Improving the Heat, Fire, and Melt Resistance of Elastomeric Seals on Military Gas Masks

by

Charles S. Hong

B.S. Textiles
Cornell University, 2001

Submitted to the Department of Materials
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Fulfillment of the Requirements for the
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Signature of Author..
Department of Materials Science and Engineering
July 6, 2009

Certified by..
David Roylance
Professor of Materials Science and Engineering
Thesis Supervisor

Accepted by..
Christine Ortiz
Chair, Departmental Committee on Graduate Studies

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Abstract:

Improvised Explosive Devices (IED's) have wreaked havoc amongst American and Coalition troops. They have been the number one killer of Coalition forces. Many times the impact knock out fuel tanks which then catch on fire, causing life threatening burn injuries. As a counter, the military unveiled new fire/melt resistant clothing.

In the case of a chemically contaminated environment, the soldier will have to rely on a gas mask with an elastomeric seal that is not resistant to fire or melting. If a soldier is traveling in a vehicle with his or her gas mask on and gets hit by an IED, facial and eye burn injuries are very possible.

New material must be found that can help prevent these injuries, particularly concerning the seal. The goal is to find the best combination of a suitable elastomer, curing agent, and filler that can give the soldier precious time to escape a burning vehicle. Various types of materials are discussed concerning thermal, other physical properties, cost, and relevant patents.

Thesis Supervisor: David Roylance

Title: Professor of Materials Science and Engineering

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Introduction

The modern battlefield in Iraq and Afghanistan proves that constant innovation in safety and security of troops is needed. Throughout history, opponents in battle have always developed ways to counter each other's war making capabilities. In modern times, this is well demonstrated by the creative and effective usage of a crude weapon called the Improvised Explosive Device (IED). IED's have killed and injured thousands of American troops. Many times, IEDs hit the fuel tanks, causing fire, which then lead to serious burn injuries. In response, the military started to unveil fire resistant clothing to just about all deployed personnel.

(www.wikipedia.org 2006)

In addition to the risk of catching fire, the heat from burning fuel can melt polyester and other man-made fabrics onto skin. In many cases the melting effect is worse of a hazard than burning due to the fact that melting synthetic textiles bond to the skin, making removal of the hot substance much more difficult. To be flame resistant, equipment must self extinguish, must not fuel a fire, must not melt, and must dissipate static electricity (particularly important to fuelers). Furthermore, it is important for the fire resistant equipment to not add bulk that could compound heat stress.

Popular "Under Armour" shirt melting and burning

(Marine Corps Times 2006)

Before the Global War on Terror, fire resistant clothing was mainly issued to air and armor crewman, fuel handlers, and certain special operations personnel who were likely to operate in confined environments that had a high probability of having a person exposed to flames (ie Navy SEALs and offshore oil platforms). The hazards of IEDs have made the need for fire protection an absolute must for all personnel deployed to combat theaters. Modern medicine has done a great deal in treating burn victims. However it is always better to prevent a burn injury than to try to heal one.

To counter burn injuries, the military has recently unveiled several different types of clothing to help protect against burn injuries, chief among them, the Marine Corps' FROG (Flame Resistant Organizational Gear) and the Army's FREE (Fire Resistant Environmental Ensemble) clothing.

Army FREE system

https://peosoldier.army.mil

Marine Corps FROG

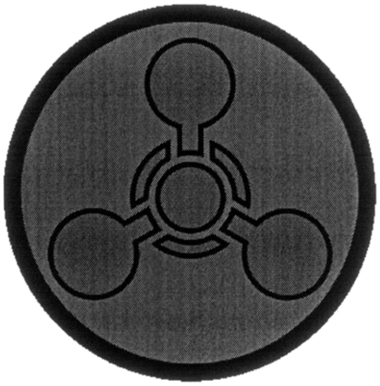
https://peosoldier.army.mil

However, one issue that has not received much attention is the fire resistant properties of chemical gas masks. Fortunately, no one has ever used chemical weapons against US Forces since World War I. During that war, the Germans were the first to prove the effectiveness of these new weapons when they unleashed Chlorine gas and caused gaps in enemy lines that were miles long. Since then, not only have people developed more deadly weapons of mass destruction (WMDs), today's soldiers are much more likely to deploy to action in vehicles that are operated by petrochemical fuel, fuel that can burn and explode.

Threats

CBRN (Chemical, Biological, Radiological, Nuclear) is the new definition of Weapons of Mass Destruction (WMD). Former names include Nuclear, Biological, and Chemical (NBC). These weapons are capable of being fatal and/or debilitating to a number of people to a much greater extent than conventional weapons or explosives. The focus of this thesis is to explore ways to improve the fire resistant capability of the military gas mask seal. However, the threats that the masks must help mitigate should be mentioned (in addition to fire/flames)

Chemical Threats



Chemical agents are classified as persistent or non persistent. Agents classified as non persistent lose effectiveness after only a few hours. Purely gaseous agents such as chlorine are non persistent, as are highly volatile agents such as sarin and blood agents. Tactically, non persistent agents are very useful against targets that are to be taken over and controlled very quickly. Apart from the agent used, the delivery mode is very important in determining persistence or non persistence. To achieve a non persistent deployment, the agent is dispersed into very small droplets comparable with the mist produced by an aerosol can. In this form not only the gaseous part of the agent, but the fine aerosol can be inhaled or taken up by the skin. Modern doctrine requires very high concentrations almost instantly in order to be effective (one breath should contain a lethal dose of the agent). To achieve this, the primary weapons used would be rocket artillery or bombs and large ballistic missiles with cluster warheads. The contamination in the target area is low or not existent after several hours and non persistent agents are not detectable anymore.

By contrast, persistent agents tend to remain in the environment for as long as several weeks, complicating decontamination. Defense against persistent agents requires shielding for extended periods of time. Non-volatile liquid agents, such as blister agents and the oily VX nerve agent do not easily evaporate into a gas, and therefore present a contact hazard. This implies that persistent deployment does not aim at annihilating the enemy but to constrain him. Possible targets include enemy flank positions (averting possible counter attacks), artillery regiments, command posts, airfields, or supply lines. Possible weapons to be used are widespread, because the fast delivery of high amounts is not a critical factor, unlike non persistent agents. A special form of persistent agents are thickened agents. These comprise a common agent mixed with thickeners to provide gelatinous, sticky agents.

In addition, chemical weapons come in four general categories. Amongst the four categories, the agents may or may not be persistent.

1) Blood Agents: Blood agents produce their effects by interfering with oxygen utilization at the cellular level. Blood agents are distributed via the blood and generally enter the body via inhalation. They inhibit the ability of blood cells to utilize and transfer oxygen. Thus, blood agents are poisons that effectively cause the body to suffocate. Various cyanide poisons are good examples of blood agents. All blood agents are non persistent.
2) Choking Agents: Amongst the first chemical agents fielded, choking agents inflict injury mainly on the respiratory tract including the nose, throat, and especially the lungs. Victims typically inhale these agents, which can lead to pulmonary edema and/or respiratory failure. Common examples include chlorine and phosgene gases.
3) Blistering Agents: Also known as "Vesicants", blister agents are highly reactive chemicals that combine with proteins, DNA, and other cellular components to result in cellular changes immediately after exposure. The most well known blister agent is mustard gas. They were the most widely used agents of World War I. The

most famous victim of this weapon was the then Corporal Adolf Hitler, who spent several days blinded after a mustard gas attack from British troops.

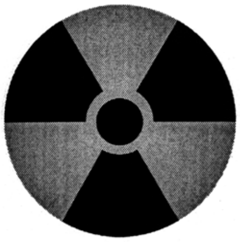
4) Nerve Agents: The most toxic of the known chemical agents. They are hazards in their liquid and vapor states and can cause death within minutes after exposure. Nerve agents acquired their name because they affect the transmission of nerve impulses in the nervous system. All nerve agents belong chemically to the group of organo-phosphorus compounds. They are stable and easily dispersed, highly toxic, and have rapid effects both when absorbed through the skin and via respiration. Nerve agents can be manufactured by means of fairly simple chemical techniques. The raw materials are inexpensive and generally readily available. The most well known are VX and Sarin gas

Biological Agents

Biological weapons (BWs) deliver toxins and microorganisms, such as viruses and bacteria, so as to deliberately inflict disease among people, animals, and agriculture. Biological attacks can result in destruction of crops, death to livestock, and death to a large numbers of people.

The effect of biological weapons depends on several factors. These include the agent itself, its preparation, its durability in the environment, and route of infection. Some agents can be disbursed as an aerosol, which can be inhaled or can infect a susceptible spot on the skin, like a cut or wound. Attackers can also contaminate food or water with some agents. Biological weapons have a long history of use. In 1346, the invading Tartar army catapulted the bodies of plague victims into the Crimean Peninsula city of Kaffa and infected its citizens (Cassiday 2009). In 1763, British troops under General Jeffrey Amherst gave the Delaware Indians blankets used by smallpox patients, infecting and decimating the susceptible native population (O'Connell 1989). Japanese troops contaminated food and released plague infected ticks during their conflict with China before World War II (Cassiday 2009). The 2001 anthrax letter attacks in the United States infected 22 people and killed five (Jernigan 2002).

Nuclear and radiological:



Nuclear: Being the most destructive of all known weapons, common sense should indicate that the development of an elastomeric seal that blocks the impact of a direct nuclear blast is impractical. However, a mask should provide protection against the radioactive fallout dust associated with the aftermath of a nuclear explosion. More is mentioned below.

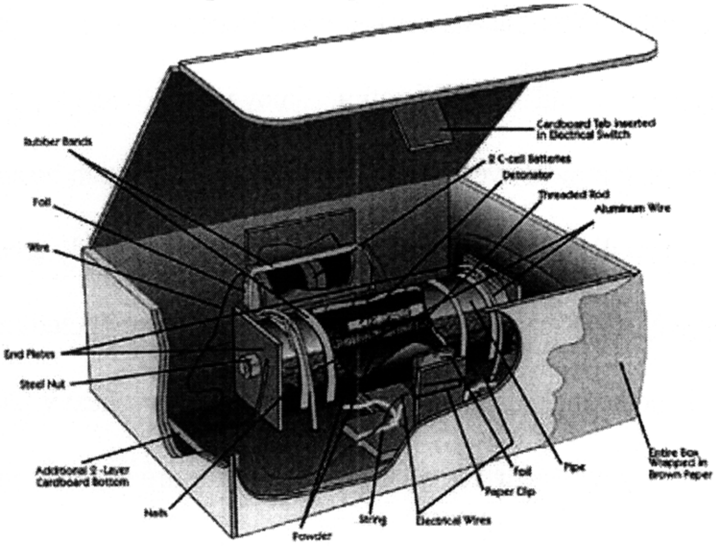
Radiological: Also known as a "Poor Man's Nuke" or "Dirty Bomb", a radiological bomb, or radiological dispersion device, is a bomb that combines conventional explosives, such as dynamite, with radioactive materials in the form of powder or pellets. The idea behind a dirty bomb is to blast radioactive material into the area around the explosion, radioactive material that is similar to radioactive fallout dust in the aftermath of a nuclear explosion. The blast itself is conventional. This could possibly cause buildings and people to be exposed to radioactive material. Most radiological bombs would not release enough radiation to kill people or cause severe illness. The conventional explosive itself would be more harmful to individuals than the radioactive material. The main purpose of a dirty bomb is to frighten people and make buildings or land unusable for a long period of time.

Conventional Explosive Devices:

The two key conventional explosive threats to soldiers in the battlefield are Improvised Explosive Devices (IEDs) and Rocket Propelled Grenades (RPGs).

Improvised Explosive Devices:

Improvised Explosive Device



www.globalsecurity.org

News media coverage of the wars in Afghanistan and Iraq made the letters "IED" a household name. An IED is a bomb fabricated in an improvised manner incorporating destructive, lethal, noxious, pyrotechnic, or incendiary chemicals and designed to destroy or incapacitate personnel or vehicles. An IED typically consists of an explosive charge (potentially assisted by a booster charge), a detonator, and an initiation system, which is a mechanism that initiates the electrical charge that sets off the device. An IED is a "homemade" device that is designed to cause death or injury by using explosives.

They may be partially comprised of conventional military explosives, such as an artillery round, attached to a detonating mechanism. IEDs may be used in terrorist actions or in unconventional warfare by guerrillas or commando forces in a theater of operations. In Iraq, IEDs have been used extensively against Coalition forces and by the end of 2007 they have been responsible for approximately 40% of Coalition deaths (http://icasualties.org/Iraq/IED.aspx). They were also used extensively by the Tamil Tiger (LTTE) organization against military and civilian targets in Sri Lanka. IEDs are often placed on the curb of roads so as to be detonated when vehicles or pedestrians pass by, and so are sometimes known as "Roadside Bombs".

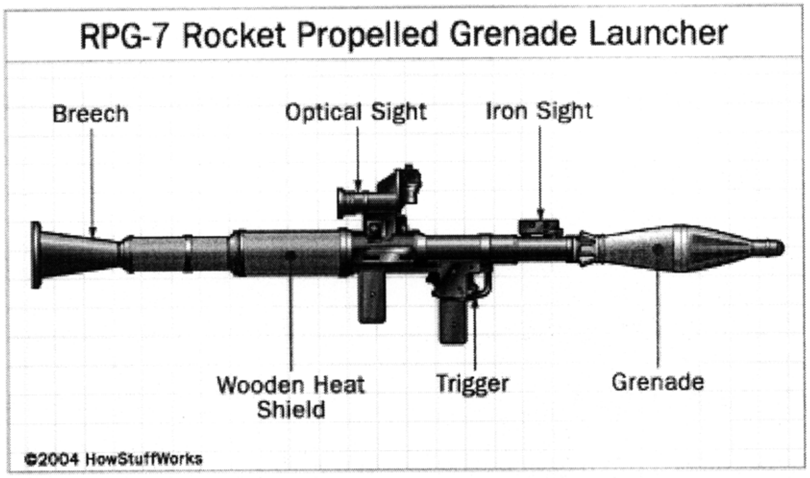
IEDs can be prepared almost everywhere, with materials that can be acquired from agricultural and medical supplies. The preparation does not require highly technical knowledge. When constructed properly, IEDs can defeat even the most highly protected threats, including main battle tanks and armored personnel carriers. Some IEDs utilize very heavy (200 pounds and more) explosive devices buried below the surface of roads where they are covered and wait for activation by remote control (usually by cellular phones). Such activation is usually dependent on a target of opportunity passing by.

IED's can also be used to spread chemical weapons. In early 2004, American soldiers were hit with an IED using a 155 mm shell containing Sarin nerve gas (MSNBC 2004). Earlier, another IED was found that was connected to an artillery projectile containing mustard gas. There is no evidence that the insurgents who planted the devices knew that the projectiles contained chemical gas. It looks as though the projectiles were unaccounted for and mixed in with conventional munitions in storage dumps during Saddam Hussein's rein. In both cases the munitions were old and hence not as effective. Ironically, the fact that an old chemical shell was used in lieu of a conventional explosive probably saved the soldiers' lives. However, these incidents do raise the possibility of a simultaneous gas and explosive IED attack that may require soldiers to wear gas masks more frequently, further justifying the need for a gas mask with a fire resistant elastomeric seal.

Rocket Propelled Grenades (RPG)

Another prevalent explosive threat comes in the form of a Rocket Propelled Grenade. Although most Westerners call "RPGs" the Rocket Propelled Grenade, the true abbreviation actually comes from the Russian phrase for "hand-held anti-tank grenade-launcher": Ruchnoi Protivotankovye Granatamyot.

An RPG is an explosive projectile weapon with two separate parts; the grenade and a device for launching it. The launcher is basically a tube that rests on the operator's shoulder. It is open at both ends, and a projectile with a small rocket engine is affixed to the front end of the tube. Firing is usually accomplished through a trigger mechanism, at which point the grenade's rocket engine is activated and a short, high-powered burst of ignited gases launches the grenade. Having a built-in rocket propulsion system, the projectile itself travels toward the target, usually exploding upon impact. When hitting a fuel tank, the effects are similar to an IED attack.

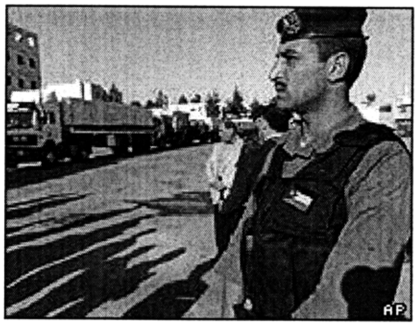


In terms of fire propagations, many times the explosives hit the fuel tanks. The most concerning of a fire scenario is a flashover, which is the simultaneous ignition of combustible vapor when ignited by a blast. Flashover is the brief but intense burst of heat and flame at the moment of an explosion resulting in temperatures well over a 1000C. A flashover is the near simultaneous ignition of all combustible material in an enclosed area when the majority of surfaces in a space are heated to the temperature at which the flammable gases that are being produced from the combustible materials in the space are hot enough to ignite. It can affect anyone who is trapped inside a vehicle or aircraft that gets hit by a roadside bomb, rocket-propelled grenade (RPG), or any other explosive device. Flashover is one of the most-feared phenomena among firefighters.

Recent Events:

So far, threats from explosive devices and Weapons of Mass Destruction (WMD) have been described in a military context, namely the conflicts in Iraq and Afghanistan. However, several other recent incidents have occurred that clearly demonstrates that the threat of a combined WMD and explosive attack to civilian/domestic target. These incidents may have more relevance to civilian law enforcement than military personnel, potentially expanding the customer base for a fire/melt resistant gas mask.

Amman Jordan (2004)



(http://news.bbc.co.uk)

Jordanian authorities intercepted an attempt by Al Qaeda operatives intent on releasing clouds of toxic sulfuric acid gas in the capitol city of Amman. Sulfuric acid can serve as a blistering agent, but it can also help propagate a fire. In gaseous form it can help initiate a flashover situation since it is volatile and combustible in gaseous form. The plot was within days of being carried out.

Had this plan succeeded, thousands would have died or been injured from this attack (cnn.com). Soldiers racing to the site with chemical weapons suits and mask could have faced tremendous burn injuries from the fire that the sulfuric acid helped propagate.

Tokyo (1995)

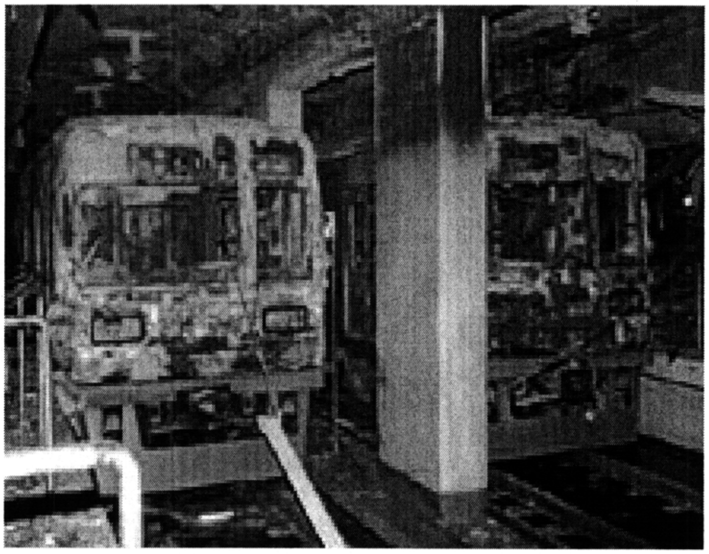
(www.wired.com)

In 1995, a group of religious fanatics known as Aum Shinriko released a toxic cloud of Sarin nerve gas into a Tokyo subway station. Fortunately, the gas was impure and crudely made. Twelve people lost their lives. In addition, thousands were injured from this attack. The subway stations with there confined space served as an effective means to help spread sarin gas to people gathering in such environments. Tokyo was experiencing a coordinated, simultaneous, multi-point assault. The attack was carried out at virtually the same moment originating from five different locations in the world's largest city: packages placed in five different trains, many kilometers apart, all converging on the center of Tokyo. The resulting deaths and injuries were spread throughout central Tokyo. Had the cult used incendiary devices as a secondary device to attack first responders, the results could have been even more deadly.

Unbelievably, this is not the first incident involving Aum Shinrikyo and sarin. Several months earlier, cult members drove a converted refrigerator truck into a residential neighborhood of Matsumoto, a city of 300,000 and 322 kilometers northwest of Tokyo (Olson 2009). Parking in a secluded lot behind a stand of trees, they activated a computer-controlled system to release a cloud of sarin. The nerve agent floated toward a cluster of private homes, a mid-rise apartment building, town homes, and a small dormitory killing seven people.

It is important to note that this was not carried out by a government entity with an organized logistics system. It was created by a group of religious fanatics. This demonstrates the simplicity of use and manufacturing of chemical weapons, further demonstrating the real threat involved.

South Korea (2003)



(cbc news 2003)

In 2003, a recently unemployed suicidal man with a history of mental problems carried two cartons of gasoline, about four liters each into a subway. The resulting ignition resulted in 192 deaths and 148 injuries. The fire quickly spread to all six coaches of the train within two minutes due to the highly flammable interior of the train. The seats, flooring and advertisement boards were not made of fireproof materials but composed of flammable fiberglass, carbonated vinyl and polyethylene. The fire had also spread to another train in the opposite direction which stopped alongside, killing all the passengers trapped in it. The complete burning of a total of twelve subway coaches generated intense heat, and poisonous smoke filled the entire station. The platform had no sprinklers. The temperature of one of the platform quickly raised to over 1000C, burning down the facilities, signposts, and ceiling of the platform. Clearly, fire resistant materials were needed to help mitigate this tragedy. However, a similar incident like this used in conjunction with a device that utilizes WMD substances could have resulted in even more tragedy.

Current Known Threats

Many US enemies have access to chemical weapons. The threat is compounded by the simplicity of these weapons. It would not be a surprise if an enemy government or organization is studying ways to further exploit vulnerabilities of the US military to IEDs. Furthermore, one should not be surprised if the enemy entity is exploring ways to efficiently use IEDs in conjunction with chemical weapons. If a soldier is caught in a chemically contaminated environment and hit with an IED, the results could be disastrous. It is very likely that the soldier will not have access to anything more than rudimentary medical care in combat. Current conflicts prove that fire resistant equipment is a must for every soldier.

Democratic People's Republic of Korea (DPRK)-North Korea

Though antiquated in its equipment and training, the vast size of its 1.2 million strong army still poses a formidable threat. The DPRK ranks among the world's largest possessors of chemical weapons. Its nuclear weapons program continues to be a cause of concern for the international community. Recent missile and nuclear tests have shown its unwillingness to heed the demands of its neighbors to stop pursuit of nuclear weapons.

It is well known that North Korea possesses the means to deliver weapons payload to South Korea and Japan. It is also suspected that the DPRK regime is developing missiles that can reach the United States. Complicating issues include the fact that the capital city of South Korea is around forty kilometers from the border with the North, putting this densely populated city (10 million in the city proper and an additional 10 million in surrounding suburbs) within artillery range. With around 100,000 special operations personnel highly trained in infiltration and saboteuring techniques, there is no doubt that North Korea possesses the tactical know how to conduct attacks with IEDs similar to those conducted against US troops in Iraq and Afghanistan..

Syria

Syria is currently believed to deploy between 100 and 200 Scud missiles fitted with sarin warheads (www.nti.org). Whether Syria's WMD capabilities are meant for offensive support or merely a counter to Israel's superior military capability is still unclear.

Israel's bombing of Syria's suspected nuclear facility site in late 2007 has brought Syria's WMD capability into international spotlight.

Its ties to certain radical groups have been well documented and established. However, it has also helped Coalition forces in its effort to counter other insurgent groups as well, particularly Al Qaeda. There is no doubt that many insurgents that have caused trouble in Iraq have entered through the Syrian border, the same insurgents who have successfully carried out IED attacks against American forces. The degree to which the Syrian government aid the insurgents operating in Iraq are not too clear.

Iran

Iran is one of the few countries in the world that has encountered chemical weapons since World War I. Iranian troops and civilians suffered tens of thousands of casualties from Iraqi chemical attacks during the Iran-Iraq War. Hence, it has publicly denounced the usage of such weapons and ratified the Chemical Weapons Convention. There is not much concrete evidence that Iran is currently developing chemical weapons, but there are documented cases of the purchase of chemical weapons precursors. Very little is known about present chemical weapons stockpiles.

Iran continues to operate suspected nuclear facilities. With the recent reelection of Mahmoud Ahmadinejad, there is likelihood that this will continue. Its ambition to build a nuclear power plant is of concern to the international community as the government of Iran continues to insist that the nuclear program is for peaceful purposes of generating electricity.

It is well known that Iran supports groups deemed by the United States to be terrorist organizations, organizations such as Hezbollah and "Special Groups" that have operated within Iraq. Reports have surfaced that the Iranians have also provided aid to their bitter enemy, the Taliban to help bloody the American soldiers operating in Afghanistan. It is also suspected that Iran provided Explosively Formed Penetrators (EFP), a deadlier form of IEDs to insurgent groups operating within Iraq. In addition many of the Special Groups are alleged to have received training from the Al Quds Brigade, the elite wing of the Revolutionary Guards.

Potential Scenario

Another violent incident on the Korean Peninsula has just commenced. North Korean Special Operations troops have begun to infiltrate the eastern part of South Korea. The Pyongyang regime had it with sanctions and the blockade of weapons and drug trade, the only real source of revenue. Some in the regime want to retaliate.

This terrain is harsh and rugged and not suitable for tanks. The Americans and the South Korean forces will not be able to use their superior technology as effectively in this environment. The North Koreans have just inserted at night. Their job is to harass the rear lines.

The route that can support heavy vehicle traffic is in the western corridor. In fact during the invasion of South Korea in 1950, the North Koreans used this route in its drive south. The goal of the North Commandoes is to help counter potential American retaliatory attacks through this same route. The emphasis is to sneak up on the enemy and saboteur his ability to respond to a provocation.

The North Korean High Command has taken a serious interest in learning of the vulnerabilities of US Forces in Iraq and Afghanistan. Rather than take the Americans and South Koreans head on, proven Al Qaeda and Al Mahdi's hit and run guerilla attacks can be more useful. The intent is to bleed the Americans and South Koreans and their will to fight. There is no question that the superior firepower of the Americans and South Koreans will make any conventional style attack suicidal.

The joint South Korean and American Commands hear of possible enemy infiltration and eventually order scouts and patrols to reconnoiter the area and to possibly intercept the North Korean Commandoes. Intelligence reports and gas detection equipment indicate that chemical agents may have been released, requiring the usage of chemical protection devices.

As the American and South Korean forces move troops to the area, a roadside bomb goes off, detonated by North Korean Commandoes observing from far off concealed positions using a simple remote controlled device learned from observing American experiences in Iraq and Afghanistan. The vehicles instantly catch on fire. Soldiers try to escape, but with their gas masks burning and melting instantaneously, they are disoriented. Some barely make it out alive, but with serious facial and eye burn injuries. Others are caught in the inferno and burn to death. For these soldiers, the mission is over. Rather than to shoot the American and South Korean soldiers, the North Korean infiltrators covertly withdraw. Firing their weapons can unnecessarily expose their position to other American/South Korean forces in the area. Secondly, knowing that a wounded soldier is more of a logistical headache for the enemy than a dead one, the justification to fire a shot is further diminished.

M50 Gas Mask

The military has recently unveiled a new mask called the M50 earlier last year with improved characteristics over the older M40 model. Some of the improvements include:

M50 Gas Mask

-Improved chemical and biological weapons protection

-Improved field of view

-Lower breathing resistance

-Reduced weight/bulk and improved "compactibility"

-Better capability of keeping out dust and dirt (of particular concern in the Middle East)

-Compatibility with night vision equipment.

Unfortunately, the new M50 is not fire and melt proof. Fire and high heat may potentially burn or melt the M50, particularly the seal, which is made of chlorobutyl rubber. The goal is to find better materials to help make the gas mask more resistant to heat and fire, with special emphasis on the seal. In addition, it is important to note that the intention of developing and fielding this new mask is not to help make a soldier a better firefighter. Even with the best available firefighting equipment, the degradation temperature in a flashover situation is mere seconds. Rather, the intention is to develop and field a product that gives the soldier precious few more seconds to escape a burning vehicle without any burn injuries.

INTRODUCTION TO ELASTOMERS

Historically most gas mask elastomeric seals were made from a small list of materials. (Vojir 2004)

Natural Rubber. Very pliable and forms a great seal. However, it has poor resistance to oil and grease which can quickly deteriorate it. The raw materials for natural rubber must also be imported, meaning that its quality and consistency is varied. Furthermore, US law severely restricts the usage of imported materials for defense applications.

Butyl Rubber. A synthetic material, this substance meets high standards for resistance to chemical agents. Its resistance to fire and heat is a little lacking. Chlorobutyl rubber, a derivative of butyl rubber has 1.2% Cl by weight. This addition slightly increases thermal resistance.

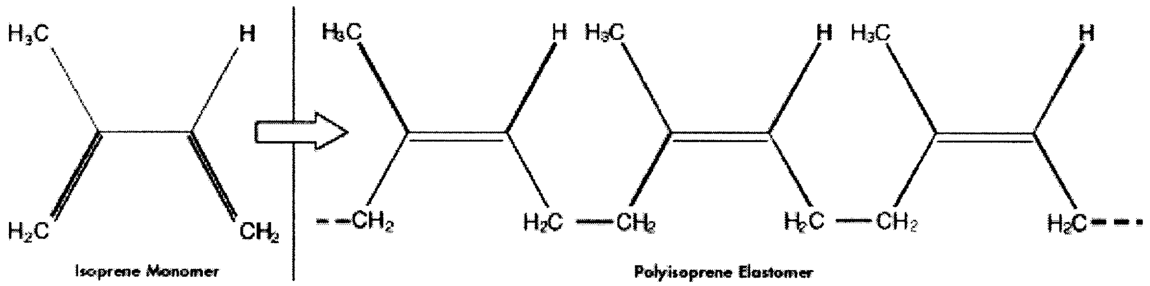
Silicone Rubber. A synthetic rubber, it is softer and more flexible than other types of rubber. It ensures a better formed fit around each individual user. However, its permeability to the outside environment can be an issue.

Perfluorocarbon Rubber. A relatively high thermal resistant rubber which is highly impermeable. However, its poor tensile properties (tears easily) and high cost makes it less attractive.

Elastomers are used in a wide variety of applications. World consumption and demand for high performance elastomers have seen a dramatic rise (Tao 2005). With continuing development and improvements in technology, these elastomers continue to see use in their current applications, as well as provide the properties necessary for a variety of new applications.

Elastomers are a class of materials with properties quite distinct from all other solid materials. They are highly elastic; in some cases capable of being stretched many times their original length, and upon release revert to their original state. Their ability to deform significantly and hence conform to the geometries of adjacent surfaces make them ideal for use in seals, sealants, gaskets, shock absorbing applications, and gas mask seals. Elastomers are a subclass of polymers –their main distinction from other polymers is their remarkable elasticity and deformability.

Elastomers may be obtained from nature or via synthesis. Natural rubber is any elastomeric material formed from a natural course of latex. The most common is the Hevea Tree, found primarily in tropical regions. Once the latex is extracted from the rubber tree, it is coagulated and further processed to fabricate the desired product. The extracted latex product from the Hevea plant is the 2-methyl 1,4 butadiene, more commonly known as isoprene. The resulting elastomer is formed when isoprene polymerizes into a chain molecule.

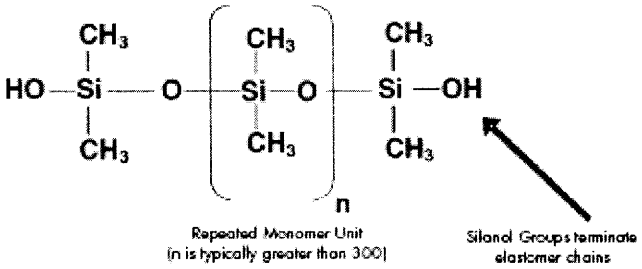


Polymerization of Polyisoprene (Natural Rubber)

(Grethlein and Craig 2004)

Synthetic elastomers on the other hand may be formulated from organic or inorganic sources. The organic elastomers are typically derived from petroleum sources. Global conflicts and periodic supply shortages of both World Wars catalyzed the development of the first synthetic analogs to natural rubber. Since the 1920's, a number of synthetic rubbers have been introduced, each a variant of the basic isoprene elastomer. Beyond establishing more reliable supplies, many of the synthetics were developed to enhance one or more elastomeric properties – usually expanding operating temperature range or improving chemical and environmental resistance. Carbon based synthetics differ from isoprene by the addition or substitution of different atoms or functional groups along the polymer chain's backbone.

Many inorganic elastomers are generally based off of silicone chemistry. Silicone polymers are fundamentally structured similarly to organic polymers. However, silicon instead of carbon is present as the backbone of the chain. More precisely, silicone's backbone is comprised of alternating Si and O atoms. The oxygen bonds between the Si atoms provide molecular stability by spacing the Silicone atoms (which are much larger that C atoms) beyond the range of their mutual repulsion.



$$HO-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-OH$$

Polydimethylsiloxane (Silicone) Elastomer

(Grethlein and Craig 2004)

The thermodynamics of elastomers are rather unique compared to other solid materials. Typically, most solids expand when heated, but elastomers under tension actually contract when heated. This behavior is known as the Gough Joule effect and is due to their internal structure. In a relaxed state, the molecules of an elastomer are tangled around themselves and adjacent molecules. When they stretch, they untangle becoming more ordered. In effect, their relative state of entropy decreases as they are extended. The thermodynamic behavior of all materials dictates that the relative state of entropy increases upon heating and decreases upon cooling. Therefore, when an already extended elastomer (in low entropy state) is heated, it must contract in response to the relative increase in entropy. Similarly, an elastomer in a relaxed state (high state of entropy) will expand when cooled.

DEGRADATION OF ELASTOMERS

Heat resistance is the maximum temperature at which elastomers are capable of operating for an extended period of time, while still retaining functionality. Elastomers exposed to heat and/ or air may show a progressive change in their physical and chemical properties. At elevated temperatures, molecules absorb heat energy leading to covalent bond cleavage and material degradation. Therefore, it is of interest to know the bond energies of the elastomer backbone.

Unsaturation in the polymer chain will make the material more susceptible to heat, because the energy required to break the second bond of C=C to form active radicals is relatively low. On the other hand, silicone elastomers and fluoroelastomers have high thermal stabilities resulting from their structure containing very strong Si-O and C-F bonds.

When exposed to heat such as a source of ignition or flame, the surface temperature of a polymer can rise to a point in which its structure will break down and will release volatile material. Physical properties which can influence this are thermal conductivities, heat capacity, and the ability to melt back away from an ignition source. The behavior of a polymer in a fire risk situation is the result of a combination of many different physical and chemical processes, which take place in the condensed phase.

Thermal decomposition of a polymer is often initiated by dissociation of covalent bonds to form radicals. Bond dissociation energies will depend on the nature of the atoms making up the bond and also the precise structural environment in which the bond occurs. Bond dissociation values can often be used to explain why one bond dissociates in preference to another, and are a particular concern for polymers which degrade by free radical mechanisms.

Scission can occur either randomly or by chain–end process, often referred to as an unzipping reaction. Volatile products may be clipped from the end of a polymer chain from the very beginning of the reaction, with a distribution that is not random, or by process of end scission or backbiting. A process of unzipping may regenerate the monomer. In addition to these cleavages, at the lowest reaction temperatures, enlargement processes can occur which increases molecular weight and increase polymeric branching.

There are many stages of polymer degradation as subsets of thermal degradation (Pielchowski 2005).

-Random initiation: where degradation occurs in the middle of the chain.

-Depropagation: another degradation method where monomers keep volatizing out of the medium.

-Intermolecular transfer: a polymer and polymer radical yield two polymers and a polymer radical.

-Terminal initiation: degradation occurring at the end of a polymer chain when a monomer is volatized out of the reaction medium.

-Unimolecular termination: where a short polymer chain breaks up into products, but this is rarely accounted for in the bulk phase.

-Termination by disproportionation: two polymer radicals share radicals and yield two non-radical polymers

-Termination by recombination: two polymer radicals join together to form non-radical products

In addition, some polymers degrade by concerted mechanisms, in which bonds are broken and formed simultaneously. These are usually lower energy processes, and take place at lower temperatures.

On the macroscopic scale, three types of changes to elastomers by heat are typical.

1) Additional crosslinkage in higher crosslink density which result in embrittlement. This can lead to the degradation of the ability of the elastomer to stretch and be pliant.

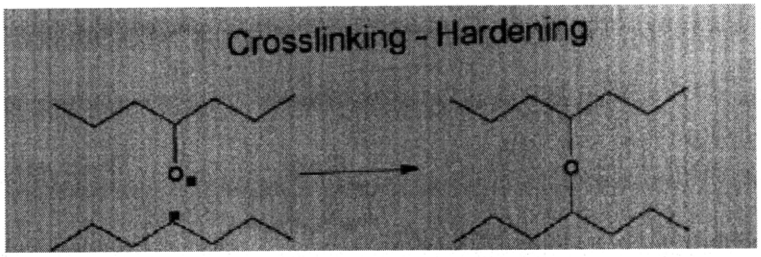


Figure 1 (Ferradino 2003)

2) Chain scission leading to a reduction in chain length and average molecular weight, leading to softening and eventual melting or "volatization". This has proven to be a major hazard in the case of soldiers' burn injuries

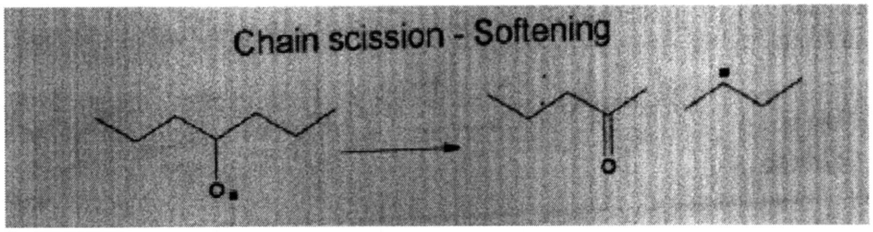


Figure 2 (Ferradino 2003)

The very popular Under Armor shirts used by soldiers serve as a great example of the hazards posed by a melting polymeric material.

3) Chemical alternation of the polymer chain by the formation of polar or other groups. This results in smaller and more volatile molecular species. This eventually leads to combustion and burning.

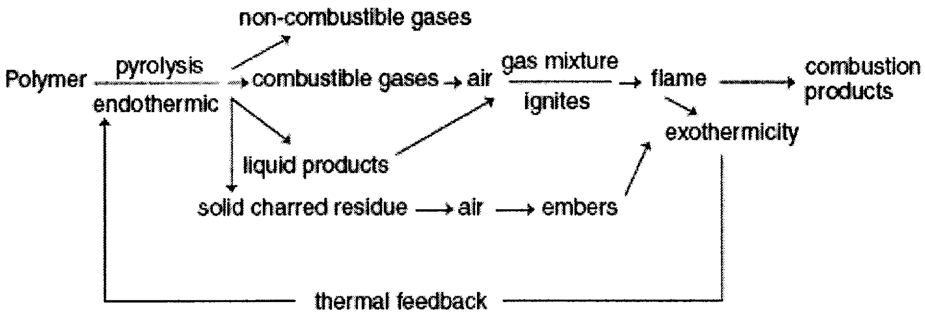


Figure 4 - Burn Process of Polymers

(Horrocks and Price 2001)

The kinetics of thermal decomposition is complicated in that it involves a large number of reactions (as described above) in parallel and in series. The existence of more than one concurrent chemical reaction accompanied by other physical phenomena such as evaporation and ablation introduce further complications for the modeling of degradation kinetics. Current mathematical models of thermal decomposition make it somewhat possible to understand the whole process of thermal degradation of elastomers. However, they are based upon oversimplification of the chemical reactions involved.

DEGRADATION METHOD 1-Burning/Combustion

Combustion is a gas phase reaction. The polymer or its decomposition products must become gaseous for the process of pyrolysis, the formation of gaseous products to initiate a fire to begin. Combustion of elastomers involves the reaction of free radicals at high temperatures.

At elevated temperatures, molecules absorb heat energy to covalent bond cleavage and material degradation. The bond energies of the elastomers are of significant interest. Moderately high temperatures may cause the exchange of crosslinks, while higher temperatures can result in scission of the bonds and hence melting. At even higher temperatures, whether through autoignition or in presence of an ignition source, combustion and/or oxidation are capable of occurring.

The rate at which oxygen reacts with a polymer approximately doubles for each 10C increase in temperature (Tao 2005). There is a likelihood that the deterioration process will go through a thermo oxidative degradation, known as autocatalytic free radical process as pictured below.

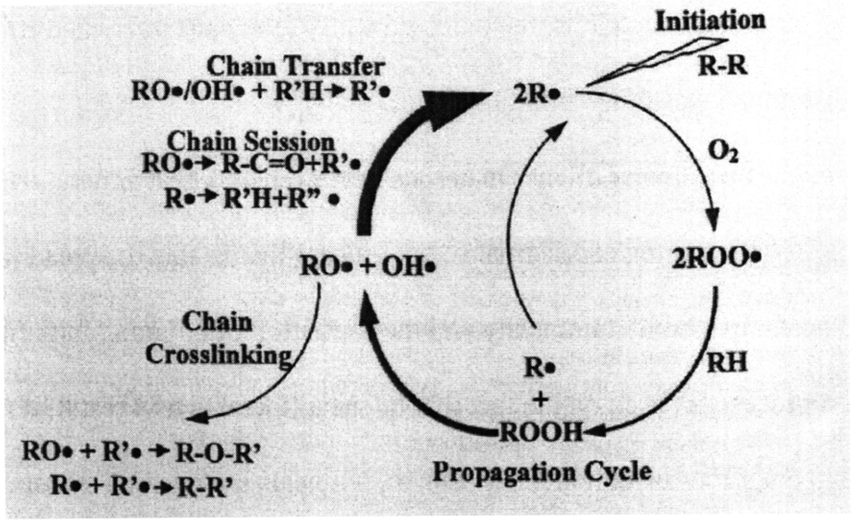


Fig 5 - The Cyclic Oxidation/Burn Cycle of Polymers

(Tao 2005)

The oxidative heat aging essentially takes place via radical reactions. It is initiated by any form of energy, such as heat, mechanical shear, or radiation, breaking the covalent bonds along the polymer backbone or side chains to produce unstable radicals. The radicals may also be initiated from other sources such as additives or contacting fluids. These radicals are so unstable that they react readily with oxygen to form peroxy radicals. The cyclic process continues by chain transfer or chain scission to produce even more new active radicals. It may undergo termination of new crosslinks, which lead to combustion.

In addition to the impact of elevated temperatures on the oxidation rate, oxidation is also affected by the oxygen density at the reaction site, which depends on the oxygen diffusion rates. The oxygen diffusion rate is dependant on the elastomer type and the composition, including factors such as the types and amount of additives and/or fillers, design of the elastomeric part, and the application. If the availability of oxygen is limited by diffusion, components with thick elastomeric layers can be considerably more resistant to elevated temperatures than those with thin layers. Additionally in some applications, the oxidized skin of the elastomer can further limit oxygen ingress to extend the elastomer's durability.

The combustion of common polymer materials is viewed as a heat generating process and is defined as a fast, self accelerating exothermal redox process that is able to spread in the environment and is accompanied by luminosity and the formation of a flame. Initiation of the polymer combustion process is based on the fact that the heat liberated as a result of the redox reaction is not able to enter the surrounding atmosphere but heats the reacting system and increases the rate of reaction. The resulting heat then causes self propagation even after the ignition source has been removed.

When the rate of heat input is equal to the rate of heat required to maintain the process plus losses to the surrounding atmosphere, then a steady state combustion process has been established. The oxygen from the air is used as an oxidizing agent in polymer combustion.

In order to burn polymers, thermal energy must be added to the material to raise its temperature sufficiently to initiate degradation. As mentioned before, this energy can come from an external source in the case of an ignition event, from autoignition, or from adjacent flame as energy feedback in the case of flame propagation.

In the case of a soldier riding in a vehicle with a gas mask on, oxygen effects will no doubt have to be considered. The diffusion rate of the oxygen is dependant on the elastomer type and the composition, including factors such as the type and amount of additives and the design of the elastomer.

Polymers will decompose or pyrolyse evolving flammable volatiles. Ignition occurs spontaneously or from the presence of an external source such as a flame or spark. If the heat evolved by this flame is sufficient to maintain the concentration of the combustible volatiles within the flammability limits for the system, then a self sustaining combustion cycle will be established.

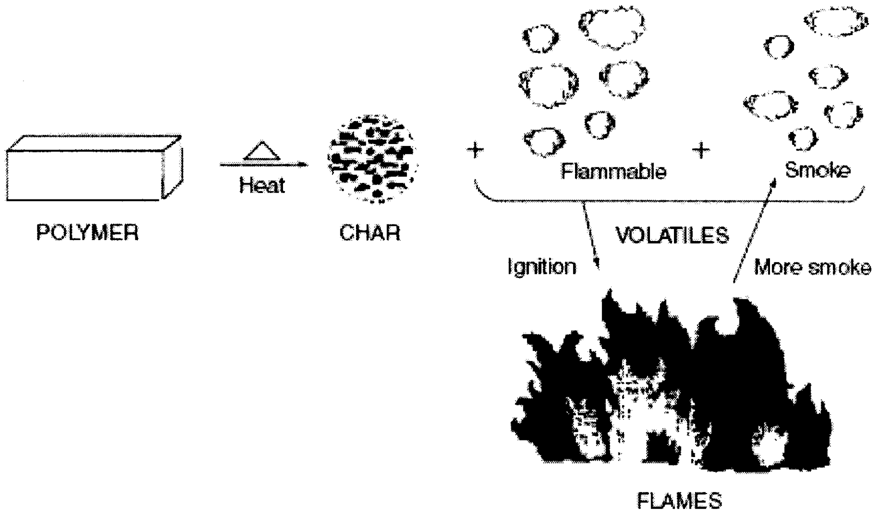
Concurrent with the rapid gas-phase reactions controlled by diffusion flames, slower oxygen dependant reactions will also take place. This reaction will give rise to smoke, soot, and carbon like residue. Some can occur in the condensed phase resulting in glow or incandescence.

Of the mentioned byproduct of burning of an elastomer (as well as many other materials), the key concern is that of smoke formation. The term smoke has a vague definition. In general use, smoke is considered to be a cloud of particles, individually invisible, which is opaque as a result of scattering and/or absorption of visible light (Horrocks and Price 2001). Fumes are considered to be a less opaque form of smoke.

It is necessary to distinguish between combustion gases and visible smoke since the two have different effects, as well as different methods of measurement and significance in fires. Among combustion gases, CO is the chief concern. Other toxic gases that can be formed include hydrogen cyanide, nitrogen oxides, hydrogen chloride, sulphur oxides, and very toxic organic compounds.

Visible smoke generation from burning polymers is generally the result of incomplete combustion. Since polymer flames are diffusion flames, proper mixing for complete burning does not readily occur. The amount of smoke produced in full-scale fires is a function of both the smoke producing tendency and the amount of material burnt. Structural factors in smoke generation are thus important, insofar as they contribute to the inherent stability of the polymer and largely determine the nature of the pyrolyzates which form the combustion fuels. The amount of smoke produced is related to the types of fuels formed on degradation and to the degree of thermal stability of the polymer. Other factors such as the sample size, sample orientation, ventilation, and heat flux contribute to the amount of smoke formed.

As mentioned before, in the presence of sufficiently intense heat source, a polymer will pyrolyse, breaking down to low molecular weight species. These species diffuse from the solid phase into the gas phase, where they form smoke observed in the absence of flame. At high heating rates and with ignition, these lower weight molecular species fuel the polymer flame.



Polymer pyrolysis, burning, and smoke evolution

(Horrock and Price 2001)

DEGRADATION METHOD 2-Melting

As one of the various forms of chain scission, this process probably will be the first to occur for thermoplastic materials. Depending on the amount of crosslinkage, the chain scission process helps break up the bulk polymer or elastomer into smaller particles to help create more particles that can eventually become volatile and take part in the pyrolytic reactions. Other cases, the chain breakage causes the elastomer to "liquify".

One of the key factors is the amount of crosslinkage. If the polymer has enough crosslinkage to classify it as a "thermoset", the material becomes more infusible and insoluble. Simple phase change is not possible.

The other key factor particularly in the case of pure thermoplastics, is the glass transition temperature. The glass transition temperature Tg, is the temperature at which an amorphous solid, such as glass or a polymer, becomes brittle on cooling, or soft on heating. Above Tg, these clusters become large, facilitating the flow of material. Above 0.75Tg, the polymers begin to soften (Ashby 2005).

Thermoplastics can soften by heating without irreversible changes to the material, provided heating does not exceed the minimum thermal decomposition temperature. The behavior of the thermoplastics is dependent on the degree or order in molecular packing (crystallinity).

For crystalline material, there exists a well-defined melting temperature, where a solid transitions to a liquid. Amorphous materials such as elastomers on the other hand transitions from a solid at low temperature to a soft and rubbery state before liquefying. Therefore a Tg can be defined as a range of temperatures for polymers. Elastomers in the rubbery state will lie on the higher temperature portion of the Tg.

If the temperature is well above the Tg, the elastomer will begin to flow. This “flow” can move the material further to the ignition source leading to a worsening fire situation if the elastomer is combustible. In addition, the potential for the hot liquid to drip can spread the combustible liquid and further aggravate the situation.

DEGRADATION METHOD 3-Crosslinkage

Formation of additional crosslinks is dominant in the oxidative process leading to some hardening of the elastomer. Moderately elevated temperature may cause the exchange of crosslinks and formation of additional crosslinks. At even higher temperature, scission of crosslinks may outweigh crosslinking formation, resulting in net softening or melting of the elastomer (the subject is mentioned above).

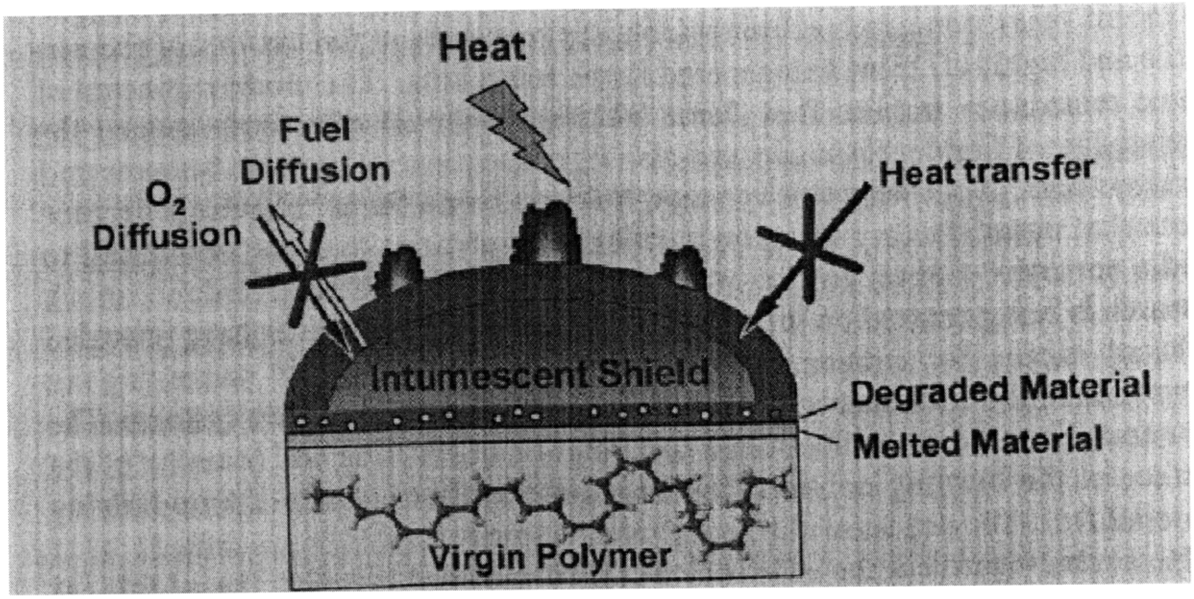
In addition, crosslinkage can promote char formation in polymers. Crosslinkage promotes the stabilization of the polymer structure by providing additional covalent bonds between the chain which have to be broken before the stepwise degradation of the chain occurs by pyrolysis. However, low degrees of crosslinking can actually decrease the thermal stability by increasing the distance between the individual chains and consequently weakening and breaking of bonds. Crosslinking may increase the viscosity of the molten polymer in the combustion zone, thereby lowering the rate of transport of the combustible pyrolysis products to the flame.

COUNTERMEASURES

Of major interest to the plastics and textiles industries is not the fact that their products burn, but how to render them less likely to ignite, and if they ignite, to burn less efficiently. Flame retarding of polymers and elastomers can occur in number of ways. Modifying the pyrolysis process to reduce the amount of flammable volatiles evolved in favor of increasing the formation of less flammable char can serve an additional duty to help insulate the bulk material from the outside heat.

A flame retardant acting via a condensed phase chemical mechanism alters the pyrolytic path of the substrate and substantially reduces the amount of gaseous combustibles produced. Pyrolysis and combustion of polymers occur in several stages, stages which flame retardants try to interrupt. The polymeric substrate heated by an external heat source is pyrolysed with the generation of combustible fuel. Usually, only part of this fuel is fully combusted in the flame by combining with the stoichiometric amount of atmospheric oxygen. The other parts remains and can be combusted by drastic means. A part of the released heat is fed back to the substrate and causes its continued pyrolysis, perpetuating the combustion cycle. Another part is lost to the environment. The energy needed to heat the polymer to the pyrolysis temperature and to decompose and gassify or volatize the combustibles and the amount and character of the gaseuous products determines the flammability of the substrate.

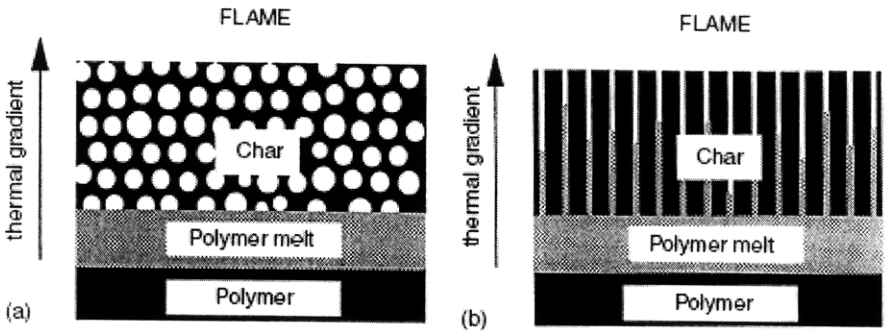
One of the key criteria that help aid heat resistance of elastomers is the formation of a charing layer. Charing is probably the most important condensed phase mechanism for modifying the combustion process. Formation of a char layer on the side exposed to heat helps serve as a barrier to heat and mass flow. The efficiency of a char as a barrier to heat degradation depends greatly on its chemical and physical structure. The ability of char formation to prevent sustained ignition will also depend on its rate of formation to other degradation mechanisms, especially the release of combustible gases. In some ways this has a similar function to passive corrosion of metals where the outer most layer forms an extremely strong oxide that prevents the bulk metal from corrosion.



Intumescence Polymeric Formation

(Le Bras 2005)

To illustrate the importance of the physical structure of char on fire retardant properties, it is useful to describe an ideal and nonideal char.



(a) Ideal char structure, (b) Poor char structure

(Horrocks and Price 2001)

The ideal char for fire retardant properties is an intact structure of closed cells containing pockets of insulating gas. For this to happen, the bubbles of gas must become frozen into the expanding and thickening polymer melt, which ultimately solidifies to produce the honeycombed structure. This prevents the flow of volatile liquids or vapors into the flame and provides sufficient thermal gradient to keep the remaining polymer or polymer melt below its decomposition temperature.

The non ideal or poor char structure does not contain closed cells, but channels or fissure through which gaseous decomposition products or polymer melt can escape. Of these two effects, the more important is the movement of liquid products which can be drawn by capillary action into hotter regions where they are more likely to decompose. This negates any heat insulating effects that the char may have on the bulk polymer underneath.

Factors which influence the type of char formed are still not properly understood, but will include melt viscosity, the surface tension of the melting gas interface, and the kinetics of gasification and polymer crosslinking.

Introduction of chlorine and bromine compounds can aid in fire retardancy. Being free radicals themselves, the Cl and Br ions scavenge the flammable free radicals of combustion and attach to them, removing the flammable radicals away (Ashby 2007). However, caution must be taken with halogens. In addition to potential toxicity, halogenation of low to moderate amount tends to increase the amount of smoke formed (Horrocks and Price 2001). Highly halogenated polymers on the other hand have reduced smoking tendencies. Reducing the heat flow back to the polymer to prevent further pyrolysis can also help. Heat sinks such as metal hydroxides aid in this effort significantly.

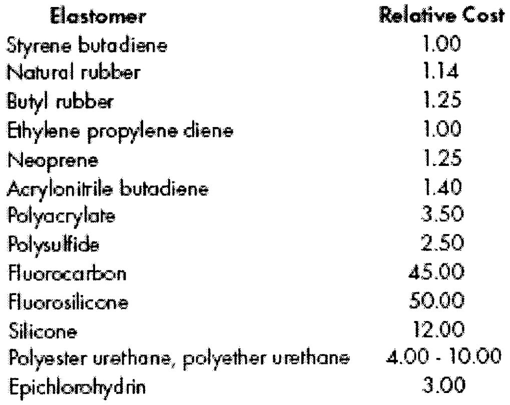
Countermeasure materials for thermal degradation mainly come in three forms.

1) Elastomer material that is relatively heat resistant.
2) An appropriate curing agent that can help the elastomer resist heat, usually by crosslinking.
3) Filler and additive materials.

COUNTERMEASURE MATERIAL 1-Flame Resistant Elastomer

In some elastomers which are inherently flame resistant, the oxidized outer skin can potentially limit the oxygen ingress to extend the elastomer's durability. Thus limitation of this rate is critical. Carboneous char can also help provide an insulating layer. This process is also known as intumescence. However, it is important to know how much damage will occur to the mask's ability to seal off outside contaminated air.

However, relying totally on an elastomer that is flame resistant may be counter productive. Even the heat resistant of a typical heat resistant elastomer such as fluorocarbon rubber only has a 200C more heat resistant than butyl rubber which has poor flame resistant capability (Grethlein and Craig 2004). However the difference in price can be a whole other story.



Elastomer	**Relative Cost**
Styrene butadiene	1.00
Natural rubber	1.14
Butyl rubber	1.25
Ethylene propylene diene	1.00
Neoprene	1.25
Acrylonitrile butadiene	1.40
Polyacrylate	3.50
Polysulfide	2.50
Fluorocarbon	45.00
Fluorosilicone	50.00
Silicone	12.00
Polyester urethane, polyether urethane	4.00 - 10.00
Epichlorohydrin	3.00

Relative Costs of Elastomers

(Grethlein and Craig 2004)

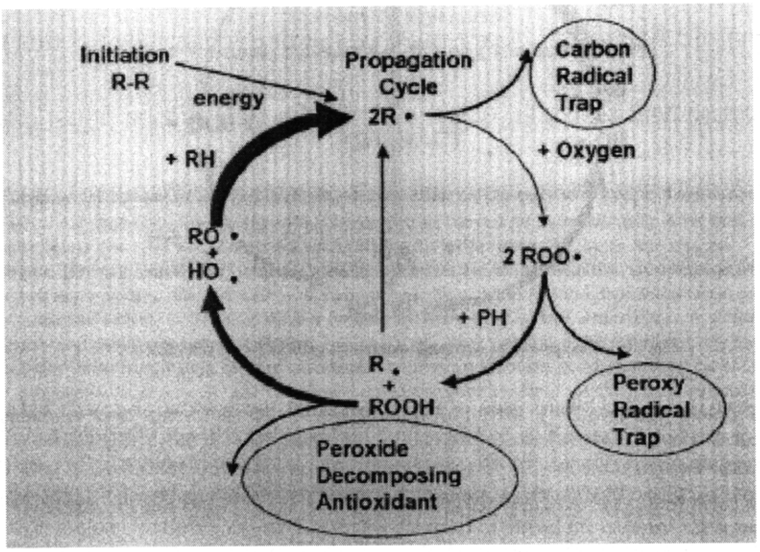
COUNTERMEASURE MATERIAL 2-Curing Agents

Concerning crosslinking, the vulcanization process used in the elastomer also plays a role in thermal stability. Vulcanization refers to a specific curing process of rubber involving high heat and the addition of sulfur or other equivalent curatives. It is a chemical process in which polymer molecules are linked to other polymer molecules by atomic bridges composed of sulfur atoms or carbon to carbon bonds. The end result is that the springy rubber molecules become crosslinked to a greater or lesser extent. This makes the bulk material harder, much more durable and also more resistant to chemical damage.

Crosslinking also makes the surface of the material smoother and prevents it from sticking to metal or plastic chemical catalysts. Care must be taken to ensure that if this method is used to make the elastomer more heat resistant, that the elastomer will still be pliant and adhesive enough to provide a seal. It is also ironic that crosslinking is a potential “damage” mechanism of heat as mentioned above. In addition, elastomers can be crosslinked with peroxides to yield rubber products with the best high temperature resistance.

Oxidation is the cyclic autocatalytic free radical process. Degradation is initiated by any form of energy that can break the bonds along the polymer backbone to produce unstable free radicals. These radicals are unstable and react readily with oxygen to form peroxy radicals. Once formed, the peroxy radicals can abstract labile hydrogen atoms from another polymer molecule to form hydroperoxide and another radical to propagate the cycle. The process then accelerates when the hydroperoxides decomposes into 2 radicals, alkoxy (RO) and hydroxy (HO). Loss of elastomeric properties (strength and elongation) occurs when the alkoxy radicals couple with carbon radicals to form crosslinks that lead to polymer embrittlement, or undergo disproportionation reactions leading to chain scission or melting. These reactions occur simultaneously.

To counter the autocatalytic free radical process, antioxidants in the curing agents scavenge and destroy the chain propagating peroxy and alkoxy radicals before they can react with the polymer. The radicals are converted to inert byproducts. Some antioxidants decompose chain-initiating hydroperoxides to non radical products. However, too much antioxidants can result in the regeneration of a pro-oxidant effect.



General antioxidant mechanism of protection

(Ferradino 2003)

Because of the free radical mechanism of the peroxide crosslinking, materials that compete with the polymer for the free radicals should be minimized. Antioxidants by function are potent free radical scavengers, competing directly with the polymer for the radicals generated by peroxides. Antioxidant selection needs to be made by considering the balance between antioxidant effectiveness and interference with peroxide crosslinking. An important trade off to consider when using antioxidants with peroxide cured elastomers is that between compression set resistance and high temperature oxidative aging resistance. In a high temperature oxidative environment, appropriately chosen antioxidants will help retain physical properties, while the unprotected compounds will rapidly embrittle. With the wrong antioxidant, undercuring and chain scission (melting) can result.

COUNTERMEASURE MATERIAL 3-Fillers and Additives

From a manufacturing point of view, the introduction of additives and fillers is the easiest and most cost effective way to make an elastomer less flammable. Development of filler material is also where nanomaterials seem to have the potential to make the biggest impact in terms of making an elastomer more fire/melt resistant (Le Bras 2003). Some fillers can decompose endothermically and hence absorb a lot of heat while liberating water. Addition of fillers with antioxidant properties may potentially protect the elastomer from further oxidation and melting. Fillers composing of less than 20% of the bulk product are called additives (Horrock and Price 2001). Filler materials should have a high heat capacity. At smaller nanoscale, the fillers tend to do a better job of protecting against heat. Hydrated fillers reduce the burn rate by inhibiting the rates of heat transfer from the flame to the underling matrix. For example, on thermal breakdown, Mg and Al hydroxides break down to their oxides, which further provide a more effective thermal barrier. The oxide becomes part of the ash that serves as the insulation barrier.

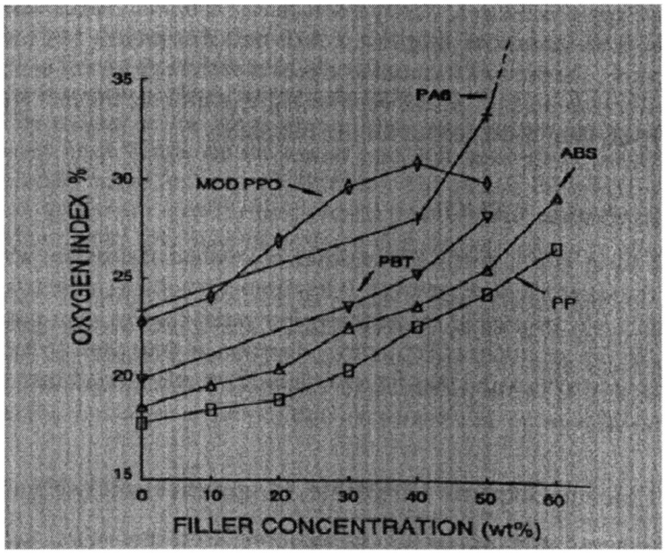


Figure 7- Influence of magnesium hydroxide fillers

on the Oxygen index of various polymers

(Le Bras 2005)

Fillers are non polymeric compounding materials. There are two classes of fillers, inert and active. Inert fillers reduce the amount of smoke generated from given mass or volume of a polymer simply by diluting or reducing the amount of combustible substrate present and also by absorbing heat to reduce the burning rate. Examples of such fillers are silica (SiO_2), clays, $CaCO_3$, and carbon black. A word of caution, it is possible that a filler may be inert in one polymer system, but active in another. Inert fillers usually give only marginal improvements in flame retardancy unless present in very high concentrations.

Active fillers promote the same diluting and heat absorption functions as inert fillers, but they absorb more heat per unit rate by endothermic processes. Gases such as water vapor, carbon dioxide, or ammonia released from these fillers during heating may also dilute the fuel volatiles and modify flame reactions. Examples of currently used active fillers include Aluminum Hydroxide $Al(OH)_3$ and Magnesium Hydroxide $Mg(OH)_2$. In these two materials, the water of hydration is released at temperatures approximating to those of polymer decomposition, producing both flame-retardant and smoke-suppressing effects.

Flame retardant additives can act by a variety of mechanisms in either the condensed phase or gas phase. They can terminate the free radical reactions in the condensed phase, act as heat sinks due to their heat capacity, form nonflammable protective coatings or char, and interrupt the flame combustion.

The gas phase activity of the active flame retardant consists in its interference in the combustion train of the polymer. Polymers, like other fuels can produce pyrolysis species capable of reaction with atmospheric oxygen. To slow down or stop the combustion, it is imperative to hinder the chain branching reactions.

In the condensed phase mechanism, chemical interaction between flame retarding agents and the polymer is postulated. This occurs at temperatures lower than those of the pyrolytic decomposition.

PATENTS

There are numerous patents containing fire, heat, or melt resistant elastomers. However, little is written about heat resistant elastomers that not only resist very high temperature but also help seal against various WMD threats. Part of the problems entails that the very science that make the elastomer soft and pliant is exactly the same science that make the elastomer less resistant to fire and heat. In addition, very few of these elastomers will stand up to a fire greater than 500C. This pales in comparison to a flashover temperature that can reach well over 1000C.

The following is the list of relevant patents. Not much is written about an elastomeric material that can withstand flashover temperatures greater than fifteen seconds, and still be soft and pliant to provide an effective seal. Considering the fact that the most modern firefighting protective gear provide only seconds of protection from a flashover, the effort to invent an elastomer that will last for a sustained period of time is counterproductive.

In terms of fire protection, much is written about textiles and clothing. However, there is very little relevance in terms of a soldier's WMD protection from breathing contaminated air. The first and foremost job of a chemical protective device is chemical protection not fire/melt protection (which is secondary).

If one produces a gas mask elastomeric seal that can withstand flashover fires of over fifteen seconds, and retain its mechanical and elastic properties, a patent should be no problem to obtain.

The following is a list of relevant patents:

Patent Number: 3438932
Title: High Strength, Heat Resistant, Fluoroelastomers
Filing Date: 12/9/1966
Date of Patent: 4/15/1969

Protections offered by this patent have been long expired. However, the fact that this patent mentions the word "heat resistant" is interesting. Temperature resistance is mentioned at 700F (371C). Usage for tires, seals, hoses, and clamping devices have been mentioned. However, little is mentioned about permeability. It is apparent that the inventor did not have chemical weapons protection in mind when developing this material because no such thing is mentioned in the patent. Its usage for chemical weapons gas mask seal must be further explored. Nothing is mentioned that describes its resistance to flashover temperatures.

Patent Number: 5875775
Title: Protective Breathing Mask
Filing Date: 4/9/1997
Date of Patent: 3/2/1999

The mask comprises of a fire resistant stretchable material shaped as a hood for wearing over and enclosing the head. The seal is provided at the neck as opposed to the face with conventional military gas masks. The mask includes a visor and filter material sealed to a stretchable material. The patent seems to indicate that this mask is meant more for temporary short term protection, because nothing is mentioned about how the filter will be replaced. In addition temperature resistance is mentioned at 250C, which is not adequate for flashover protection.

Patent Number: 5922799
Title: Organopolysiloxane Compositions Which can be Crosslinked to give Flame-Resistant Elastomers
Filing Date 2/24/1997
Date of Patent: 7/13/99

This patent essentially describes a silicon based flame resistant elastomer with boron carbide filler. The use is described of boron compounds chosen from the group consisting of boron carbide and metal borides mixed with non-reinforcing fillers, with the provision that at least 75% by weight of the non-reinforcing fillers are heat-stable up to 1200C as flameproofing agents in organopolysiloxane compositions which can be crosslinked to flame-resistant elastomers.

The high percentage of filler materials will likely make this elastomer unsuitable for use as a gas mask seal. Fillers of this amount are well known to negatively affect the mechanical properties of the elastomer. A gas mask that tears when a soldier attempts to don a gas mask is useless. Secondly, the elastomer is silicon based. Silicon, though more heat resistant to other elastomers, has issues with permeability. More testing is needed if a material such as this is suitable for use as an elastomeric seal

Patent Number: 6892725
Title: Protective Hoods and Neck Seals for use Therein
Filing Date: 4/26/02
Date of Patent: 5/17/05

The main features of this patent is new design features for a gas mask. A neck seal is included that helps seal off outside contaminated air. This is in addition to the seal for the nose and mouth. A section fabricated from a heat sealable material at the hood is included. The mask's resistance to various agents, both chemical and biological were mentioned. However, nothing is mentioned about its resistance to high temperatures.

SUMMARY AND CONCLUSION

It is important to mention again that the primary function of the military gas mask is and should still be the filtration of contaminated air, and this function should be the first in consideration in design above all else. However, with more soldiers going into combat operated by combustible fuel, the dangers of burn injuries are ever present. Today's soldier is burdened by a myriad of hazards. Countermeasures to one hazard can make a soldier more vulnerable to another. The best example is that of tank armor. A heavier tank has more protection, but the compromised mobility caused by added weight can be just as deadly.

In terms of gas masks, it is possible that selecting materials solely for heat resistance can affect its ability to provide an effective seal or impermeability to the outside environment (ie silicon). Other properties such as resistance to corrosive material (particularly blistering chemical agents), mechanical durability, and adhesiveness to the skin (to provide maximum seal from the chemically contaminated environment) can be compromised as well. The physical properties of polymers are often badly affected by the addition of fillers and additives. For example, high impact resistant polymers such as ABS, suffer massive reduction in impact strength in the presence of fillers, often making filler treatments impractical in some applications. Loss of impact and tensile properties in other polymers can be somewhat reduced by the addition of impact modifiers. The best combination of fillers, elastomers, and curing agents must be produced and tested

Also, the potential material should not be toxic. For example, one may think of using PCB's as an elastomer material and asbestos as potential filler. Both materials have excellent heat/ fire resistance. Time has shown that asbestos and PCB's to be toxic materials. Further testing by the military will be needed to determine the appropriate mix of various properties before the development and fielding of the new seal material. Certain new nanomaterials that have been developed such as carbon nanotubes (its high thermal conductivity may be an issue with usage as a filler/additive) have been documented to cause lung scarring similar to the precancerous scarring that occurs from asbestos.

The primary intended customer is the United States military. If a quality product is achieved, the military is certain to purchase the product. In addition, law enforcement and militaries of allied nations (i.e. Israel, South Korea, and Japan in particular) will take serious interest in this fire resistant gas mask.

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