



# **A Discussion of Polymeric Materials for Fire-Safe Naval Applications**

*Enhanced Reliability, Fire and Damage Tolerance*

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Technical Memorandum

DRDC Atlantic TM 2007-051

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## Abstract

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Fire fighting is one of the most labour intensive operations aboard ship, and poses a significant threat to crew. The incorporation of fire-safe materials can reduce the threat by decreasing the likelihood of ignition or slowing the spread, should a fire start. The right choice of materials can result in smaller fires, requiring fewer crew to be at risk while fire fighting. This paper reviews shipboard fires on both commercial and non-commercial vessels. It discusses the mechanism for fire and how organic materials such as polymers undergo combustion, with emphasis placed on the typical polymeric fire loads on board: cable insulation/sheathing and textiles/furnishings. This review concludes with a survey of current efforts in fire/flame retardant materials. The recommended areas for future research include investigations into the mechanism of char formation, examination of nanocomposite materials based on nanometal hydroxides, exfoliated nanoclays and nanosized versions of traditional fire retardant additives, understanding polymer degradation mechanisms, and achieving a balance between mechanical properties, fire retardant properties and smoke inhibiting properties.

The goal of this review is to provide background on what is currently known about the fire properties of polymeric materials used in marine applications and to provide some insight as to what future research is relevant in a naval context.

## Résumé

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La lutte contre l'incendie à bord d'un navire constitue une des activités les plus exigeantes en main-d'œuvre, en plus de présenter des risques importants pour l'équipage. L'incorporation de matériaux résistant au feu peut réduire les risques, en diminuant la probabilité que l'inflammation se produise ou, du moins, en ralentissant la propagation de l'incendie, s'il se déclare. Le choix judicieux de matériaux adéquats peut permettre de réduire l'importance de l'incendie et, du même coup, le nombre de membres d'équipage exposés à des risques lorsqu'il faut combattre le feu. Le présent document contient les résultats d'une analyse des données disponibles sur les incendies pouvant se produire à bord de navires commerciaux et d'autres types. On y discute des différentes étapes du déclenchement et de la propagation d'un incendie et des mécanismes de combustion des substances à base de composés organiques comme les polymères ; l'accent est mis sur la nature et l'importance de la charge combustible typique constituée par les polymères à bord d'un navire, à savoir les matériaux isolants de câbles et ceux composant leur gaine, ainsi que divers textiles et meubles. On y présente enfin une liste des travaux en cours portant sur les matériaux ignifuges. Les domaines recommandés de recherches futures comprennent l'étude du mécanisme de formation des produits de carbonisation, l'examen de matériaux nanocomposites à base d'hydroxydes de métaux de dimensions nanométriques, de nanoargiles expansées et d'additifs ignifuges classiques de dimensions nanométriques, la

compréhension des mécanismes de dégradation des polymères, ainsi que les conditions qui permettent d'atteindre un juste équilibre des propriétés mécaniques, ignifuges et d'inhibition de la fumée des matériaux en question.

L'analyse qui fait l'objet du présent rapport a pour but d'offrir un survol des connaissances de base actuelles sur les propriétés ignifuges des matériaux polymères utilisés dans des conditions propres au milieu marin et de fournir un aperçu des recherches futures pertinentes dans le domaine naval.

# Executive summary

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## A Discussion of Polymeric Materials for Fire-Safe Naval Applications: Enhanced Reliability, Fire and Damage Tolerance

Royale S. Underhill, John Hiltz, Howard Moyst; DRDC Atlantic TM 2007-051; Defence R&D Canada – Atlantic; August 2007.

**Background:** The Canadian Navy has identified the reduction of through-life costs as a priority. One way to address this is through optimized crewing levels. One of the most labour intensive operations on board a ship is fire control. Effective fire suppression systems can reduce the amount of manpower needed to fight a fire. Fire suppression systems can be either active (*e.g.*, sprinklers, water mist, *etc.*) or passive (*e.g.*, fire resistant coatings, inherently non-combustible materials, *etc.*). This report considers the latter to address naval fire concerns, with emphasis placed on organic polymeric materials.

**Significance of Review:** This review discusses recent ship fires, summarizing their causes. It then goes on to cover the science of fire and how organic polymers burn. By understanding the mechanism of burning, one can hypothesize which physical characteristics are desirable for fire-safe materials. For example, char retards flame spread, thus slowing burning. By understanding the mechanism by which char forms, materials can be tailored to maximize this desirable reaction.

The two major polymeric fire loads on board a ship are cable insulations/sheathing and textiles/furnishings. By understanding how the products burn, one can explore new materials to reduce the fire load.

Gaps in the current fire literature are identified and fall under the main categories of understanding the mechanisms under which flame retardants work, developing more robust and processable flame retardant composites and improving the polymers with respect to environment limitations.

This review has identified a number of areas where materials research can impact fire-safe naval applications. The main topics include: (1) developing methods to predict char formation as a means to determine efficacy of a fire retardant material, (2) exploring nanocomposites to exploit the maximum fire retardant properties of new materials, (3) developing methods to evaluate and predict polymer degradation, which causes the polymer flammability to change over time and may affect overall fire loads, and (4) standardization of testing.

**Future Work:** As this report has shown, fire safe materials and an understanding of how materials respond to fire is of great importance to the Navy. The development of new materials combined with active suppression systems will help reduce the number of people needed to fight fires.



# Sommaire

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## A Discussion of Polymeric Materials for Fire-Safe Naval Applications: Enhanced Reliability, Fire and Damage Tolerance

Royale S. Underhill, John Hiltz, Howard Moyst ; DRDC Atlantic TM 2007-051 ; R & D pour la défense Canada – Atlantique ; août 2007.

**Introduction :** La réduction des coûts de cycle de vie de ses navires constitue une des priorités établies par la Marine canadienne. Pour atteindre ce but, on vise, entre autres, à optimiser les besoins en membres d'équipage. Les travaux de prévention et de maîtrise des incendies comptent parmi les activités les plus exigeantes en main-d'œuvre à bord d'un navire. Les systèmes efficaces d'extinction des incendies peuvent permettre de réduire le nombre d'intervenants requis pour combattre les incendies ; ces systèmes peuvent être de nature active (par exemple, des extincteurs automatiques, des dispositifs d'extinction par brouillard d'eau, etc.) ou passive (par exemple, des revêtements résistant au feu, des matériaux intrinsèquement non combustibles, etc.). Les données du présent rapport portent sur l'utilisation de ces derniers, plus particulièrement des matériaux polymères organiques, pour répondre aux préoccupations liées aux risques d'incendies à bord de navires.

**Portée de l'étude :** La présente étude comprend une discussion portant sur des incendies récents survenus à bord de navires et un résumé de leurs causes. On y traite aussi des connaissances scientifiques de base sur les incendies et des mécanismes de combustion des polymères organiques. La bonne compréhension de ce mécanisme permet de faire des hypothèses au sujet des caractéristiques physiques que doivent posséder de bons matériaux résistant au feu. Ainsi, les produits de carbonisation retardent la propagation des flammes et, de ce fait, ralentissent la vitesse de combustion. En établissant clairement le mécanisme de formation des produits de carbonisation, on pourra élaborer et fabriquer des matériaux sur mesure et optimiser cette réaction propice.

À bord d'un navire, les deux principales charges combustibles à base de polymères sont les matériaux isolants de câbles et ceux composant leur gaine, et les divers textiles et meubles. On peut se baser sur les connaissances sur la nature de la combustion de ces produits pour les remplacer par de nouveaux matériaux qui permettent de réduire la charge combustible totale.

L'ensemble des documents actuels traitant des incendies comporte certaines lacunes. On a identifié ces dernières, qui se classent dans les grandes catégories suivantes : la compréhension des mécanismes qui régissent le comportement des agents ignifuges, la mise au point de composites ignifuges plus solides et présentant une meilleure aptitude au traitement, et l'amélioration des polymères au chapitre des facteurs limitatifs relatifs à l'environnement.

L'étude faisant l'objet du présent rapport a permis d'identifier un certain nombre de domaines où les travaux de recherche sur les matériaux peuvent avoir des retombées en matière d'applications navales de sécurité-incendie. Les principaux sujets comprennent : 1) la mise au point de méthodes permettant de prévoir la formation de produits de carbonisation et de déterminer ainsi l'efficacité de matériaux ignifuges, 2) l'examen de nanocomposites afin de tirer le meilleur avantage des propriétés ignifuges de nouveaux matériaux, 3) la mise au point de méthodes permettant d'évaluer et de prévoir la dégradation des polymères, un phénomène qui entraîne, avec le temps, une variation de leur inflammabilité et qui pourrait influencer sur la nature des charges combustibles totales, et, 4) la normalisation des essais.

**Recherches futures :** Les données du présent rapport démontrent clairement que la détermination des propriétés des matériaux résistant au feu et la compréhension du comportement des matériaux en présence de feu constituent des connaissances d'une grande importance pour la Marine canadienne. L'élaboration de nouveaux matériaux et la mise au point de systèmes d'extinction des incendies de nature active permettront de réduire le nombre d'intervenants requis pour combattre les incendies.

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# 1 Introduction

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The Canadian Navy has identified as a priority, the reduction of through-life costs of its ships. Part of achieving this goal is an optimization of crewing levels. One of the most labour intensive operations is fire control. A fire on a ship is a major concern, which can occur under the least expected circumstances and timing. Aside from the human element in controlling a fire, there is a materials component. The first goal when considering fire-safe materials is to reduce the likelihood of ignition. The second goal is to reduce the spread of a fire should it start. For both these goals, inherently or engineered non-combustible materials play an important role.

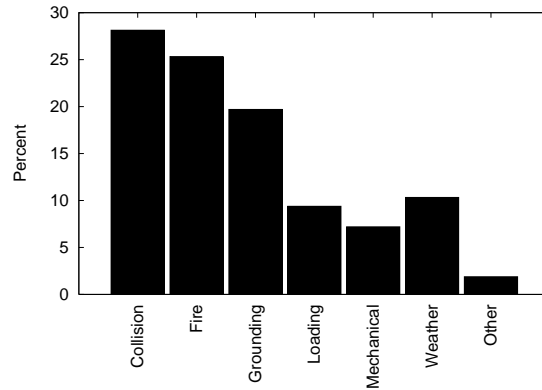
## 2 Background

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There have been a number of fires aboard both commercial and non-commercial vessels operating in Canadian waters. Canada's Transportation Safety Board (TSB) statistics indicate that over the past ten years there has been an average of 71 fire/explosion incidents per year. In 2004, fire/explosion incidents accounted for approximately 12.2 % of all shipping incidents [1]. Forty-one percent of these incidents occurred on commercial or "other" vessels. Commercial vessels include cargo vessels, passenger ships and ferries, tankers, barges, and tugs. "Other" refers to government, research, oil exploration, exploitation and support vessels, and pleasure craft. These numbers do not include naval vessels. Research into passenger ship accidents by Bichler-Robertson found that fire accounted for approximately 25 % of the events that resulted in casualties between 1950 and 1998 (Figure 1) [2]. Analysis of the 2003 International Maritime Organization (IMO) serious marine casualty statistics indicates that approximately 9 % of serious marine casualties were fire related incidents [3]. These statistics confirm that shipboard fires do occur and result in casualties, loss of life and loss of property.

The TSB has investigated a number of fire related shipping accidents over the past number of years. These include a roll-on/roll-off passenger ferry (the *Joseph and Clara Smallwood* [4]), a passenger vessel (the *Statendam* [5]), a shrimp factory freezer trawler (the *Katsheshuk* [6]), a bulk carrier (the *Windoc* [7]), an offshore platform supply and diving vessel (the *Thebaud Sea* [8]), and a container vessel (the *Kitano* [9]). These accident reports provide insight into the circumstances that surround the initiation and propagation of a shipboard fire and the measures that could assist in the prevention or mitigation of such an event. Each of the accident reports is a valuable source for "lessons-learned" in risk prevention.

The fire on the *Joseph and Clara Smallwood*, occurred on a vehicle deck in or around a tractor-trailer [4]. The firefighting effort was praised and it was noted that the deluge system was effectively utilized to contain the fire. Even though boundary cooling was applied, the



**Figure 1:** Nature of events resulting in passenger ship casualties 1950-1998. (adapted from ref. [2])

fire caused damage to the thermal insulation, buckled the deck above the fire, and damaged various electrical fixtures including heat detectors and local wiring. The fire created thick smoke that contributed to 4 minor smoke inhalation injuries out of a total of 218 people aboard. The fire fighting effort brought the fire under control within 180 min and was declared out 265 min from the time it was first sensed. After the fire was discovered, the ship proceeded to dock at Port aux Basques, where it received additional firefighting support from the local volunteer fire department. The deck above the fire was designed to comply with an A60 fire rating, which required thermal insulation. The material details were not reported, but an A60 division retards the transmission of heat so that the average temperature on the unexposed side of the boundary does not exceed 139°C over a period of 60 min (see Table 1).

In another incident, the passenger ship *Statendam*, experienced a fire in the main switchboard room when a diesel generator circuit breaker failed with a violent release of energy [5]. The generated electrical arc damaged circuit breakers, relays and switchgear on either side, above and below, and vapourized the bus bars in the immediate vicinity. There was

**Table 1:** Structural and thermal fire boundary [5]

Structural Boundary	Thermal Boundary			
	0 min	15 min	30 min	60 min
0 min	C <sup>a</sup>	-	-	-
30 min (flame only)	B-0	B-15	B-30	-
60 min (flame and smoke)	A-0	A-15	A-30	A-60

<sup>a</sup>must be noncombustible

also damage to high tension, control and electrical cables beneath the Engine Control Room (ECR) deck plates; most likely a result of radiant heat transmitted from the Main Switchboard Room (MSR) to the ECR through the deck head. There was no thermal insulation on the MSR deck head, nor was it required by regulation. The fire in the ECR was extinguished immediately and MSR fire was doused in 65 min. The fire produced dense black smoke and created poor visibility for the firefighting team in the MSR. There were no reported injuries. Two relevant and significant factors arising from this report were that there was no thermal insulation between the MSR and the ECR and the MSR was not fitted with a CO<sub>2</sub> fire suppression system. The TSB report also identified five other instances where fires had occurred on passenger ships [5]:

- *Regent Star* (1990), which was disabled in the Delaware River, USA .
- *Celebration* (1995), where the fire was extinguished by a fixed halon system.
- *Sun Vista* (1999), which sank after all passengers and crew abandoned the ship in the Malacca Strait.
- *Columbia* (2000), which was disabled southwest of Juneau, Alaska.

As stated by the TSB, a fire once started can spread rapidly and exponentially. The report stressed the importance of structural fire protection and fixed-extinguishing systems to restrict and extinguish a fire [5]. These were not the only fire incidents, but have been summarized here to illustrate some of the issues involved when fires occur at sea.

Naval vessels also experience fires, and although the examples discussed previously occurred on civilian ships, the concerns they raise can be extrapolated to naval vessels. The example of the *Joseph and Clara Smallwood* illustrated how fire loads can change with the addition of cargo. The ferry was specifically designed to carry vehicles. This is relevant to the navy because future naval vessels may have a requirement to carry vehicles, while current naval vessels store payloads on exterior and interior decks. Payloads, containers and/or vehicles can be a source of increased fire load. On an exterior sweep deck the significance of a fire incident would depend on a number of factors including the thermal insulation protecting the compartments below, and the firefighting capacity of the crew. The consequences of a fire event increase when the payload is stored below deck.

Between 1994 and 2004, the CF Navy Damage Control School reported 120 fires [10, 11]. Examples of fires aboard naval vessels include engine fires and electrical fires. The most publicized, was the recent tragedy on the *HMCS CHICOUTIMI*. This was precipitated by inadequate electrical cable sheathing [12]. Other nations have experienced naval ship fires. The Royal Navy reported over 1,726 fires on naval ships between 1983 and 1989, costing approximately 6,790,000£ [13]. One hundred and eighty two (182) of these were electrical fires [13]. In the U.S., the *USS Tattnell* (DDG-19) experienced a fire originating in a locked compartment, resulting in the loss of life and preventing the ship from carrying out

its mission [14]. The cause of the fire was attributed to cableway discrepancies. Follow-up surveys on other ships found that 15 % to 20 % of all dead end cables were still electrically energized. Based on the literature, electrical faults are the most frequent source of fires on naval combatants in non-combat situations. The U.S. Navy Integrated Deckhouse Program reported that the major fire sources for naval ships were electrical, followed by matches/smoking, open flame/welding/hot work, and arson [15]. The majority of these fires occurred in the engineering spaces followed by storerooms and crew living spaces.

Although these are a small sample of maritime fire investigation reports, the importance of using methods to prevent ignition and retard the progression of fire throughout the ship, as well as the difficulties the crew encounter with smoke while firefighting, are common themes. Materials can make a positive contribution to the prevention of fire incidents by retarding the ignition and spread of a fire and reducing the production of smoke. The objective of this report is to investigate passive material systems to improve naval combatant fire safety through preventative measures. Investigating materials that can reduce the ignition and spread of fire through a ship mitigates the loss of property [16], and the potential for fatalities and injuries [17]. Seventy-five percent of fire related deaths are caused by the inhalation of smoke and toxic combustion gases, such as carbon monoxide [18]. Addressing material properties to reduce or eliminate the production of these gases is essential.

In this report, research aimed at developing materials that prevent or retard the ignition and spread of fire and the generation of smoke are reviewed. The work focuses on polymeric materials used in cable insulation/jackets/sheathing and furniture/furnishings. Fire retardant materials used in marine applications are compared to those used in other industries, such as the aeronautical or nuclear power industries. An assessment of the gaps where materials research could/should be focused to develop passive fire retardant systems for naval combatant purposes has been included.

This review was designed to act as a foundation for more specific and comprehensive research into the topics identified.

### **3 The Science of Fire**

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Combustion is a rapid, oxidative process requiring fuel, an oxidizing agent (typically oxygen) and energy. In a ship, the structure and contents serve as the fuel; oxygen from the air acts as the oxidizer. The three stages to initiate combustion are heating, thermal decomposition and ignition of volatile components. The basic sources of ignition are chemical, electrical or mechanical. Chemical based sources usually lead to spontaneous combustion. Electrical fires originate from induction, dielectric processes, arcing, and/or static electricity. Mechanical sources of ignition are typically from heat due to compression or friction.



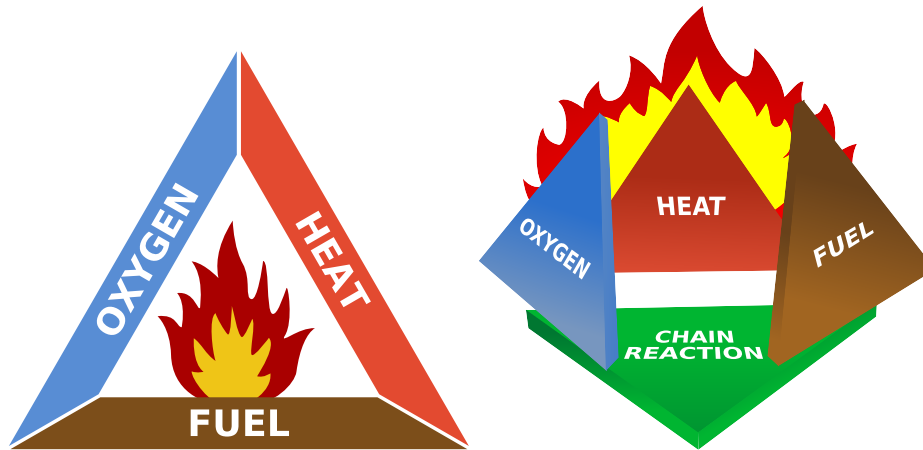
The flammability behaviour of a material can be described by a number of factors, such as [19]:

- Ease of ignition or how readily a material ignites.
- Flame spread or how rapidly fire spreads across a surface.
- Fire endurance or how rapidly fire penetrates a wall or barrier.
- Heat release rate (HRR) or how much heat is released and how quickly.
- Ease of extinction or how rapidly/easily the flame chemistry leads to extinction.
- Smoke production; the amount, evolution rate and composition of smoke during the stages of a fire.
- Toxic gas production; the amount, evolution rate and composition of gases released during the stages of a fire.

Fires can be classified by the combustion process, rate of growth, basis of ventilation, or fire stage. Material properties have a great effect on the ignition and heat released by a fire. These material properties include temperature resistance, decomposition temperature, mode of decomposition, softening temperature, flash-ignition temperature, rate of heat release, oxygen index, and heat of combustion.

Two models used to describe the combustion process (primarily used in firefighting) are the fire triangle and fire tetrahedron, shown in Figure 2. The three main constituents of the fire triangle are fuel, energy (such as heat), and oxidant (typically oxygen). Although the fire triangle is useful, it fails to identify the fourth, essential element of fire: the sustaining chemical reaction (see the fire tetrahedron shown in Figure 2b). As defined by Faraday's experiments with a candle [20], there are four types of fire processes: 1) diffusion controlled flaming, 2) smouldering 3) spontaneous and, 4) premixed flaming combustion. In typical fire scenarios, one encounters diffusion flames, spontaneous combustion and/or smouldering. A burning match, or building fire are examples of diffusion controlled flaming combustion. The diffusion flame is a result of oxygen diffusing into the gaseous fuel. This type of combustion requires a pilot flame such as a flame, spark, electrical arc, or glowing wire, to initiate combustion of a material or its vapours. Smouldering combustion is the oxidation of a solid without a flame, which usually results in an increase in temperature and/or the production of smoke. Spontaneous combustion or ignition is the process by which oxygen combines slowly with the fuel, usually at its surface, with the slow evolution of heat energy [21]. The fire starts when the material reaches its ignition temperature. In a premixed flame the gases required for combustion are premixed, then ignited (*e.g.*, an oxy-acetylene torch).

There are a number of different ways to consider fires. These include fire load, fire growth/spread or heat release rate. The fire load (fuel) of a ship compartment is the mass



**Figure 2:** Fire models: (a) Fire Triangle [22](reproduced under the GNU Free Documentation License), (b) Fire Tetrahedron [23](author released this image for use to the public domain)

of combustible material per square metre of floor space ( $\text{kg}/\text{m}^2$ ) [16]. This characterizes the hazard of a space by estimating the length of time that a space is expected to burn. This assumes that ignition has taken place and the fire has reached the point of established burning. Fire growth and spread also assumes burning has been established and the energy produced by the initial fire determines if the fire will spread beyond a compartment. Heat release rate (HRR) is defined as energy released per unit time (J/s or Watts). HRR is the single most important variable in describing fire hazard because it is the driving force for fire, most other variables (such as smoke and toxic gas generation) are related to HRR, and HRR numbers can be directly related to threat of life.

The material used to outfit a compartment with the necessary décor and furnishings is a major contributor to fire load. The other aspect of fire load is material brought on by the crew. Polymeric materials, such as those within bedding, furnishings, computers, televisions, floorings, bulkhead and ceiling materials, and cable sheathings, are a significant contributor to the fire load. A modern naval combatant uses many electrical and electronic components. It can have over 100 tons of cable, potentially providing 50–75 tons of insulating and shielding materials to a ship's total fire load [13].

## 4 Polymeric Materials and Combustion

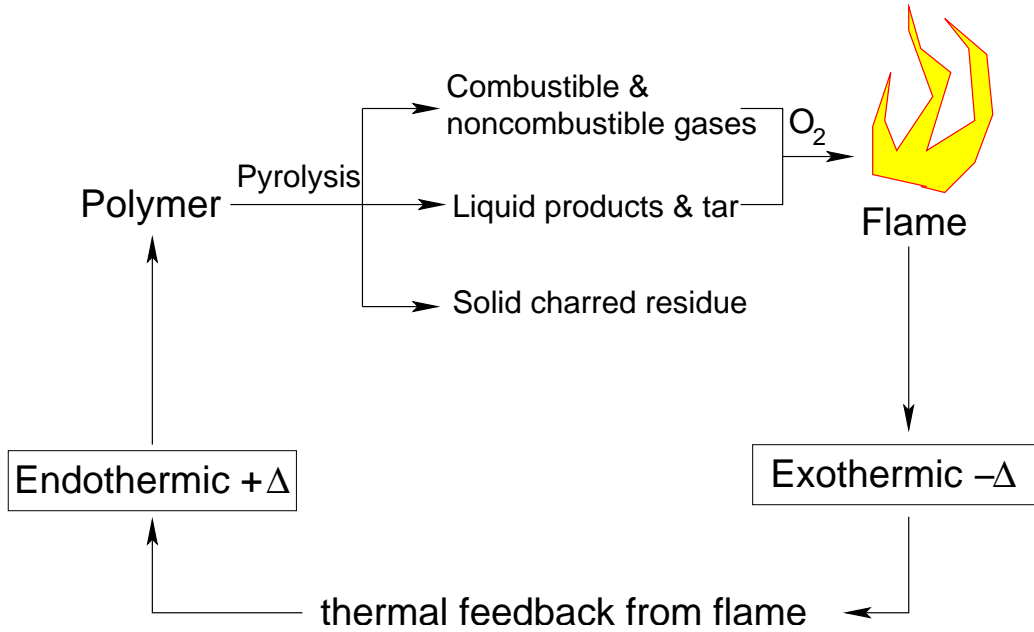
Materials can be classified into four main groups: metals, polymers, ceramics, and composites. Depending on the application, desirable material characteristics include; availability, low cost, energy efficiency, strength, stiffness, and dimensional stability at operating temperatures, low density, corrosion resistance, fire resistance, environmental-friendliness and biodegradability [24].

The selection of a material for an application is a complex process, involving an understanding of the many relationships that exist between design, performance characteristics, manufacturing processes, and cost. Therefore, selecting or evaluating currently used materials and potential replacements for fire retardant applications is a complex process, especially when considering fire properties such as burning behaviour, fire gas composition, and smoke development. The way a material burns depends on many factors. These factors include the chemical composition, phase (solid, liquid or gas), physical form (size and shape), and degradation mechanism(s) of the materials, its ability to form char, the thermal conductivity, heat release rate, moisture content, melting and ignition temperatures, and net heat of combustion of the material, ventilation and environmental conditions, source of ignition, and materials configuration during ignition and combustion [21].

Polymers, or macromolecules, are long-chain molecules of very high molecular weight and can be either natural (*e.g.*, wool, cotton, starch) or synthetic materials (*e.g.*, nylon, polyethylene, polymethyl methacrylate). A typical organic polymer has chains containing between 1000–5000 carbon atoms. If macromolecules contain oxygen, nitrogen or halogens, these heteroatoms change the chemical composition and therefore burning characteristics of the material. Hydrocarbon plastics, such as polypropylene, polyethylene, polybutadiene, or polystyrene, contain only carbon and hydrogen and burn hotter than the plastics containing heteroatoms because the entire molecular chain can be consumed as fuel [21]. In general plastics containing oxygen burn slower. This is because oxygen replaces some of the fuel that would be available on the hydrocarbon molecular chain. However, there are exceptions such as polyacetal and cellulose nitrate. Both of these polymers contain oxygen in their backbones, but are highly flammable. Zhang claims the ideal fire retardant polymer has a high decomposition temperature, a low volatile release rate, a low heat of combustion of those volatiles, high char yield, an endothermic phase transition or decomposition, and releases a chemical flame retardant chemical species (halogen, water, *etc.*) [25].

Organic polymers can degrade due to several specific processes, such as weathering from photo-oxidation, fatigue and melt degradation through mechano-oxidation, and through flammability and ablation in pyrolysis and vapour phase oxidation [26]. The polymer burning process can be represented in a number of ways. The general polymer burning process is illustrated in Figure 3 [25].

A polymer undergoes combustion when there is sufficient energy in the form of heat to facilitate either decomposition or pyrolysis. The heating source can be radiant energy, a flame, or the thermal feedback from an already ignited fire, as shown in Figure 3. Thermoplastics will soften and start to flow when exposed to the initial heat, whereas thermosetting plastics will not. Depending on the polymer structure, the decomposition temperatures vary within certain limits and these limits vary if the polymer is compounded with additives. Decomposition or pyrolysis results in the release of volatile organic compounds that can subsequently be ignited. The flammable products that evolve from the polymer during heating mix with the oxygen in the air and when their flammability limit is reached,



**Figure 3:** Polymer burning process. Adapted from ref. [25].

they ignite in the presence of a flame or spark. Ignition depends on variables such as oxygen availability, temperature, and the polymer's physical and chemical properties. Once ignition has taken place, the burning process is exothermic. If sufficient energy is produced, it will overcome the endothermic requirements for polymer decomposition/pyrolysis, and flame spread will be initiated.

Flame spread occurs when there is sufficient heat to sustain the polymer decomposition/pyrolysis process. The diffusion flame will advance along the surface of the material and the extent of flame spread will be affected by the heat of combustion of the polymer. The heat of combustion represents the total energy that is released during the complete combustion of the material. The greater the heat of combustion the greater amount of heat liberated into the flame to sustain the burning cycle. In general the combustibility of a material correlates with its heat of combustion, however some polymers such as cotton have combustibilities that do not directly correlated with the heat of combustion (*e.g.*, cotton has a low heat of combustion but is very flammable). Price *et al.* [27] show that the rapid flame spread from gas-phase reaction is controlled by the diffusion flame and the slower oxygen limited processes are responsible for the generation of smoke, soot and carbon like residues.

## 4.1 Retarding Fire

Fire suppression systems are designed to disrupt the constituents of fire as shown in Figure 2b by cooling the fire, displacing oxygen, and/or inhibiting the chemical reaction in the flame. Suppression systems can be water, gas and/or foam based. Retarding the ignition

or flame spread of polymer materials would allow a wider use of these materials. Flame-retardants can be effective by [27]:

- Reducing the heat evolved to below that required to sustain combustion.
- Modifying the pyrolysis process to reduce the release of flammable volatiles.
- Promoting the formation of less flammable insulating char.
- Forming a layer that isolates the polymer degradation products from the oxygen/air supply.
- Releasing flame inhibitors such as halogens that interfere with the pyrolysis process (*i.e.*, radical scavenging which interferes with the polymer degradation process)
- Reducing the heat flow back to the polymer (*i.e.*, reducing the amount of energy given back to the endothermic pyrolysis reaction).

Flame retardant processes used to suppress polymer ignition or flame spread are discussed in Horrocks and Price, Troitzsch, and Zhang [17, 25, 28].

Less flammable polymeric materials can be developed only through understanding thermal degradation and decomposition. Key areas that must be addressed include polymer thermal degradation and decomposition kinetics, material degradation and decomposition, the dynamics of heat and mass transfer, and the experimental study of the degradation and decomposition behaviours [29].

## 4.2 Char

An important process that assists in retarding flame spread is the development of char. An ideal char is comprised of an intact structure of closed cells containing pockets of gas. This porous structure prevents the evolution of flammable vapours (from polymer degradation) into the flame. In addition, it forms an insulating layer that keeps the polymer solid or melt below its decomposition temperature. Some of the more important properties of char are density, continuity, coherence, adherence, oxidation resistance, thermal insulation, and permeability. Low density, high porosity chars tend to be good thermal insulators and can significantly inhibit flow of heat from the gaseous combustion zone back to the condensed phase, thereby slowing the thermal decomposition process [30].

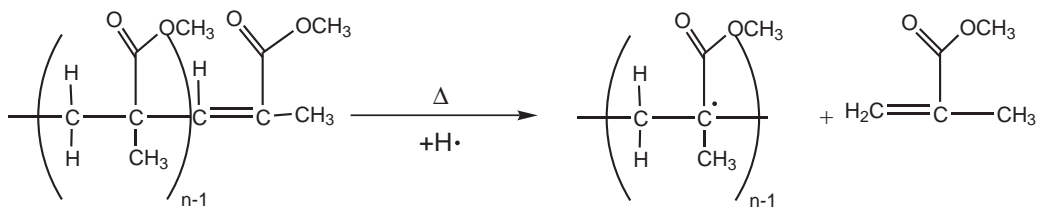
Although the process whereby char forms is not fully understood, a number of factors influence char formation. These include the polymer melt viscosity, surface tension at the melt-gas interface, the kinetics of gasification, polymer crosslinking and the polymer degradation mechanism. Char forms between 300–1500°C . A polymer passes through several steps during the formation of char: crosslinking, aromatization, fusion of aromatics,

turbostratic char formation and graphitization [31]. Generally, polymers degrade through free-radical processes initiated by bond dissociation at elevated temperature. There are four main processes for degradation; random chain scission, depolymerization (unzipping), side-group elimination, and interchain condensation [32]. The first two processes occur in polymers where the weakest bonds are in the backbone of the polymer. A polymer which undergoes chain scission experiences random breakage of chemical bonds, producing fragments of the original polymer. Depolymerization involves a reverse polymerization, yielding the monomer (see Figure 4). The final process applies to polymers where the weakest bonds are those attaching the pendant groups. Side-group elimination removes pendant groups, leaving unsaturated polyolefins that can further decompose to form aromatic compounds (see Figure 5).

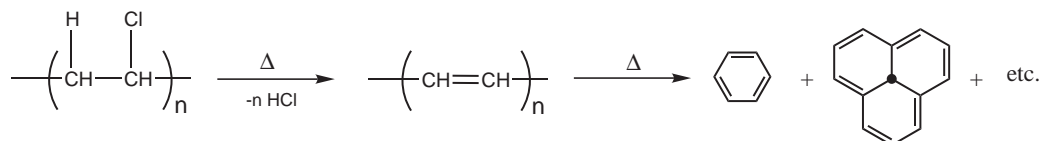
Based on the chemical processes governing thermal degradation, polymers can be classified by the amount of char that forms. Polymers that degrade by chain scission and depolymerization produce minimal amounts of char (*e.g.*, polyethylene (PE), polypropylene (PP), and polymethylmethacrylate (PMMA)). Polymers that degrade through side-group elimination, produce moderate amounts of char (*e.g.*, polyvinyl chloride (PVC), polyvinyl acetate (PVA), polyacrylonitrile (PAN)). Polymers that produce moderate to high levels of char typically contain aromatic rings from interchain condensation that can crosslink simultaneously with chain scission reactions (*e.g.*, Kevlar, Nomex, aromatic polyamide (PA), polyphenylene sulfide (PPS), polycarbonate (PC), polyimide (PI)) [31].

There are a number of different ways to take advantage of char producing materials. In the best case, the polymer used is inherently a good char producer, but when this fails changes can be made to either the polymer or by using additives to improve char production. Char production can be improved by enhancing the polymer's thermal stability, increasing the rate of the reductive coupling mechanism, altering the oxidative dehydrogenation mechanism or reducing the concentration of volatile fuel components at the surface of the polymer.

Aromatic polymers tend towards higher thermal stability than vinyl polymers or aliphatic polymers containing heteroatoms. Aromatic moieties in the backbone of the polymer (*e.g.*, polyphenylene oxide), increase char yield over polymers with pendant aromatic groups (*e.g.*, polystyrene) that can produce a lot of smoke when burning. Halogenated polymers containing backbone aromatic groups usually produce more char than their non-



**Figure 4:** Depolymerization (unzipping) of polymethylmethacrylate (PMMA)



**Figure 5:** Side-group elimination of polyvinylchloride (PVC)

halogenated counterparts. Studies have shown that the more aromatic and more compact the char, the more stable it will be due to the chemical structure and morphology of the char being more resistant to thermo-oxidative degradation. When polymers based on aromatic moieties are not desirable, cross-linking has been shown to increase thermal stability of polymers and enhance char formation.

In polymers that produce minimal char, additives are frequently used to enhance char formation. Inorganic metal-containing additives catalyse char formation by catalysing reductive coupling. For example, low-valent metals such as copper and its salts cause reductive coupling of PVC to form very significant amounts of char. Smoke production from the burning of PVC can be suppressed with the addition of transition metal oxides, which also promote char formation via the reductive coupling mechanism. Iron compounds reduce flammability and smoke production in PVC and PVC/ABS blends and have a synergistic effect in both halogen containing and halogen free fire retardant systems. Tin compounds have also been used as condensed and vapour phase fire retardants in the presence of halogenated compounds [31].

Chars obtained under pyrolytic conditions are different from those obtained when thermal degradation occurs in vacuum or under an inert atmosphere. Oxidative dehydrogenation is an important step in char formation [31]. Partial oxidation forming hydroxyl-, peroxy-, or ketonic groups that can then be eliminated through dehydration also aid in fire retardancy. It is believed that oxidative dehydrogenation catalysts have potential as additives to improve the fire-retardant properties of polymers. Oxidative dehydrogenation catalysts accelerate char formation under oxidative conditions only and have no value as heat or mass transfer promoters.

Silica gel and  $\text{K}_2\text{CO}_3$  have been shown to be effective fire retardant additives with the ability to increase char yields for many polymers. The silica gel accumulates near the sample surface forming a barrier stopping volatile components leaving the surface of the polymer [33]. Silica gel can reduce the HRR of a polymer [33].

There have been extensive studies on the mechanisms of action of various phosphorus containing fire retardants. The additives function in both the gas and the condensed phases where the additives degrade to phosphoric acids. There are a number of mechanisms by which phosphorous-based additives work. They can crosslink with the polymer to limit the volatilization of polymer and the diffusion of oxygen to the polymer surface, degrade endothermically, or scavenge radicals. There is some evidence that polymers that are

sensitive to acids decompose at lower temperatures. This may be beneficial if it results in the rapid accumulation of protective surface char layer.

NASA Langley Research Centre has investigated high performance polyimide foams as candidate materials for acoustic and thermal insulation, gaskets and seals, and other applications [34]. Polyimides are inherently flame retardant because of their aromatic and heterocyclic structures which result in char formation [28]. Char is formed during thermal decomposition and can offer various roles in fire retardancy, including: insulating capability to the base polymer, trapping of free radicals, or releasing additives to enhance char formation. Williams *et al.* found that changes in the surface area or cell structure of the foams have a large affect on the flame retardant properties [34]. A polyimide formulation noted as TEEK-CL had the lowest surface area, the lowest HRR and the highest thermal stability [34]. This is an active area of research.

The study of char formation is an active area of polymer science research. However much work has yet to be done to understand how char formation improves the fire properties of a polymer materials fire properties. Further study is needed to better understand char formation and thermal stability [31], and the chemical reactions that occur at high temperatures [34].

#### **4.2.1 Intumescent Materials**

Intumescent materials swell when exposed to heat and literature suggests that they can be used to improve the fire resistance of polymeric materials [35–37]. Intumescent tend to be silicate hydrate materials that release water when heated. The water vapour acts as a blowing agent, causing the softened silicate structure to foam, forming a hardened ceramic once the water is released. The ceramic remains solid until it reaches its glass-softening point [37]. The benefits of intumescent materials are the temperature-control and the formation of a swollen char capable of insulating/protecting the underlying material from the action of the flame. It is believed that the char acts as a physical barrier, protecting the polymer against heat transmission, diffusion of oxygen toward the surface and diffusion of combustible degradation products of the polymer away from the surface, outward toward the flame. The vapour released is only water, thus reducing the presence of toxic fumes. In addition, the char formed slows fire propagation by preventing the polymer from dripping and decreasing flame-feeding requirements during pyrolysis. This contributes to flame extinguishment. General reviews of intumescent systems are discussed in Grand and Wilkie [38] and Horrocks and Price [17]. The most common intumescent coatings have been based on alkali silicates. Unfortunately these coating have limitations: sodium silicate and potassium silicate react with carbon dioxide, causing the coating to lose its intumescent properties and become brittle, and lithium silicate coatings are not reactive to carbon dioxide, but have inherently lower intumescence and form brittle coatings. Langille and Nguyen in collaboration with DRDC Atlantic have developed an intumescent coating based on combined sodium silicate/potassium silicate/lithium silicate that provides



increased environmental stability and a higher degree of intumescence over any of the three components individually [37]. Camino and Delobel have described the chemistry of ammonium polyphosphate pentaerythritol [39]. Camino and Lomakin concluded that the prediction of the effectiveness of intumescent systems is difficult and that the fire performance of the resulting foamed char is not yet understood [40]. In fact there is limited understanding of the physical and chemical mechanisms of intumescence.

### 4.3 Smoke and Combustion Gases

Smoke hampers firefighters and can increase escape time for persons in a burning space. Increasing the time required for escape increases the hazard from combustion gases and heat. It is important to distinguish between smoke and combustion gases. Smoke can be defined as a cloud of particles individually invisible but due to light scattering and/or absorption of light the particles appear opaque. Combustion gases are gaseous molecules; predominantly carbon monoxide, carbon dioxide, hydrogen cyanide, nitrogen oxides, hydrogen chloride and sulfur oxides resulting from the degradation (oxidative or pyrolytic) of the substrate.

Smoke is the result of incomplete combustion of the polymer fuel. Coaker *et al.* describe soot formation and the chemistry of flames in reference [41]. It is important to understand that the species formed during pyrolysis are a major factor in smoke formation. That is, smoke is not an inherent property of the material. The production of smoke is dependent on the burning conditions and the amount of material burnt and as such, no single test gives a comprehensive representation of smoke production from a polymer in a fire. Various tests for smoke production exist, but are of secondary importance to other flammability tests. The understanding of smoke production tendencies of specific polymeric materials is however, very important as it is a major fire hazard that creates fear, slows down the rate of escape, and hampers the firefighting effort. The inhalation of smoke and combustion gases, predominantly carbon monoxide, is the main cause of death in fires.

The cone calorimeter is a common test apparatus used to provide an indication of the smoke generated by a specific polymer. Despite standardized tests, results may vary from lab to lab [42]. Results are complicated due to polymers having different additives that may influence the flammability properties of the material and its tendency to produce smoke. A polymer's flammability and ability to produce smoke is influenced by its chemical structure. In general, polymers that are largely aliphatic and contain oxygen have a tendency toward low smoke generation [27]. On the other hand, polymers containing double bonds or polyenic backbones and those with pendant aromatic groups decompose, yielding smoke. Poly(vinylchloride) and poly(vinylidene chloride) are exceptions to these rules. Although they contain unsaturated backbones, their decomposition products are stable, resulting in little smoke formation.

## 5 Cable Insulation, Jackets or Sheathing

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The fire on the *Statendam*, in the Main Switchboard Room (MSR) was caused by an electric arc [5]. The arc vapourized the bus bars inside the cabinet and significantly damaged control and high-tension cables. The investigation report concluded that the spread of the fire to the Engine Control Room (ECR) was due to radiant heat from the MSR igniting cables located in the space above the deck head and below the ECR false floor. In this case, there was no regulatory requirement for thermal insulation to be installed between the spaces. This is a case in point where additional thermal insulation, beyond regulatory requirements, may have assisted in the prevention of fire spread.

The recommended practise for marine electrical cables for use on ships and fixed or floating platforms are delineated in IEEE STD 1580-2001. For military platforms, various U.S. Military Standards can be sourced (*e.g.*, MIL-C-28661, MIL-M-20693, MIL-C-137776, DOD-STD-2003-3). IEEE Std 1580-2001 recommends that cable insulation types be polyvinyl chloride, polyvinyl chloride/nylon, ethylene propylene rubber, crosslinked polyethylene, low-smoke, halogen-free crosslinked propylene rubber, low-smoke, halogen-free cross-linked polyolefin, silicone rubber, or crosslinked polyolefin. The recommended cable jacketing materials are polyvinyl chloride, neoprene, chloro-sulfonated polyethylene, chlorinated polyethylene, crosslinked polyolefin, or polyolefin. The recommended minimum material properties for these materials can be found in the standard. MIL-C-28661 is a specification for insulated, shielded, high voltage power cable. The specification calls for crosslinked polyethylene, ethylene propylene rubber, or high molecular weight polyethylene. Cable sheathings are specified to the National Electrical Manufacturers Association (NEMA) standards WC5 or WC7. There are many cable and electrical installation standards available through ASTM, MIL, NEMA, Underwriters Laboratories (UL), International Electrotechnical Commission (IEC), American Petroleum Institute (API), and the Canadian Standards Association (CSA). Many of these are cross-referenced. Assimilating these standards and specifications into a single document for design and construction is a major task. It raises the question: *How much effort is spent considering the fire protection properties of insulation and sheathing of materials during the selection of a cable system for an application?*

The literature on fire resistant electrical systems and components has focused on developing fire retardant materials for electrical sheathing/jackets, assessing fire performance of electrical cabinets, and the impact on plant operations and safety. This is a concern to many industries, not just the military. The nuclear power industry has actively investigated electrical cabinet fires. There have been a number of electrical fires in nuclear plants around the World. The U.S. Nuclear Regulatory Commission initiated research into power plant fire incidents, some of which have led to cable failures and operational challenges including loss of power to various plant systems [43].

Small and large electrical cabinet fires, the potential for a fire to spread to adjoining

cabinets, and the impact on a room's environment are the biggest concerns in the US Nuclear Regulatory Commission review [44,45]. In many of the tests, the fire was initiated under a cable or wire bundle and the HRR, mass loss, carbon dioxide, carbon monoxide, and smoke production rates, and gas and wall temperatures in the cabinets were measured as a function of time. The conclusions from these studies are summarized below:

- Where flashover occurred within the cabinet, the maximum HRR was 100-350 kW [44].
- The test results were dependant on ventilation conditions, cabinet structure, the fire loading and location of fire loads within the cabinet, mechanical locking mechanism failures, and gaps in the cabinet walls [44].
- Experiments using real cabinet/cable set-ups were performed to determine the lowest ignition power needed to initiate an established burn. The individual cable required 0.5 kW for 4.5 min (150kJ), while the bundle required 3.2 kW for approximately 10 min (1.9 MJ) [44]. These data suggest thicker and tighter bundled cables require higher ignition energy.
- Fire spread occurred via several mechanisms. The most common involved molten plastic flowing across a corridor or dropping under a cabinet or false floor [44]. Therefore, secure containment of the bottom of a cabinet becomes a very important design and construction characteristic.
- Cables that do not pass flame spread test standards easily ignite and propagate the fire onto other combustible materials. Fire qualified cables within the cabinet were more difficult to ignite and were less likely to sustain a fire but a fully involved cabinet fire was possible [45].
- Peak fire intensities were as high as 1300 kW, and were reached within 10 min. Handheld extinguishers were found to be ineffective 5 minutes after ignition, which emphasized the need for early suppression. Twenty feet above the cabinet fire, the peak ceiling temperature was observed to reach a high of 262°C [45]. The peak temperatures within the cabinets were found to depend on the size of the enclosure and the ventilation rate provided throughout the fire.
- Smoke build up and deposition of soot was found to be a problem within the cabinets. Visibility was obscured within 6–15 min [45].
- Smoke and heat pose a significant risk to circuitry in adjacent cabinets and it is anticipated that control components would experience calibration drifts or failure at the temperatures observed [45].

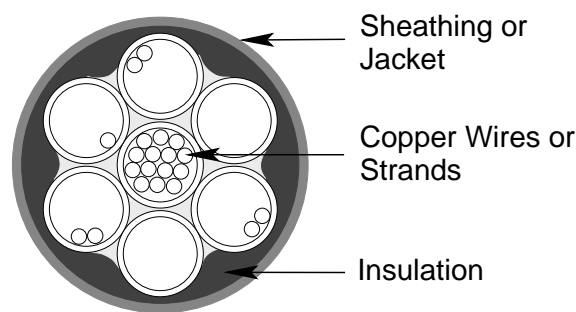
Cables are often qualified using full-scale cable tray tests. The cable sheathing or jacket material is the main concern, followed by its insulation and the filler (Figure 5). Cable

sheathing typically contains a halogen, such as chlorine, which has become an environmental concern when a fire occurs. The concern is the generation of toxic and corrosive by-products such as HCl, during and after the fire. Smoke and soot toxicity and their potential affect on other shipboard materials and electrical components long after the fire cleanup are also of concern. A fire on a new British submarine in 1976 resulted in scrapping the entire ship because of the long term economic and safety risks associated with the potentially affected equipment and cable/electrical insulation. In particular there was concern that corrosive compounds had condensed onto or absorbed into the materials and/or critical equipment surfaces [13]. This is a very real concern aboard the *HMCS CHICOUTIMI*.

Fei *et al.* investigated cable fires in a plenum, simulating communication cable insulated with high-density polyethylene (HDPE) and sheathed with linear low-density polyethylene (LLDPE) [46]. The plenums in this case were compartments or voids used for the distribution of circulating air for heating and air conditioning. They are typically between a structural ceiling and a suspended ceiling or under a raised floor. The objective of the tests was to simulate potential fire hazard scenarios caused by active and/or abandoned cables in plenums representative of realistic practises occurring in buildings. The tests indicated that cables in plenums present a large fire hazard even at relatively low fire loads.

Fire performance testing of polymer cable insulation/jackets or polymer materials used in electrical applications (*e.g.*, enclosures), is an active area [41, 47, 48]. Toxicological and environmental factors are driving the investigation of alternative fire retardants to replace halogenated materials. Some alternatives currently being explored include red phosphorous, melamine polyphosphate, and their combination in high impact polystyrene [48]. High impact polystyrene is used for electronic enclosures. Braum and Schartel demonstrated that the combination of melamine polyphosphate and red phosphorous reduced the HRR, the average steady HRR, and the total heat evolved per unit mass of polymer loss, but there was an increase in smoke and carbon monoxide production [48]. The reduction in HRR was achieved through reducing the efficiency of the burning process.

The use of nanotechnology to improve the fire performance of polymers for electrical applications shows great potential. Jiao *et al.* have studied the fire retardant efficiency



**Figure 6:** Cable cross-section (Adaptation from [13])

and mechanical properties of ethylene vinyl acetate copolymer (EVA) filled with nano-metal hydroxides (NMH) and nanosized layered double hydroxides (NLDH) [49]. The high loadings of NLDH improved the fire retardancy of EVA but had detrimental effects on the mechanical properties (53 % decrease in original tensile strength and 3–10 % decrease in the original elongation to break). The char structures were observed to be quite different for the samples loaded with NMH or NLDH. The NLDH filled sample had a loose char, while the NMH char filled sample had a more compact char with low porosity [49]. A benefit of a loose char is that it can dilute combustion gases, decrease the rate of burning in the gas phase and retard the pyrolysis of the polymer.

Beyer studied a blend of carbon nanotubes and organoclays as a fire retardant for a polymers used for cable applications [50]. Based on the peak HRR values, Beyer found that multiwall carbon nanotubes (MWNT) were a very efficient flame retardant at low filler contents in PE, whereas PE filled with single wall carbon nanotubes (SWNT) did not show any improvements in fire performance. An optimized MWNT/organoclay mixture was developed for PVA wire insulation. Based on small scale fire tests, HRR and ignition times, polymers filled with blends of MWNT, organoclays and aluminium trihydrate performed best.

Breulet and Steenhuizen investigated the test methods used to classify cables, with regard to the ability of these tests to measure essential performance parameters such as fire properties [51]. Their work is part of the European effort to develop a harmonized system for classification of cables based on fire properties. Two test methods were investigated, EN 50266-2-4 and FIPEC (fire performance of electric cables) SMT4-CT96-2059:2000. Cables with different sheathing materials were tested. The study concluded that more investigation was needed to assess the test methods ability to discriminate between cable samples, sensitivity for smoke testing, and the test methods validity in selecting the cable with the best fire performance. Statistical analysis of the test results showed that the results from the different tests might not correlate. This study highlights the limitations of test methods and their ability to categorize a materials' fire properties. Troitzsch has provided an overview of the test methods and standards that are used by various nations [28].

Polymeric materials degrade over time. This may lead to a change in the fire retardant properties for the cable materials after they have been in service for a number of years. Based on the review by Gillen *et al.*, it does not appear that there has been specific research on time dependant cable material degradation in a marine environment with emphasis on the fire properties [52]. This raises the question of the marine shipboard environment impact on electric cable material and fire performance properties, the associated risks under asset life extension programs, and material performance in various fire scenarios.

## 6 Textiles and Furniture/Furnishings

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Statistics indicate that in 20 % of dwelling fires, textiles were the first materials ignited. The 1997 statistics show that fire originating in upholstered furniture has caused 3100 fires, resulted in an estimated 100 deaths, 460 injuries, and \$50 million in property damage annually in the U.S [19]. Many ship compartments are similar to rooms in a residential dwelling. That is, items such as bedding, drapes, mattresses, chairs, desks, cupboards, computers, televisions, wardrobes, sofas, *etc* are present. Each item contributes to the ships potential fire load. The March 2006 fire on the cruise ship *Star Princess* in the Caribbean illustrates this hazard and potential consequences [53]. The accident report indicates that the fire caused 1 fatality, 11 injuries and the damage of over 100 cabins [53].

The fabric covering upholstered furniture strongly influences the ignition behaviour of the item. Textile products are considered to pose a significantly high fire hazard because many items fabricated from these materials tend to have a large surface area, which is easily accessible to atmospheric oxygen. An indicator of a textile products ability to ignite is the limiting oxygen index (LOI). LOI values below 21 % indicate the material is easily ignitable, cotton has an LOI of 18 %. Fibres with a LOI >26 % are considered flame retardant (*e.g.*, Kevlar, an aromatic polyamide with an LOI of 29 %).

This is not the only fire performance measurement used. Other textile characteristics, including the glass transition temperature, melting temperature, pyrolysis temperature, ignition temperature, and the HRR of the fibres used in the textile are related to flammability. The lower the respective ignition and pyrolysis temperatures, the greater the HRR, and the more flammable the fibre is. The burning behavior of a fabric is influenced by many factors, including the fibre used in its manufacture, the ignition source and the time the fabric is exposed to the ignition source, the fabric orientation and point of ignition, the ambient temperature and relative humidity, and velocity of the air. A fabric's flammability is thus determined by the fibre properties, the weave used to prepare the fabric [54], and ambient conditions.

Upholstered furniture represents a considerable fire hazard. The major hazard with upholstered furniture is the rate of fire growth, heat release, and the associated generation of smoke and toxic combustion gases. Research has shown that these factors are related to the upholstery and filler materials and the design and construction of the furniture itself [17,55]. Since the implementation of the United Kingdom's furniture and furnishings regulations, which made it mandatory for the sale of flame retardant upholstered furnishing fabrics, there has been a reduction in the number of fires and related casualties due to textile related fires [56].

The emphasis of fabrics related research has been directed at the development of flame retardant textiles, testing of furniture and furnishings, and harmonization of tests to evaluate fire retardant textiles. Fire retardants used with textiles can be added as a finish,

added during fibre production, or introduced through polymer modifications. Examples of flame retardants include: organophosphorous compounds; nitrogen containing monomeric components; antimony-organohalogenated systems used as finishes on cotton fibres; and zirconium hexafluoride complexes used as additives during wool processing. Polyester fibres utilize organophosphorus based additives introduced through copolymer modifications or during processing. Other examples and applications of flame retardant textiles can be found in Troitzsch [28] and Horrocks [17].

For environmental reasons, there has been an effort to replace antimony-halogen systems in textile back coatings and to introduce formaldehyde-free treatments in durable finishes [56]. There has also been an effort to improve char formation and efficiency for better thermal barrier properties. Intumescent flame-retardant fibre combinations have had some success but the challenge is to prepare combinations that can survive the textile laundering processes [56]. Horrocks *et al.* have recently reviewed the developments in flame retardant textiles with respect to enhanced char formation and environmentally sustainable flame-retardants [56]. One of Horrocks conclusions was that there has been very little research undertaken in nanocomposites textiles, although the use of nanoclays as flame retardants in textiles has been investigated.

Hirschler surveyed test methods for several individual furnishings as well as the acceptance criteria [57]. Fire performance of these items has been based on flaming ignition of full-scale items to obtain the HRR. Review of regulatory requirements for various product systems appear to be somewhat arbitrary. Babrauskas and Wetterlund [58] developed an improved procedure for preparing and testing upholstered furniture composites in the cone calorimeter to address problems with test reproducibility including those associated with sample preparation and operator bias. This work was part of the European furniture fire program for international standardization of cone calorimeter procedures for testing. The results of the study were to be incorporated into the new version of ASTM E 1474 [58].

The aerospace industry is also concerned with reducing fire threats and imposes stringent criteria and demands on material flammability. For example, cushion materials must have high flame resistance ( $LOI > 30\%$ ), low density, and negligible particulate formation [59]. Polyimide foam has been evaluated as a fire barrier for spacecraft cushion materials because of its intrinsic flame resistance. Test results indicate that it slows flame spread, increases the minimum heat flux required for ignition, and can significantly reduce the peak HRR, mass burning rate and the generation of carbon monoxide and smoke in flaming combustion when used as a barrier on polyurethane foam [59].

Polyurethane (PU) foams are widely used in upholstered furniture and mattresses across numerous industries. Unfortunately, PU is very flammable. Flammability and flame spread is affected by the chemical properties, which are determined by the choice of short chain diol, isocyanate and crosslinker used in polymerization as well as the physical properties of the foam, such as density and porosity [60]. Lefebvre *et al.* investigated the influence

of conventional PU foam composition on fire properties and thermal behaviour [60]. They were able to compare formulations of short chain diol, isocyanate and water on fire properties such as, HRR, total volume of smoke produced, time to ignition, and fire growth rate. They observed that the higher the short chain diol content, the longer time to ignition. There was no observed influence on the total volume of smoke production or the HRR. However an increase in the isocyanate content resulted in a reduction in the time to ignition, although it had no influence on the intensity of the first peak in the HRR. Also, an increase in water index (reduction in density) reduced the time of combustion of the foam, increased the intensity of the first peak rate in the HRR and increased the production of smoke. These all correlate with an increase in flame spread. It was concluded that the amounts of components and additives used in the manufacture of conventional polyurethane foams influences their fire properties. The blowing agent level was found to have a major influence on the combustion of the foam [60].

The flame retardant properties of upholstery can be improved by re-engineering the outer fabric or using a barrier material to form a non-flammable interlayer between the outer covering fabric and filling material [61]. Flambard *et al.* studied the impact of two methods of seat manufacturing on flammability [61]. The first method used a blend of wool and poly-*p*-phenylenediamine-terephthalamide (*i.e.*, Kevlar<sup>®</sup>29) as a seat covering. The goal was to improve the overall flame retardancy of the textile. The second method utilized flax or hemp combined with flame retardant products such as urea polyborates or polyphosphates to form a felt interlayer. Both methods yielded upholstery that was satisfactory for transportation applications.

Horrocks *et al.* have reviewed the status of developments in flame retardant textiles [56]. They concluded that there had been few significant developments in the last 25 years with the exception of nanoclays in polymers. They indicate that enhancing char-formation, replacing antimony-halogen systems in textile back coatings, and the identification of formaldehyde-free treatments for durable finishes are areas of interest.

Hirschler investigated the use of the small-scale HRR tests as a means to predict the contribution of individual furnishings to the propagation of a fire [57]. The main driving force for this study was that many specifications and regulations use an HRR limit for individual products. Many of these limits and the regulations that incorporate them are based on hazard assessments, but some are based solely on expert judgement. Hirschler's empirical investigation explored the understanding of what was needed to develop safe products. A major concern was contradictory test results. For example, materials passed full scale testing but the results of small-scale suggest that the materials are unsafe. In other instances small-scale tests predicted a material was 'safe', while full-scale tests indicated that they were not. Hirschler's analysis indicated that HRR could be used to assess the fire hazard of most individual furnishings [57]. The results from a number of tests were analyzed. In one case, cone calorimetry correctly predicted that 20 systems tested would not cause a self-propagating fire, while six others would. However, there were cases where



the cone calorimetry predicted that certain systems would result in severe fires when in fact they had excellent fire performance. One observation was that the fabric fire behaviour had a greater effect on cone calorimeter test results than was observed for full-scale testing. The analysis indicated that a HRR between 100 and 200 kW is a threshold for distinguishing between products that are unlikely to cause self-propagating fires and products that are unsafe [57].

## 7 Current Efforts in Fire Research

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Worldwide, there are many test standards and material specifications used to aid in selection of materials for particular applications. Attempts to harmonize standards and specifications, especially in the European Union, are an active area of discussion between countries.

A National Bureau of Standards study showed how important the use of materials with superior fire and flammability properties can be [19]. The study found that use of fire/flame retardant materials resulted in:

- A fifteen fold increase in escape time in room burn tests.
- A 50 % reduction in the amount of material consumed compared to non-fire retardant product.
- One quarter of the total heat release compared to non-fire retardant products.
- A reduction in carbon monoxide release.

The overall conclusion was that the proper selection and application of fire retardant materials could improve overall fire safety [19]. However, smoke production is still a concern with many fire retardant materials.

Some of the other general active polymeric research areas in the literature include:

- Polymer nanocomposite applications in aerospace [62] and flammability properties of nanocomposites [63] [64].
- Block copolymer based nanocomposite materials [65].
- How flame retardants work with polymers [66] and studies on flammability characteristics of various polymers before and after a fire retardant system is applied [67–71].
- Harmonization of testing standards [72].

An overview of potential military applications of polymeric composite materials included for surface ships [73]:

- Hull & Deck Machinery
- Gun Enclosure
- Radomes
- Mast
- Deckhouse
- Intake Louvers & Ducting
- Exhaust Stack
- Doors & Hatches
- Deck Equipment Enclosures
- Hangar Doors
- Life Rails
- Propulsors
- Rudders
- Propulsion Shafts
- Auxiliary Machinery
- Decks & Bulkheads
- Non-Structural Partitions
- Foundations
- Sonar Dome

and for submarines:

- Bow Dome
- Torpedoe Shutters
- Bow Planes
- Missile Tube Components
- Snorkel, Antenna, Masts and Periscope Fairings
- Sail
- Towed Sonar Fairings
- Logistics Trunk and Escape Hatches
- Rudder and Dive Planes
- Tail Cone
- Propulsor
- Main Propulsion Shaft
- Air Flasks
- Non-Built-In Tanks
- Water-Tight Compartment Doors
- Main Ballast Tank Louvers
- Acoustic Windows
- Main Ballast Tank

The main drawback to polymer composites for marine applications are their poor flammability characteristics. Once these are addressed, they will become more mainstream and marine applications will benefit from their corrosion resistance, and low density.

## 8 Potential Areas of Future Exploitation

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### 8.1 Gaps in Current Research

A number of reviews on fire retardant materials exist. Horrocks and Price [17], and Nelson and Wilkie [74] have reviewed the fire properties of polymeric materials. Lewin suggests that some of the unsolved problems pertinent to flame retardants for polymers include [75]: the development of a durable weatherable and non-water leachable flame-retardant system for cotton and cotton blends, flame retardant treatment for lignocellulosic products, better understanding of the gas and condensed phase mechanisms of flame retardants, flame retardants derived from sulfur derivatives, weatherable flame-retardant coatings, and development of flame retardants based on nanoparticles.

Nelson suggests that there is a need to develop more robust and processable flame retardant

resins to meet more stringent moulding conditions. The goal is to produce fire retardant resins that can go through multiple moulding operations with minimal degradation [19].

Environmental issues will demand more stringent limitations on the chemistry of fire retardants. Some of the areas that must be addressed include the development of effective vapour phase flame retardants that do not contain halogens, efficient intumescent coatings for a variety of products, and environmentally stable intumescent coatings. That is, hydrophobic intumescent systems that will not hydrolyse or decompose and will remain stable at high temperatures for significant periods time.

Although not exhaustive, Table 2 represents some pertinent topics in polymeric flame retardant materials research, including requirements and/or gaps in research that exist.

Table 2: Summary of Research Questions and Gaps in the area of Improved Fire Retardant Polymeric Materials

Author or Source	Questions or Gaps
Lewin (2005) [75]	<ul style="list-style-type: none"> <li>● To what extent is the effectiveness of halogen flame-retardants compromised as the temperature increases?</li> <li>● What is the role of ammonia and nitrogen in flame-retardants for polymers?</li> <li>● What is the role of melamine as a flame retardant for polymers?</li> <li>● What are the preferred systems of application of brominated and phosphorus based flame-retardants in polymers. As additives or by copolymerization?</li> <li>● How does ammonium polyphosphate (APP) work? Is it a catalyst or a binder for the resulting char? How does APP contribute to the formation of the char network?</li> <li>● What are the interactions between ammonium polyphosphate (APP) and co-additives that result in such large increases in the fire retardant effect of the APP?</li> <li>● What happens in the time between the formation of the char precursors and the formation of the char on the surface of a polymer?</li> <li>● How can smoke production of polystyrene be lowered at a reasonable cost?</li> <li>● What are the mechanisms governing the activity of metallic compounds in the fire retardancy of polymers?, in both endothermic and intumescent formulations?</li> </ul>
Le Bras & Bourbigot (1997) [76]	<ul style="list-style-type: none"> <li>● What is the relationship between the cell structure and the fine structure of nano-units?</li> </ul>

Author or Source	Questions or Gaps
as noted in ref [75]	
Levchik & Wilkie (2000) [31]	<ul style="list-style-type: none"> <li>• Studies are needed to correlate char formation and the thermal stability of polymers.</li> </ul>
Horrocks & Price (2001) [17]	<ul style="list-style-type: none"> <li>• There is a gap in the full understanding of what influences the type of char formed when polymeric materials burn or smoulder. Factors such as melt viscosity, the surface tension of the melt-gas interface, the kinetics of gasification, and polymer crosslinking must be better understood.</li> <li>• The application of phosphorus and nitrogen compounds and systems within intumescent systems needs to be investigated.</li> <li>• There is no single smoke test that is universally recognized for its predictive ability or high correlation with real fire situations.</li> <li>• There is a need to develop polymers that have effective smoke suppressant capabilities and that increase the time available to escape fires or improve the environment for fire fighters.</li> </ul>
Zhang (2004) [25]	<ul style="list-style-type: none"> <li>• There has been qualitative analysis and identification of the decomposition products of most know polymers but little has been done on the quantitative analysis of the pyrolysis gases by using mass spectrometry as a detector.</li> <li>• The FAA in association with a number of other organizations (<i>e.g.</i>, NIST, the U.S. Army) has established a research cluster to investigate fire-safe polymers and polymer composites at the Centre for University of Massachusetts/Industry Research on Polymers (CUMIRP). The goal is to aid in identification and design of new fire safe polymeric materials by elucidating the intrinsic relationships between polymer structures and compositions and their fire behaviour.</li> <li>• Although most countries have standards and codes for the classification of materials with respect to their combustion behaviour, methods used to classify materials vary considerably depending on the nature, size, and shape of the polymeric materials tested. Tests used in the U.S. can only be used as guides and they suffer from lack of precision and reproducibility.</li> <li>• The structural integrity of materials as they burn is an important issue. It requires that the residual mechanical properties of materials during the decomposition process be evaluated.</li> <li>• Molecular modeling has the potential to give a better understanding of the thermal decomposition and fire-resistance mechanisms of polymer materials. Modeling of high temperature decomposition mechanisms is required.</li> </ul>

Author or Source	Questions or Gaps
Breulet <i>et al.</i> (2006) [51]	<ul style="list-style-type: none"> <li>• Searching for environmentally friendly and efficient flame-retardants is a promising research direction.</li> <li>• Breulet <i>et al.</i> have identified limitations with the harmonized Euro classification of cables with existing cable testing standards. The results of specific tests do not correlate and they do not enable flame-spread measurements. Further investigation is needed to determine whether the test measurements are sensitive enough to reliably predict which cables generate low amounts of smoke.</li> </ul>
Horrocks & Price (2001) [17]	<ul style="list-style-type: none"> <li>• Seating materials are required to have low HRRs. Is there a minimum HRR criteria for textile materials used on naval combatants and aircraft? If no, should one be developed?</li> </ul>
Troitzsch (2004) [28, 29]	<ul style="list-style-type: none"> <li>• Di Blasi (published in Troitzsch) highlighted the need to investigate polymer thermal degradation and decomposition kinetics, material decomposition and how this influences the dynamics of heat and mass transfer, and the different degradation and decomposition behaviours for polymer materials.</li> </ul>

## 9 Conclusions

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Fire is a major concern due to loss of life, damage of property and disruption of missions. With the appropriate choice of materials, the likelihood of ignition or spread of fire can be reduced. This paper has concentrated on the flammability of polymeric materials, specifically their uses in electrical/electronic equipment and furniture/furnishings. A brief review of the literature shows R&D is needed to improve the fire resistance and smoke inhibiting properties of polymers.

Materials on naval combatants can be exposed to shock, explosion and CBRN agents, adding another dimension of requirements that civilian applications do not consider. Combining these requirements with fire resistance will lead to a new class of multifunctional materials.

## 10 Future Research

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Char formation is the primary mechanism by which flame spread is reduced. Further study is needed to better understand char formation and stability in polymers.

Nanotechnology has contributed to improving material properties in a number of areas and has potential for future fire safe materials. The literature indicates that this is the area from which the next generation of high performance polymeric fire retardant materials will emerge. The high surface area of nanometer sized fillers modify the fire properties of the composite at much lower filler contents than micron-sized particles. The lower filler contents allow for less change in other composite properties. In the future, more work will be needed to understand the science of nanocomposite fire resistant materials. Copolymer blends, composites, nanocatalysts and nanoparticle additives are all potential areas for future research. Investigating composite additives may include such materials as; low valent metals and salts, nanometal hydroxides, Nano LDH, carbon nanotubes, organoclays, aluminium trihydrate, APP, and nanocatalysts. There may be room to re-examine intumescent systems, within the realm of nanometer-sized particles.

With a trend towards lifecycle extensions, polymer degradation and its effect on mechanical and fire retardant properties must be considered. There has been little investigation on how a marine environment affects polymer ageing. Condition monitoring techniques and analytical methods are needed to evaluate polymer life expectancy.

Fire retardant polymeric material selection and application is a complex subject. Evaluation of the fire and flammability properties of materials using laboratory scale tests does not always reflect a material's performance in a fire. The ability to compare standard tests and cross-reference materials specifications would ease selection decisions. Development of

small scale fire performance tests that more accurately assess a polymeric material smoke production performance in an actual fire scenario.

Investigation of fire stop design and materials used to prevent the spread of fire between spaces or compartments (penetrations) is relevant to the new support vessels, now in the concept design stage. An investigation of existing technology and requirements for current and future fleet applications would be appropriate.

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## List of symbols/abbreviations/acronyms/initialisms

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£	British Pound
API	American Petroleum Institute
APP	Ammonium polyphosphate
ASTM	American Society of Testing of Materials
ATH	Aluminium hydroxide
°C	Degrees Celsius
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon dioxide
CSA	Canada Standards Association
DND	Department of National Defence
DRDC	Defence Research and Development Canada
ECR	Engine Control Room
EVA	Ethylene vinyl acetate
HCL	Hydrochloric Acid
HDPE	High density polyethylene
HMCS	Her Majesty's Canadian Ship
HVAC	Heating ventilation and air conditioning
IEC	International Electrotechnical Commission
IEEE	Institute for Electrical and electronic Engineers
IMO	International Maritime Organization
K	Potassium
K	Degrees Kelvin
kJ	Kilojoules
kW	Kilowatts
LLDPE	Linear low density polyethylene
MH	Magnesium hydroxide
MIL	Military
MIR	Marine Investigation Report
MJ	Mega joules
MPa	Mega Pascal
MSR	Main Switchboard Room
NEMA	National Electrical Manufacturers Association
NMH	Nanometal hydroxide
NMR	Nuclear magnetic resonance
O <sub>2</sub>	Oxygen
PA	Polyamide
PAN	Polyacrylonitrile
PC	Polycarbonate

PE	Polyethylene
PI	Polyimide
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PS	Polystyrene
PVA	Polyvinyl alcohol
PVC	Poly(vinyl chloride)
RFP	Request for Proposal
RHR	Rate of Heat Release
SBI	Single burning item
Std	Standard
T	Temperature
TSB	Canadian Transport Safety Board
U.S.	United States
UL	Underwriter Laboratories
WC	Wire and cable



# Glossary

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Technical term <sup>1</sup>	Definition
Auto-ignition	Initiation of fire by chemical process inherent in the material; specific fuel concentration and temperature is usually needed.
Auto-ignition temperature	The lowest temperature at which a mixture of fuel and oxidizer can propagate a flame without the aid of an initiating energy source (pilot).
Char	Carbonaceous material formed by pyrolysis or incomplete combustion.
Critical heat flux	A threshold level of heating below which ignition (or flame spread) is not possible.
Fire retardant	A substance added, or a treatment applied to a material in order to suppress, significantly reduce or delay the combustion of the material.
Flame resistance	The ability of an element of building construction to fulfil for a stated period of time the required load bearing function, integrity and/or thermal insulation specified in the standard fire resistance test (see ISO 834).
Flammability	A measure of a materials propensity to burn or, conversely, its resistance to ignition.
Flame spread	The propagation of the flame away from the source of ignition across the surface of a liquid or solid. The tendency of a material to spread flame as it burns (ASTM E 176). The propagation of a flame front.
Flashover	The phenomenon that may occur during a fire, whereby the surface of everything in a compartment appears to break into flame at the same time.
Flash point	The minimum temperature of a liquid at which it produces vapours sufficient to form an ignitable mixture with the air at the surface of the liquid or near the container.
Heat of combustion	The total amount of energy (heat) released during the complete combustion of a material.
Heat flux	A measure of heat impinging onto a surface per unit of time, usually from a radiant heating device.

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<sup>1</sup>For a complete list of terms, refer to Troitzsch [28], Fire [21] or the National Fire Protection Assoc.

Heat release rate (HRR)	The thermal energy released per unit time by a material during combustion under specified test conditions.
Limiting Oxygen Index (LOI)	The limiting concentration of oxygen in the atmosphere necessary for sustained combustion. A material with an LOI of more than 21 should not burn in air at room temperature.
Pyrolysis	Irreversible chemical decomposition caused by heat usually without oxidation. Pyrolysis of polymers can produce shorter-chain polymers (lower molecular weight) or the original monomer.

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Fire fighting is one of the most labour intensive operations aboard ship, and poses a significant threat to crew. The incorporation of fire-safe materials can reduce the threat by decreasing the likelihood of ignition or slowing the spread, should a fire start. The right choice of materials can result in smaller fires, requiring fewer crew to be at risk while fire fighting. This paper reviews shipboard fires on both commercial and non-commercial vessels. It discusses the mechanism for fire and how organic materials such as polymers undergo combustion, with emphasis placed on the typical polymeric fire loads on board: cable insulation/sheathing and textiles/furnishings. This review concludes with a survey of current efforts in fire/flame retardant materials. The recommended areas for future research include investigations into the mechanism of char formation, examination of nanocomposite materials based on nanometal hydroxides, exfoliated nanoclays and nanosized versions of traditional fire retardant additives, understanding polymer degradation mechanisms, and achieving a balance between mechanical properties, fire retardant properties and smoke inhibiting properties.

The goal of this review is to provide background on what is currently known about the fire properties of polymeric materials used in marine applications and to provide some insight as to what future research is relevant in a naval context.

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fire safe materials, fire retardant materials, char, polymer, polymer degradation, polymer decomposition

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