is suppressed, as occurs with organic peroxide cross-linking. Overall, this suggested that either organic peroxide or a low-sulphur cross-linking system may be the most suitable for a fire retardant rubber compound.

The use of carbon black was compared with the inorganic fillers, precipitated silica and calcium carbonate, both individually and blended together within rubber compounds. Calcium carbonate filler reduced the thermal stability of the polyisoprene compared to carbon black and silica, when decomposed by TGA in air, but reduced the mass loss between 400 and 450°C, indicating an increased yield of a temporary char structure. LOI values were similar at around 19.5% for all formulations except for a compound entirely filled with calcium carbonate which had a level 1.5% lower. Within the cone calorimeter, material containing carbon black formed a char-like residue which provides some reduction in the rate heat release, and did not contribute to the fuel load. The use of inorganic fillers in the study yielded more rapid burning behaviour, confirming carbon black as the most suitable reinforcing filler for use within fire retardant formulations.

The use of carbon black was further investigated at filler loadings from 0 to 80 pphr to better understand the influence on decomposition and burning. The progressive incorporation of carbon black had little influence on TGA in nitrogen, but slowed the rate of polymer mass loss in air. The absence of carbon black resulted in a rubber compound with rather low LOI (17.5%), compared to any of the carbon black filler compounds which had similar values of around 19% regardless of the loading level. In the cone calorimeter the unfilled compound displayed significantly high heat release, melting after ignition into a liquid source of fuel. The carbon black filler compounds all had lower levels of heat release, with the burning compounds seen to remain more stable so restricting the rate of fuel release into the gas phase. Increasing levels of carbon black did not proportionally reduce heat release however, suggesting that whilst the presence of carbon black was of use, increasing this level has only very modest benefits.

Overall, it is apparent that the thermal decomposition of rubber compounds is controlled by a complex interaction of the decomposing elastomer modified by the presence of carbon black. Moreover, in TGA conditions, the thermal stability of the carbon black is compromised by the presence of the elastomer. Contrary to literature reports, suggesting detrimental influences on the flammability of rubbers after the incorporation of carbon black, its presence seems essential for the maintenance of both physical properties, and reduced flammability, as replacement with alternative fillers has indicated.

In Chapter 4 (Fire Retarded Polyisoprene) different approaches suggested within Chapter 2 were taken to attempt to fire retard polyisoprene rubber compounds.

Intumescent formulations were prepared using ammonium polyphosphate (APP), pentaerythritol and melamine, and separately using expandable graphite (EG). Many of the physical properties were degraded with the use of APP, with high water absorption and increased compression set. TGA in air indicated that the use of APP reduced the initial thermal stability of the compounds with mass loss occurring at lower temperatures, but led to some temporary char development and an increased temperature of oxidation for the carbon black. APP alone was of little benefit to LOI, and when used with pentaerythritol and melamine gave only a minor improvement. In the early stages of burning within the cone calorimeter, the use of APP/PER/MEL produced a significant reduction in peak HRR, but a second peak was more pronounced in the FR compounds with a significantly higher peak HRR measured. This second peak was attributed to a significant level of intumescence which develops after around 2 minutes in the cone calorimeter, increasing the surface area of polymer available for combustion. The combination of APP and a higher loading of carbon black yielded an excessive level of intumescence which has opened the material plaque up to expose a large interior surface, which underwent rapid burning, and a subsequent high rate of heat release. APP based systems did not show sufficient promise to merit further investigation in polyisoprene. The lack of success is most likely due to the lack of the additives to generate any conversion of the polymer into a char residue.

Expandable graphite (EG) was incorporated into rubber compounds at varying levels as an intumescent fire retardant. This had a detrimental effect on the physical properties due to the large particle size of EG flakes, but these were acceptable at additions below 10 phr. The thermal decomposition in air showed that the use of EG reduced the thermal stability of the polyisoprene in the initial stages of mass loss, due to the intumescence increasing the surface area, and hence the heat absorbed by the sample, but increased the proportion of a short-lived char between 400 and 500°C. LOI was only modestly improved with EG addition, but in the cone calorimeter a significant reduction was observed in the early stages of heat release. A substantial barrier of EG builds up, providing an insulating barrier to the underlying polymer, but in the later stages of burning the entire sample volume expands, releasing higher levels of heat. The best compromise of maintaining physical properties, and improving burning behaviour, was from the use of 5 – 10pphr EG.

Formulations were prepared incorporating aluminium hydroxide (ATH) and magnesium hydroxide (MH). Calcium carbonate was used in a control formulation as diluent filler with little fire retardancy. Some physical properties, such as tensile strength, showed significant reductions of up to 50% from a compound filled only with carbon black, probably due to a lack of polymer-filler interaction, which may be attributable to the incompatibility of a non-polar hydrocarbon polymer with a polar metal hydroxide. Thermal decomposition studies show a distinct mass loss, as water is lost, in compounds containing ATH at a peak of around 310°C; whereas MH loses mass at a similar decomposition temperature as for polyisoprene, around 390°C. Blends of huntite and hydromagnesite were also investigated, which have greater thermal stability than ATH. When ATH was added at 50 pphr, a moderate improvement in LOI was measured (21.5%), and at 100 pphr LOI was improved to 24.7%, demonstrating that ATH is around twice as effective as calcium carbonate, with an LOI of 21.5% at 100 pphr. A blend of huntite/hydromagnesite gave a similar LOI to ATH, but MH gave an improved LOI at 27.1%. An equal blend of ATH and MH also gave an improved LOI of 26.9%, which also resulted in the best rating for the horizontal flammability test, with rapid self-extinguishment. In the cone calorimeter the lowest heat release and MARHE values were obtained for the equal blend of ATH and MH, somewhat better than either ATH or MH alone. The blends of huntite and hydromagnesite gave slightly higher levels of heat release than ATH. 50 pphr of ATH performed similarly to 100 pphr of calcium carbonate. 50 phr of MH gave significantly lower heat release than 50 pphr of ATH.

Using ATH, and MH, filled formulations, the effect of additives providing a proposed synergistic benefit were considered, including zinc hydroxystannate (ZHS) as an additive or filler coating, zinc borate (ZB), red phosphorus (RP) and expandable graphite (EG) chosen based on favourable literature reports in other polymers. These additions had little effect on the physical properties apart from RP which caused a greasy surface bloom to occur, thought to originate from the oil used to encapsulate it. These additives caused little change to the thermal decomposition as measured by TGA. In small scale flammability testing, the highest LOI for an ATH based formulation was the addition of EG, with a 3.5% increase compared to 100 pphr ATH (24.7%). The other additives used with ATH gave no improvement in LOI. Formulations based on MH had a higher starting LOI at 27.1%, and the addition of 10 pphr ZHS increased the LOI by 1.6%.

In the cone calorimeter, for ATH, the addition of 10 pphr ZHS gives a modest reduction in peak heat release but an increase in smoke yield; although one of the benefits claimed for ZHS is as a smoke suppressant. The addition of ZB had little effect on heat release and also caused an increase in smoke yield, contrary to the reported benefit of smoke suppression. The most significant reduction in average heat release was for the addition of EG with ATH, with the only reduction in smoke yield compared to ATH. The use of red phosphorus led to increased peak heat release, together with a large increase in CO yield. The CO increase indicated some flame quenching in the gas phase from the phosphorus, but this did not confer a reduction in heat release. It is suggested that RP and ATH are an antagonistic combination of fire retardants, hence the reduction in fire retardance.

The use of ZHS in MH gave no benefit, with increased heat release and smoke yield. The additive caused excessive intumescence within the samples, so causing the samples to open up and burn rapidly. The use of ZHS resulted in a reduction in the observed residue strength, making it more friable, reducing the barrier properties, and possibly accounting for the greater swelling. Since some benefits were seen for ZHS, it may be that the loading level was not correct for optimised performance. In any future study lower levels of ZHS should be considered.

Blends of hydrated fillers were investigated, based on ATH and MH, to find an optimised ratio of addition for the lowest flammability. ATH was added at 0, 25, 50, 75 and 100 pphr with the remainder MH for a combined 100 pphr loading. Increasing levels of MH led to improved physical strength and elongation at break values, but reduced processability. The formulation with 75 pphr MH and 25 pphr ATH gave the highest LOI and lowest horizontal burning rate. In the cone calorimeter however, this ratio gave the highest level of peak heat release and smoke yield. The lowest HRR and smoke values were recorded for 25 pphr MH and 75 pphr ATH. The lowest MARHE value was for an equal mix of ATH/MH at 50 pphr each, and can be judged to provide the best compromise of all properties. This suggests that the continuous endothermic loss of water occurring from 240 to 390°C provides the optimum protection for polyisoprene, giving a clear improvement over a larger evolution of water over a smaller temperature range. Possibly the ATH decomposes and fuses on the surface before the polyisoprene starts to break down, forming a protective layer. It is concluded that the use of a blend of MH and ATH is successful because the wide range of decomposition temperatures gives endothermic cooling and water release to the polymer for a longer period so slowing the rate of fuel production available for burning over a longer period.

Overall it is concluded that from the work undertaken, the use of hydrated fillers was the most successful technique for the fire retarding of polyisoprene rubber compounds. Importantly the use of a blend of aluminium hydroxide and magnesium hydroxide had the greatest benefit. The beneficial effects of expandable graphite were also reported, both alone, and in conjunction with ATH. Although some temporary char structures were generated under TGA, all attempts to generate graphitic char from polyisoprene proved unsuccessful using char promoting additives such as ammonium polyphosphate. Of the standard additives used in rubber, a nominal addition of carbon black was found to be beneficial to prevent more rapid burning of the decomposing polymer.

Recommendations for further evaluation

The use of zinc hydroxystannate (ZHS) gave mixed results, but showed some potential in ATH with some improvement in LOI. The level of ZHS used may have not been optimal, so it is recommended that it be re-evaluated with hydrated fillers at a range of addition levels, from 1 to 15% of the filler loading.

Further work is recommended with ATH and MH blended together, but to introduce variation in particle size and coatings to improve physical properties and burning behaviour. In addition the use of silane coupling agents can be evaluated to improve the filler compatibility with the elastomer. The addition of varying levels of expandable graphite (EG) should be evaluated with an ATH/MH blend to increase the benefit of addition seen by EG when used with ATH.

The wide range of decomposition temperatures benefited the fire retardancy of polyisoprene, so it is feasible that a third hydrated filler may improve the progressive release of endothermic cooling. Candidate materials for this role are the UltraCarb materials, a blend of huntite and hydromagnesite, with some of the decomposition occurring in two steps between the ATH and MH mass losses.

An area of work not undertaken due to limitations of time was the evaluation of nano-scale additives such as montmorillonite clay and carbon nano-tubes. These additives can be used as secondary additives with hydrated fillers as primary fire retardants, but a method of mixing technology needs to be identified to ensure nano-dispersion. It is generally considered that the use of conventional low shear mixing technology will not result in the dispersion levels necessary for the realisation of the benefits promoted for nano-scale additives.

Reference list

1. Kind, D. J. Elastomeric body with elastic fire retardant coating. United States Patent application No. 20100183856 2010.

2. Brydson, J. A. *Plastics Materials;* 7th ed.; Butterworth Heinemann: Oxford, 1999.

3. Billmeyer, F. W. The science of large molecules. In *Textbook of polymer science*, third ed.; Billmeyer, F. W., Ed.; Wiley: New York, 1984; p 21.

4. Nagdi, K. Basic Principles of Rubber Chemistry. In *Rubber as an Engineering Material*, Nagdi, K., Ed.; Hanser: Munich, 1993; pp 1-7.

5. Billmeyer, F. W. Hydrocarbon Plastics and Elastomers. In *Textbook of polymer science*, third ed.; Billmeyer, F. W., Ed.; Wiley: New York, 1984; pp 361-382.

6. *BS ISO 1629:2007*; Rubber and latices. Nomenclature; British Standard Institution, London, 07.

7. *ASTM D 1418-06*; Standard Practice for Rubber and Rubber Latices-Nomenclature; ASTM International, West Conshohocken, PA, USA, 06.

8. Mathew, N. M.; . Natural rubber. In *Rubber Technologists Handbook*, White, J. R., De, S. K., Eds.; RAPRA Technology Ltd: 2001; pp 11-45.

9. Fernando, M.; Hull, C.; Clark, J. Flame Retardant Natural Rubber Formulations. 176th Technical Meeting of the Rubber Division of the American Chemical Society: 2009.

10. Bryant, C. L. Acrylonitrile-Butadiene (Nitrile) Rubbers - NBR. In *Rubber Technology and Manufacture*, Second ed.; Blow, C. M., Hepburn, C., Eds.; Butterworths: London, 1985; pp 130-136.

11. Hoffman, W. *Vulcanization and vulcanizing agents;* MacLaren and Sons Ltd: London, 1967.

12. Brydson, J. A. *Rubbery materials and their compounds;* Elsevier Applied Science: 1988.

13. Mouseman, M.; Ingham, J. D. Smoke Properties of Highly FIlled Ethylene-Propylene-Diene Terpolymer Rubbers. *Rubber Chem. Technol.* **1978,** *51* (5), 970-976.

14. Arnold, R. G.; Barney, A. L.; Thompson, D. C. Fluoroelastomers. *Rubber Chem. Technol.* **1973,** *46* (3), 619-652.

15. Polmanteer, K. E. Silicone rubber, its development and technological progress. *Rubber Chem. Technol.* **1988,** *61* (3), 470-502.

16. Horn, J. B. Materials for Compounding and Reinforcement. In *Rubber Technology and Manufacture*, second ed.; Blow, C. M., Hepburn, C., Eds.; Butterworths: London, 1982; pp 202-308.

17. *ASTM D2000-08*; Standard Classification System for Rubber Products in Automotive Applications; ASTM International, West Conshohocken, PA, USA, 08.

18. Dick, J. S.; Annicelli, R. A. *Rubber technology: compounding and testing for perfomance;* Hanser Publishers: 2001.

19. Balthasar, M.; Mauss, F.; Knobel, A.; Kraft, M. Detailed modeling of soot formation in a partially stirred plug flow reactor. *Combustion and Flame* **2002,** *128* (4), 395-409.

20. Lockwood, F. C.; Van Niekerk, J. E. Parametric study of a carbon black oil furnace. *Combustion and Flame* **1995,** *103* (1-2), 76-90.

21. *ASTM D 1765-10*; Standard Classification System for Carbon Blacks Used in Rubber Products; ASTM International, West Conshohocken, PA, USA, 10.

22. Precipitated silica used in 100 M tyres over the past 15 years. *Focus on Pigments* **2007,** *2007* (5), 3.

23. Mouri, H.; . Fillers. In *Rubber Technologists Handbook*, White, J. R., De, S. K., Eds.; RAPRA Technology Ltd: 2001; pp 131-165.

24. Zhao, Q.; Tannenbaum, R.; Jacob, K. I. Carbon nanotubes as Raman sensors of vulcanization in natural rubber. *Carbon* **2006,** *44* (9), 1740-1745.

25. Frogley, M. D.; Ravich, D.; Wagner, H. D. Mechanical properties of carbon nanoparticle-reinforced elastomers. *Composites Science and Technology* **2003,** *63* (11), 1647-1654.

26. Morrell, S. H. The Chemistry and Technology of Vulcanisation. In *Rubber Technology and Manufacture*, Second ed.; Blow, C. M., Hepburn, C., Eds.; Butterworths: London, 1985; pp 171-201.

27. Datta, R. N.; Ingham, F. A. A.; . Rubber Additives - Compounding Ingredients. In *Rubber Technologists Handbook*, White, J. R., De, S. K., Eds.; RAPRA Technology Ltd: 2001; pp 167-208.

28. Cataldo, F. On the ozone protection of polymers having non-conjugated unsaturation. *Polymer Degradation and Stability* **2001,** *72* (2), 287-296.

29. Crowther, B. G.; Lewis, P. M.; Metherell, C. Compounding. In *Natural Rubber Science and Technology*, Roberts, A. D., Ed.; Oxford University Press: 1998; pp 177-233.

30. Drysdale, D. Fire Science and Combustion. In *An Introduction to Fire Dynamics*, second ed.; Drysdale, D., Ed.; Wiley: Chichester, 1998; pp 2-30.

31. Cullis, C. F.; Hirschler, M. M. Polymer Combustion: Fundamental Studies. In *The Combustion of Organic Polymers*, Culls, C. F., Hirschler, M. M., Eds.; Clarenden Press: Oxford, 1981; pp 93-228.

32. Billmeyer, F. W. Polymerization conditions and polymer reactions. In *Textbook of polymer science*, third ed.; Billmeyer, F. W., Ed.; Wiley: New York, 1984; pp 126-148.

33. Heal, G. R. Thermogravimetry and Derivative Thermogravimetry. In *Principles of Thermal Analysis and Calorimetry*, first ed.; Haines, P. J., Ed.; The Royal Society of Chemistry: Cambridge, 2002; pp 10-54.

34. Laye, P. G. Differential Thermal Analysis and Differential Scanning Calorimetry. In *Principles of Thermal Analysis and Calorimetry*, Haines, P. J., Ed.; The Royal Society of Chemistry: Cambridge, 2002; pp 55-93.

35. Warrington, S. B. Simultaneous Thermal Analysis Techniques. In *Principles of Thermal Analysis and Calorimetry*, Haines, P. J., Ed.; The Royal Society of Chemistry: Cambridge, 2002; pp 166-189.

36. Mastovskβ, K.; Lehotay, S. J. Practical approaches to fast gas chromatography-mass spectrometry. *Journal of Chromatography A* **2003,** *1000* (1-2), 153-180.

37. BS EN 60695-1-10:2010. Fire hazard testing. Guidance for assessing the fire hazard of electrotechnical products. General guidelines; British Standard Institution, London. 2010.

38. BS 2782-1: Method 140A:1992 ISO 1210:1992. Part 1: Thermal properties - Method 140A: Determination of the burning behaviour of horizontal and vertical specimens in contact with a small-flame ignition source; British Standard Institution, London. 1992.

39. ISO 4589-2:1996. *Plastics – Determination of burning behaviour by oxygen index – Part-2: Ambient temperature test*. Geneva, Switzerland, ISO.

40. *BS 476-15:1993 ISO 5660-1:1993*; British Standard Institution, London: Fire tests on building materials and structures - Part 15: Method for measuring the rate of heat release of products, 93.

41. Huggett, C. Estimation of rate of heat release by means of oxygen consumption measurements. *Fire and Materials* **1980,** *4* (2), 61-65.

42. ISO 5659-2:2006. *Plastics - Smoke generation - Part 2: Determination of optical density by a single-chamber test*. Geneva, Switzerland, ISO.

43. Stoliarov, S. I.; Lyon, R. E. *Thermo-Kinetic Model of Burning*;DOT/FAA/AR-TN08/17; U.S. Department of Transportation: Washington DC, 08.

44. *BS EN ISO 1716*; Reaction to fire tests for building products - Determination of the heat of combustion; British Standard Institution, London, 02.

45. Hshieh, F. Y.; Hirsch, D. B.; Beeson, H. D. Predicting heats of combustion of polymers using an empirical approach. *Fire and Materials* **2003,** *27* (1), 9-17.

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

47. Messenger, T. H. Heats of Combustion of Rubber, Gutta-Percha, and Balata. *Rubber Chem. Technol.* **1929,** *5*, 71-83.

48. van Krevelen, D. W. Product properties (II) Environmental behaviour and failure. In *Properties of polymers*, Third ed.; van Krevelen, D. W., Ed.; Elsevier: 1990; pp 725-744.

49. Janowska, G.; Kucharska-Jastrz-àbek, A.; Rybinski, P.; Wesotek, D.; Wojcik, I. Flammability of diene rubbers. *Journal of Thermal Analysis and Calorimetry* **2010,** *102* (3), 1043-1049.

50. Johnson, P. R. A General Correlation of the Flammability of Natural and Synthetic Polymers. *Rubber Chem. Technol.* **1976,** *49* (1), 158-169.

51. Fabris, H. J.; Sommer, J. G. Flame Retardation of Natural and Synthetic Rubbers. In *Flame Retardancy of Polymeric Materials*, Kuryla, W. C., Papa, A. J., Eds.; Marcel Dekker: 1973; pp 135-199.

52. Fabris, H. J.; Sommer, J. G. Flammability of Elastomeric Materials. *Rubber Chem. Technol.* **1977,** *50* (3), 523-569.

53. Green, J. *Flame Retarding Rubber - Materials, Markets*; Rubber & Plastics News, Jan 18, 93.

54. Rogers, T. H.; Fruzzetti, R. E. Flame Retardance of Rubbers. In *Flame retardant Polymeric Materials*, Lewin, M., Atlas, S. M., Pearce, E. M., Eds.; Plenum Press: New York, 1975; pp 223-237.

55. Schultz, D. *Flame retarding materials*; Rubber World, Aug 1, 92.

56. Dufton, P. W. *Fire - Additives and Materials*; RAPRA Technology Ltd, Shrewsbury: May, 95.

57. Nakagawa, Y.; Komai, T. Correlation between the Thermogravimetric Analysis and Some Other Flammability Tests on Covers of Rubber Conveyor Belts. *Journal of Fire Sciences* **1990,** *8* (6), 455-476.

58. Lawson, D. F. Recent Developments in the Flammability of Elastomeric Materials. *Rubber Chem. Technol.* **1986,** *59* (3), 455-481.

59. Hirsch, D. B.; Beeson, H. D. Improved Test Method to Determine Flammability of Aerospace Materials. National Institute of Standards and Technology: 2011.

60. Mayer, H. A.; Day, A. C. Halogen-free Flame Retardant Compounds and Cables. 1988.

61. Myers, R. E.; Dickens, E. D. J.; Licursi, E.; Evans, R. E. Ammonium Pentaborate: an Intumescent Flame Retardant for Thermoplastic Polyurethanes. *Journal of Fire Sciences* **1985,** *3* (6), 432-449.

62. Ismawi, D. H. A.; Harper, J. F.; Ansarifar, A. Influence of Flame Retardant Additives on the Flammability Behaviour of Natural Rubber (NR). *Journal of Rubber Research* **2008,** *11* (4), 223-236.

63. Wu, Y.; Huang, H.; Zhao, W.; Zhang, H.; Wang, Y.; Zhang, L. Flame retardance of montmorillonite/rubber composites. *Journal of Applied Polymer Science* **2008,** *107* (5), 3318-3324.

64. Lawson, D. F.; Kay, E. L.; Roberts, D. T. Mechanism of Smoke Inhibition by Hydrated Fillers. *Rubber Chem. Technol.* **1975,** *48* (1), 124-131.

65. Khattab, M. A. Decabromobiphenyl oxide aluminum hydroxide system as a flame retardant for styrene butadiene rubber. *Journal of Applied Polymer Science* **2000,** *78* (12), 2134-2139.

66. Vinod, V. S.; Varghese, S.; Kuriakose, B. Aluminum powder filled nitrile rubber composites. *Journal of Applied Polymer Science* **2004,** *91* (5), 3156-3161.

67. *Flame Retardance in Vamac*; Doc. Ref. VAM020925_2, v.1; DuPont: http://www2.dupont.com/Vamac/en_US/assets/downloads/vamac_flame_retardant_compounds.pdf, Sep, 02.

68. Yang, L.; Hu, Y.; Lu, H.; Song, L. Morphology, thermal, and mechanical properties of flame-retardant silicone rubber/montmorillonite nanocomposites. *Journal of Applied Polymer Science* **2006,** *99* (6), 3275-3280.

69. BS 6853:1999. Code of practice for fire precautions in the design and construction of passenger carrying trains. British Standard Institution, London.

70. Hudson, S. *Train Fires - Special Topic Report*; Controller, Safety Strategy & Risk Railway Safety: 01.

71. Galea, E. R. Modelling human behaviour and evacuation within the rail environment, Fire Protection of Rolling Stock, London. 2007.

72. Braun, E. *A Fire Hazard Evaluation of the Interior of WIMATA Metrorail Cars*; NBSIR 75-971; National Bureau of Standards: 75.

73. Braun, E. *Fire Hazard Evaluation of BART Vehicles*;NBSIR 78-1421; National Bureau of Standards: 78.

74. Peacock, R. D. *Fire Safety Guidelines for Vehicles in a Downtown People Mover System*;NBSIR 78-1586; National Bureau of Standards: 79.

75. Kaminski, A. Study of Smoke Emission of Materials Used in Passenger Rail Vehicles. *Journal of Fire Sciences* **1988,** *6* (4), 267-289.

76. Troitzsch, J. H.
Fire Safety Regulations and Testing - their Impact on the Use of Polymers and Flame Retardants. 2009.

77. Tooley, D. A comparison of New European fire standards with UK standards and the impact on UK vehicle design. *Proceedings of the Institution of Mechanical Engineers, Part F: Journal of Rail and Rapid Transit* **2011,** *225* (4), 403-416.

78. Brazier, D. W. Applications of thermal analytical procedures in the study of elastomers and elastomer systems. *Rubber Chem. Technol.* **1980,** *53* (3), 437-511.

79. Sircar, A. K. Identification of elastomers by thermal analysis. *Rubber Chem. Technol.* **1972,** *45* (1), 329-345.

80. Sircar, A. K. Identification of natural and synthetic polyisoprene vulcanizates by thermal analysis. *Rubber Chem. Technol.* **1977,** *50* (1), 71-82.

81. Sircar, A. K. Analysis of Elastomer Vulcanizate Composition by Tg-Dtg Techniques. *Rubber Chem. Technol.* **1992,** *65* (3), 503-526.

82. Brazier, D. W.; Nickel, G. H. Thermoanalytical methods in vulcanizate analysis ii. Derivative thermogravimetric analysis. *Rubber Chem. Technol.* **1975,** *48* (4), 661-677.

83. Straus, S.; Madorsky, S. L. Thermal Degradation of Unvulcanized and Vulcanized Rubber in a Vacuum. *Industrial and engineering chemistry* **1956,** *48* (7), 1212-1219.

84. Cataldo, F. Thermal depolymerization and pyrolysis of cis-1,4-polyisoprene: preparation of liquid polyisoprene and terpene resin. *Journal of Analytical and Applied Pyrolysis* **1998,** *44* (2), 121-130.

85. Colin, X.; Audouin, L.; Verdu, J. Kinetic modelling of the thermal oxidation of polyisoprene elastomers. Part 1: Unvulcanized unstabilized polyisoprene. *Polymer Degradation and Stability* **2007,** *92* (5), 886-897.

86. Reshetnikov, S. M.; Reshetnikov, I. S. Oxidation kinetic of volatile polymer degradation products. *Polymer Degradation and Stability* **1999,** *64* (3), 379-385.

87. Colin, X.; Audouin, L.; Verdu, J.; Le Huy, M. Kinetic modelling of the thermal oxidation of polyisoprene elastomers. Part 2: Effect of sulfur vulcanization on mass changes and thickness distribution of oxidation products during thermal oxidation. *Polymer Degradation and Stability* **2007,** *92* (5), 898-905.

88. Choi, S. S. Correlation of crosslink density with pyrolysis pattern of natural rubber vulcanizates with efficient vulcanizing cure system. *Journal of Analytical and Applied Pyrolysis* **1999,** *52* (1), 105-112.

89. Jiang, D. D.; Levchik, G. F.; Levchik, S. V.; Dick, C.; Liggat, J. J.; Snape, C. E.; Wilkie, C. A. Thermal degradation of cross-linked polyisoprene and polychloroprene. *Polymer Degradation and Stability* **2000,** *68* (1), 75-82.

90. Mizuno, K.; Ueno, T.; Hirata, A.; Ishikawa, T.; Takeda, K. Thermal degradation and flame retardancy of polynorbornene by a zeolite. *Polymer Degradation and Stability* **2007,** *92* (12), 2257-2263.

91. Liu, L.; Jia, D.; Luo, Y.; Li, B. Structure and flammability properties of NR-organoclay nanocomposites. *Polym Compos* **2009,** *30* (1), 107-110.

92. Wang, J.; Yang, K.; Zheng, X. Studies on the effect of 4A zeolite on the properties of intumescent flame-retardant agent filled natural rubber composites. *Journal of Polymer Research* **2009,** *16* (4), 427-436.

93. Jincheng, W.; Yuehui, C. Synthesis of an Intumescent Flame Retardant (IFR) Agent and Application in a Natural Rubber (NR) System. *Journal of Elastomers and Plastics* **2007,** *39* (1), 33-51.

94. Peacock, R. D.; Braun, E. *Fire Safety of Passenger Trains, Phase I: Material Evaluation (Cone Calorimeter)*;NISTIR 6132; National Institute of Standards and Technology: 99.

95. Moon, S.; Jo, B.; Farris, R. J. Flame Resistance and Foaming Properties of NBR Compounds With Halogen-Free Flame Retardants. *Polym Compos* **2009,** *30* (12), 1732-1742.

96. Bugajny, M.; Le Bras, M.; Bourbigot, S.; Delobel, R. Thermal behaviour of ethylene-propylene rubber/polyurethane/ammonium polyphosphate intumescent formulations--a kinetic study. *Polymer Degradation and Stability* **1999,** *64* (1), 157-163.

97. Zhang, Q.; Tian, M.; Wu, Y.; Lin, G.; Zhang, L. Effect of particle size on the properties of Mg(OH)2-filled rubber composites. *Journal of Applied Polymer Science* **2004,** *94* (6), 2341-2346.

98. Cusack, P. A. Tin-coated inorganic fillers with enhanced fire retardant activity, High Performance FIllers. 2005.

99. Fang, S.; Hu, Y.; Song, L.; Zhan, J.; He, Q. Mechanical properties, fire performance and thermal stability of magnesium hydroxide sulfate hydrate whiskers flame retardant silicone rubber. *Journal of Materials Science* **2008,** *43* (3), 1057-1062.

100. Schartel, B.; Hull, T. R. Development of fire-retarded materials - Interpretation of cone calorimeter data. *Fire and Materials* **2007,** *31* (5), 327-354.

101. *CEN/TS 45545-2*; European Committee for Standardization (CEN): Railway Applications-Fire Protection of Railway Vehicles, Brussels, Belgium, 09.

102. ASTM E662. 2009. Standard Test Method for Specific Optical Density of Smoke Generated by Solid Materials.

103. *Fire Statistics, United Kingdom 2008*; UK government statistical report Department for Communities and Local Government: London, 08.

104. Hull, T. R.; Stec, A. A.; Lebek, K.; Price, D. Factors affecting the combustion toxicity of polymeric materials. *Polymer Degradation and Stability* **2007,** *92* (12), 2239-2246.

105. Stec, A. A.; Hull, T. R.; Lebek, K.; Purser, J. A.; Purser, D. A. The effect of temperature and ventilation condition on the toxic product yields from burning polymers. *Fire and Materials* **2008,** *32* (1), 49-60.

106. Hilado, C. J.; Huttlinger, N. V. Relative Toxicity of Gases From Overheating of Rubbers and Plastics. *Journal of Elastomers and Plastics* **1980,** *12* (2), 94-103.

107. Hilado, C. J.; Huttlinger, P. A. Carbon Monoxide Evolution From Elastomers. *Journal of Elastomers and Plastics* **1980,** *12* (4), 197-200.

108. *NFX 70-100*; Analysis of pyrolysis and combustion gases. Tube furnace method. Part 1, Methods of analysis of gas generated by thermal degradation. Part 2, Method of thermal degradation using tube furnace, AFNOR, France, 01.

109. Janowska, G.; Slusarski, L. Effect of Carbon-Black on the Thermal-Properties and Flammability of Cis-1,4-Polyisoprene Vulcanizates. *Journal of Thermal Analysis* **1991,** *37* (4), 713-720.

110. Janowska, G.; Slusarski, L. Effect of mineral fillers on thermal properties and flammability of cis-1,4-polyisoprene vulcanizates. *Journal of Thermal Analysis* **1995,** *45* (6), 1579-1588.

111. Derham, C. J.; Plunkett, A. P. Fire resistance of steel-laminated natural rubber bearings. *NR Technology* **1976,** *7*, 29-37.

112. Simpson, R. B. *Rubber Basics;* Rapra Technology, Shrewsbury: 2002.

113. Yao, Q.; Wilkie, C. A. How does cross-linking affect the thermal stability of polyisoprene? *Polymer Degradation and Stability* **2000,** *69* (3), 287-296.

114. Troitzsch, J. H. Fire Retardant Plastics. In *International Plastics Flammability Handbook: Principles, Regulations, Testing and Approval*, Second ed.; Troitzsch, J. H., Ed.; Hanser: Munich, 1990; pp 43-62.

115. Price, D.; Pyrah, K.; Hull, T. R.; Milnes, G. J.; Ebdon, J. R.; Hunt, B. J.; Joseph, P.; Konkel, C. S. Flame retarding poly(methyl methacrylate) with phosphorus-containing compounds: comparison of an additive with a reactive approach. *Polymer Degradation and Stability* **2001,** *74* (3), 441-447.

116. National Research Council (U.S.) *Materials: state of the art;* National Academy of Sciences: 1977; Vol. v. 1.

117. Trexler, H. E. The Formulation of Nonburning Elastomer Compounds. *Rubber Chem. Technol.* **1973,** *46* (4), 1114-1125.

118. Price, D.; Bullett, K. J.; Cunliffe, L. K.; Hull, T. R.; Milnes, G. J.; Ebdon, J. R.; Hunt, B. J.; Joseph, P. Cone calorimetry studies of polymer systems flame retarded by chemically bonded phosphorus. *Polymer Degradation and Stability* **2005,** *88* (1), 74-79.

119. Cullis, C. F.; Hirschler, M. M. Polymer Combustion: Inhibition. In *The Combustion of Organic Polymers*, Culls, C. F., Hirschler, M. M., Eds.; Clarenden Press: Oxford, 1981; pp 229-318.

120. Kandola, B. K. An Overview of Flame Retardancy. 2008.

121. Weil, E. D.; Levchik, S. V. Commercial Flame Retardancy of Polyurethanes. *Journal of Fire Sciences* **2004,** *22* (3), 183-210.

122. Harashina, H.; Tajima, Y.; Itoh, T. Synergistic effect of red phosphorus, novolac and melamine ternary combination on flame retardancy of poly(oxymethylene). *Polymer Degradation and Stability* **2006,** *91* (9), 1996-2002.

123. Jincheng, W.; Shenglin, Y.; Guang, L.; Jianming, J. Synthesis of a New-type Carbonific and Its Application in Intumescent Flame-retardant (IFR)/Polyurethane Coatings. *Journal of Fire Sciences* **2003,** *21* (4), 245-266.

124. Duquesne, S.; Delobel, R.; Le Bras, M.; Camino, G. A comparative study of the mechanism of action of ammonium polyphosphate and expandable graphite in polyurethane. *Polymer Degradation and Stability* **2002,** *77* (2), 333-344.

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

126. Price, D.; Pyrah, K.; Hull, T. R.; Milnes, G. J.; Ebdon, J. R.; Hunt, B. J.; Joseph, P.; Konkel, C. S. Flame retarding poly(methyl methacrylate) with phosphorus-containing compounds: comparison of an additive with a reactive approach. *Polymer Degradation and Stability* **2001,** *74* (3), 441-447.

127. Menon, A. R. R.; Pillai, C. K. S.; Nando, G. B. Modification of natural rubber with phosphatic plasticizers: a comparison of phosphorylated cashew nut shell liquid prepolymer with 2-ethyl hexyl diphenyl phosphate. *European Polymer Journal* **1998,** *34* (7), 923-929.

128. Menon, A. R. R. Flame-Retardant Characteristics of Natural Rubber Modified with a Bromo Derivative of Phosphorylated Cashew Nut Shell Liquid. *Journal of Fire Sciences* **1997,** *15* (1), 3-13.

129. Horacek, H.; Grabner, R. Advantages of flame retardants based on nitrogen compounds. *Polymer Degradation and Stability* **1996,** *54* (2-3), 205-215.

130. Jincheng, W.; Yuehui, C. Effect of Microencapsulation and 4A Zeolite on the Properties of Intumescent Flame-retardant Natural Rubber Composites. *Journal of Fire Sciences* **2008,** *26* (2), 153-171.

131. Hollingbery, L. A.; Hull, T. R. The fire retardant behaviour of huntite and hydromagnesite - A review. *Polymer Degradation and Stability* **2010,** *95* (12), 2213-2225.

132. Hull, T. R.; Witkowski, A.; Hollingbery, L. Fire retardant action of mineral fillers. *Polymer Degradation and Stability* **2011,** *96* (8), 1462-1469.

133. Horn, W. E. Inorganic Hydroxides and Hydroxycarbonates: Their Function and Use as Flame-Retardant Additives. In *Fire retardancy of polymeric materials*, Grand, A. F., Wilkie, C. A., Eds.; Marcel Dekker Inc: New York, 2000; pp 285-352.

134. Hornsby, P. R. Fire Retardant Fillers for Polymers. *International Materials Reviews* **2001,** *46*, 199-210.

135. Hornsby, P. R.; Rothon, R. N. Fire Retardant Fillers for Polymers. In *Fire Retardancy of Polymers - New Applications of Mineral Fillers*, Le Bras, M., Wilkie, C. A., Bourbigot, S., Eds.; The Royal Society of Chemistry: Cambridge, 2005; pp 19-41.

136. Hollingbery, L. A.; Hull, T. R. The thermal decomposition of huntite and hydromagnesite--A review. *Thermochimica Acta* **2010,** *509* (1-2), 1-11.

137. Kirschbaum, G. S. Huntite/Hydromagnesite - Mineral flame retardants as alterative and complement to metal hydroxides. 1998; pp 151-162.

138. Horrocks, A. R.; Smart, G.; Price, D.; Kandola, B. Zinc Stannates as Alternative Synergists in Selected Flame Retardant Systems. *Journal of Fire Sciences* **2009,** *27* (5), 495-521.

139. *Zinc stannates in halogen-free polymer formulations*;Technical Bulletin No.2; ITRI: 92.

140. Fire Retardant Effects of Polymer Nanocomposites. *Journal of Nanoscience and Nanotechnology* **2009,** *9*, 4478-4486.

141. Shen, K. K.; Kochesfahani, S.; Jouffret, F. d. r. Zinc borates as multifunctional polymer additives. *Polym. Adv. Technol.* **2008,** *19* (6), 469-474.

142. Troitzsch, J. *Plastics flammability handbook: principles, regulations, testing, and approval;* Hanser: 2004.

143. Shen, K. K. Borates As Fire Retardants - A Review, The Global Outlook for Environmentally Friendly Fire Retardant Systems. Missouri, USA, 1990.

144. Han, Z.; Dong, L.; Li, Y.; Zhao, H. A Comparative Study on the Synergistic Effect of Expandable Graphite with APP and IFR in Polyethylene. *Journal of Fire Sciences* **2007,** *25* (1), 79-91.

145. Avalos, F.; Ortiz, J. C.; Zitzumbo, R.; L≤pez-Manchado, M. A.; Verdejo, R.; Arroyo, M. Effect of montmorillonite intercalant structure on the cure parameters of natural rubber. *European Polymer Journal* **2008,** *44* (10), 3108-3115.

146. Wilkie, C. A. An Introduction to the Use of Fillers and Nanocomposites in Fire Retardancy. In *Fire Retardancy of Polymers - New Applications of Mineral Fillers*, Le Bras, M., Wilkie, C. A., Bourbigot, S., Eds.; The Royal Society of Chemistry: Cambridge, 2005; pp 3-15.

147. Liu, Q.; Zhang, Y.; Xu, H. Properties of vulcanized rubber nanocomposites filled with nanokaolin and precipitated silica. *Applied Clay Science* **2008,** *42* (1-2), 232-237.

148. Maiti, M.; Bhattacharia, M.; Bhowmick, A. K. Elastomer Nanocomposites. *Rubber Chem. Technol.* **2008,** *81* (3), 384-469.

149. Kumar, A. P.; Depan, D.; Singh Tomer, N.; Singh, R. P. Nanoscale particles for polymer degradation and stabilization--Trends and future perspectives. *Progress in Polymer Science* **2009,** *34* (6), 479-515.

150. Ye, L.; Wu, Q.; Qu, B. Synergistic effects and mechanism of multiwalled carbon nanotubes with magnesium hydroxide in halogen-free flame retardant EVA/MH/MWNT nanocomposites. *Polymer Degradation and Stability* **2009,** *94* (5), 751-756.

151. Ismail, N. I. N.; Singh M; Mustafam A; Ahmad, M. A. Some Properties of Carbon Nanotube Filled Natural Rubber Using Rubber Latex Masterbatch Technique. *Rubber Technology Developments* **2010,** 30-34.

152. Cusack, P.; Perrett, T. The EU RoHS Directive and its implications for the plastics industry. *Plastics, Additives and Compounding* **2006,** *8* (3), 46-49.

153. *European Chemicals Agency (ECHA)*; Candidate List of Substances of Very High Concern for authorisation (SVHC), http://echa.europa.eu/home_en.asp, 11.

154. Horrocks, A. R. Overview of Plastics, Flammability and Flame Retardancy. 2009.

155. ASTM D5289-07a. Standard Test Method for Rubber Property-Vulcanization Using Rotorless Cure Meters. 2007. ASTM International, West Conshohocken, PA, USA.

156. BS ISO 48:2007. *Rubber, vulcanized or thermoplastic. Determination of hardness (hardness between 10 IRHD and 100 IRHD)*. London, British Standard Institution.

157. BS ISO 2781:2010. Physical testing of rubber. Determination of density; British Standard Institution, London. 2010.

158. BS ISO 37:2005. Rubber, vulcanized or thermoplastic. Determination of tensile stress-strain properties. London, British Standard Institution.

159. BS ISO 34-1:2004. Rubber, vulcanized or thermoplastic. Determination of tear strength. Trouser, angle and crescent test pieces. London, British Standard Institution.

160. BS ISO 188:2007. Rubber, vulcanized or thermoplastic. Accelerated ageing and heat resistance tests; British Standard Institution, London.

161. BS 903-A6:1992, ISO 815:1991. Physical testing of rubber. Method for determination of compression set at ambient, elevated or low temperatures. London, British Standard Institution.

162. BS ISO 1817:2005. 2005. Rubber, vulcanized. Determination of the effect of liquids; British Standard Institution, London.

163. ISO 11345. Rubber - Assessment of carbon black and carbon black/silica dispersion - Rapid comparative methods.

164. ASTM D945-06. Rubber Properties in Compression or Shear (Mechanical Oscillograph); ASTM International, West Conshohocken, PA, USA. 2006.

165. BS ISO 814:2007. *Rubber, vulcanized or thermoplastic. Determination of adhesion to metal. Two-plate method*. London, British Standard Institution.

166. Flory, P. J. *Principles of Polymer Chemistry;* Cornell University Press: 1953.

167. ISO 11358:1997. *Plastics -- Thermogravimetry (TG) of polymers -- General principles*. Geneva, Switzerland, ISO.

168. BS ISO 9924-1:2000. *Rubber and rubber products. Determination of the composition of vulcanizates and uncured compounds by thermogravimetry. Butadiene, ethylene-propylene copolymer and terpolymer, isobutene-isoprene, isoprene and styrene-butadiene rubbers*. London, British Standard Institution.

169. BS 476-15:1993 ISO 5660-1:1993. Fire tests on building materials and structures - Part 15: Method for measuring the rate of heat release of products. British Standard Institution, London.

170. DD/CEN TS 45545-2. *Railway Applications-Fire Protection of Railway Vehicles*. 2009. Brussels, Belgium, European Committee for Standardization (CEN) .

171. Conesa, J. A.; Marcilla, A. Kinetic study of the thermogravimetric behavior of different rubbers. *Journal of Analytical and Applied Pyrolysis* **1996,** *37* (1), 95-110.

172. van Krevelen, D. W. Thermal Decomposition. In *Properties of polymers*, Third ed.; van Krevelen, D. W., Ed.; Elsevier: 1990; pp 641-653.

173. Byers, J. T. Silane coupling agents for enhanced silica performance. *Rubber World,* **1998**.

174. Cusack, P. Novel coated fillers enhance flame-retardant properties. *Plastics, Additives and Compounding* **2007,** (July/August), 26-29.