

Silicone Rubber Flame Resistance

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Abstract

The requirements for a material to combust are heat, fuel, and oxygen. Limiting the interaction of a material with at least one of these requirements will impede the combustion process and impart a level of flame resistance. This is achieved by modifying the composition of a material to include chemicals that specifically target impedance of the combustion process. The level of flame resistance required from a material is specific to the end application and can be measured by one of the many test methods available. Silicone rubber is often selected as the design elastomer because of its excellent flame resistance and low smoke toxicity. Arlon has developed a number of calenderable silicone rubber compounds capable of meeting the flame resistance requirements for even the most stringent flame resistance requirements.

Key words: silicone rubber, flame resistance

Introduction

Flame resistance is a complex property of a material that depends in part on its composition, construction, thermal stability, and environment. The composition of a material can have a significant effect on its flame resistance. Silicone rubber compounds often contain additive packages to impart color, modify rheology, improve adhesion or release, neutralize acids, and initiate cure. An additive package can have a pronounced effect on flame resistance. Pigments containing cadmium or lead, low molecular weight silicones used to modify rheology, certain filler systems and acid by-products have a negative effect on flame resistance. Catalysts can have either a negative or positive effect on flame resistance. The construction of a material can also play a significant role in its flame resistance. Composites of silicone rubber and a supporting fabric such as fiberglass will have a lower degree of flame resistance under specific conditions than a homogeneous silicone rubber sheet. This is due to delamination of the silicone rubber from the supporting fabric during burning. Pockets within the composite material fill with flammable degradation products that support combustion as they escape through the flame impingement point. Increasing the thermal stability of a material will improve its flame resistance. In general, solid materials do not burn as easily as smaller molecular fragments of a material. Higher thermal stability equates to less decomposition and

fewer molecular fragments; therefore, improving flame resistance. The environmental effect on flame resistance can be observed by evaluating the performance of a material using several different methods. The environment of the UL94 flame resistance standard is different from that of FAR 25.853, which is different from FAR 25.856. The variations from one method to another can produce widely different results from an identical test material.

Improving Flame Resistance (FR) through Composition

The flame resistance of silicone rubber can be improved by admixing with flame retardant additives such as the well-known halogens and metal hydrates or the lesser known platinum, rhodium, and iridium complexes. Intumescent or ceramifying additives do not actually impart flame resistance, but they can be used as a form of passive flame resistance. Multiple methodologies may be combined into a single product to achieve the highest level of flame resistance possible.

Halogenated Flame Retardants

Halogenated flame retardants (HFR) are among the most well-known and scrutinized flame retardants. Recently implemented legislation, such as Directive 2002/95/EC on the Restriction of Hazardous

Substances (RoHS), limits the use of brominated flame retardants in certain materials because of resultant negative effects on the environment. Brominated and chlorinated flame retardants work in the gas phase by neutralizing free-radicals that are responsible for the degradation of the material and the formation of flammable by-products [7]. HFR's are effective at moderate loadings (typically 10%w), because the halogen radical is regenerated in the combustion process [8]. Brominated flame retardants are more effective than chlorinated flame retardants. The bromine radical is released over a narrower temperature range than the chlorine radical producing a higher concentration of bromine in the flame front [8].

Metal Hydrates

Aluminum trihydroxide (ATH) and magnesium dihydroxide (MDH) are two metal hydrates that are used to impart flame resistance. The metal hydrate releases water during thermal decomposition. During combustion, the released water absorbs heat, volatilizes, and cools the burning material. The volatilized water dilutes the degradation products and oxygen at the surface of the material. Additionally, the metal hydrate becomes a metal oxide after dehydration which is non-flammable and insulates the part. A Thermal Analysis Q100 DSC was used with a 5°C/min. heating rate to measure the endotherm and temperature associated with dehydration of ATH and MDH (FIG. 1).

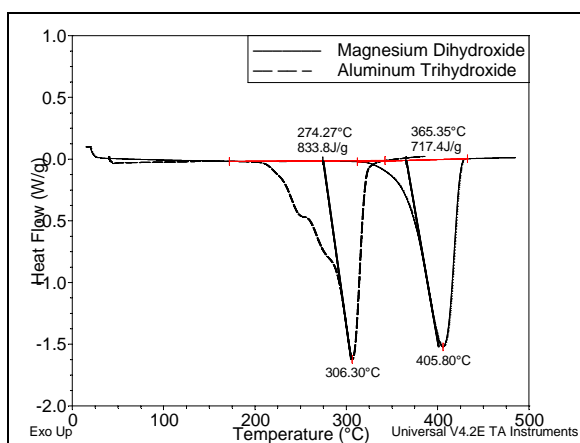


Figure 1: DSC thermograms of ATH and MDH.

It can be seen that both metal hydrates are strongly endothermic and that the dehydration temperature of ATH is lower than MDH. The selection of ATH or MDH can be made based on the required processing temperature or required operating temperature of the part. Materials requiring temperatures near 200°C and above should use MDH to prevent premature

dehydration which may occur with ATH. Both metal hydrates are effective flame retardants, but they require high loading (typically > 30%v) which can negatively affect the physical properties of the polymer.

Transition Metal Complexes

Platinum, rhodium, and iridium complexes impart improved flame resistance to silicone rubber at low loadings (typically < 1%wt) [5, 6]. Platinum is particularly useful because it serves as both a flame retardant and a catalyst for addition cure silicone rubber. The catalytic action of platinum makes it a powerful flame retardant in silicone rubber. During thermal oxidation, the platinum compound catalyzes the formation of methylene-bridges, both inter- and intramolecularly, reducing the potential for thermal degradation [5]. This can be seen in TGA scans of a silicone rubber with and without ppm order of platinum complex added (FIG. 2) [5].

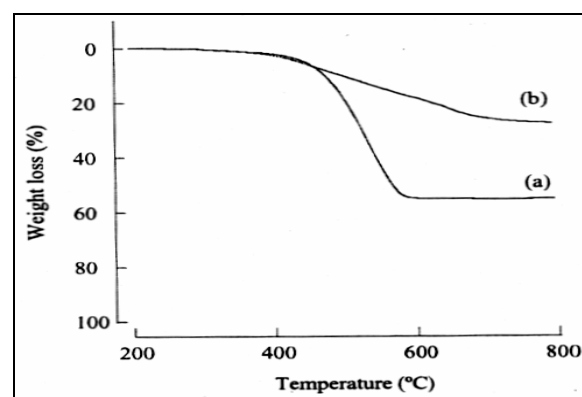


Figure 2: TGA scan of (a) silicone rubber without platinum complex and (b) silicone rubber with platinum complex [5].

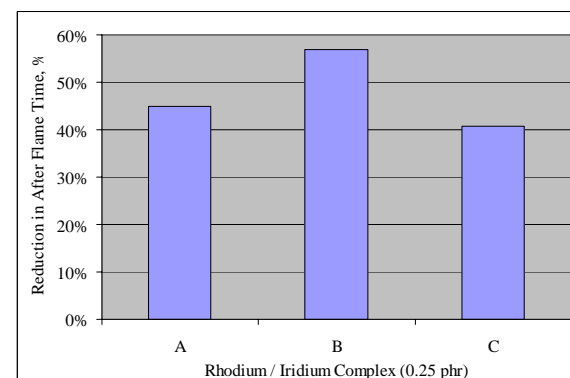


Figure 3: Reduction in after flame time after adding 0.25 phr (A) bis(1,5-cyclooctadiene diridium(I) dichloride, (B) iridium(III) acetylacetonate or (C) rhodium(III) acetylacetonate.

The reduction in thermal degradation afforded by the addition of a platinum complex translates directly into improved flame resistance. Addition of 1.0%w organo-platinum complex dispersed in polysiloxane (*Syl-Off 4000, Dow Corning, Midland, Michigan*) to silicone rubber (*SE 6140, GE Silicones, Waterford, New York*) reduces the after flame time 78% and the char length 68% as measured by FAR 25.853. Addition of 0.25 phr iridium or rhodium complex reduces the after flame time by as much as 57% as measured by FAR 25.853 (FIG. 3).

Ceramifying Components

Intumescent silicone rubber formulations contain a binder, a blowing agent, and an acid source that are designed to form a sacrificial surface that insulates the underlying part. The binder is designed to melt below the degradation temperature of the material. The blowing agent releases a non-flammable gas, such as water vapor, carbon dioxide, nitrogen or ammonia, causing the melted binder to foam. The acid source releases an acid that reacts with the foamed binder forming rigid foam with a high melting temperature [7]. The foamed structure protects the material by insulating it from external heat sources. The foamed structure also prevents the escape of degradation products and interaction with oxygen. Intumescent require heat to function. The required heat can come from the combustion of the material or from external sources. Intumescent materials are used in applications as protective coatings for structural steel supports and in barrier materials to prevent the passage of fire from one area to another.

Improving FR through Construction

Product construction can have a significant effect on flame resistance. Multi-layer composites of silicone rubber and a supporting substrate such as fiberglass are common in the hose and duct industry and flexible heater industry. When multi-layer composites are tested to FAR 25.856 the after flame time will increase as the number of layers increases but the flame propagation distance will remain fairly stable (FIG. 4). This occurs because of interlayer delamination of the composite caused by reduced adhesive strength and increased pressure from decomposition by-products. The blister vents flammable by-products at the point of impingement fueling the after flame.

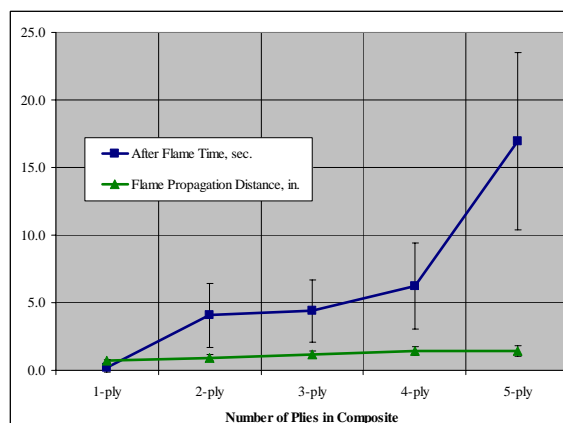


Figure 4: FAR 25.856 results as a function of number of plies on a multi-layer composite of silicone rubber and fiberglass

Improving FR through Polymer Selection

Molecular Structure

Solid materials are often resistant to combustion; however, breakdown of those materials into smaller molecular fragments facilitates combustion. Thermal oxidative degradation is one process that can break down a polymer into smaller, more combustible components. Silicone rubber can undergo thermal oxidative degradation as early as 149°C in an aerobic atmosphere. At 149°C the degradation is weakly detectable, but the rate increases with increasing temperature. At 220°C silicone rubber operates for thousands of hours in flexible heater and motor insulation applications. However, five hours at 300°C can oxidize ~12% of the methyl groups [1]. Increasing the temperature to 350°C can oxidize ~85% of the methyl groups [1]. By 600°C, the methyl groups are completely oxidized and the remaining residue is silicon dioxide. Oxidation also produces carbon monoxide, water, formaldehyde, carbon dioxide, methanol and formic acid [1]. The formaldehyde, methanol and formic acid volatilized during degradation are a source of fuel in a combustion process. The Andrianov mechanism accounts for the volatile oxidation products and the eventual formation of silicon dioxide as shown in figure 5 [1]. Commercially available silicone rubber contains mostly methyl functionality with a few mol percent vinyl, but specialty grades contain phenyl to improve high temperature stability and low temperature flexibility. The following order of thermal stability has been established for the aforementioned functional groups: phenyl > vinyl > methyl [1]. In addition to substitution of the organic functional groups, the siloxane monomer can be copolymerized with a variety of organic groups to

improve the thermal stability of the polymer[1-4]. The silphenylene-siloxane copolymers maintain low temperature flexibility while extending high temperature stability [2-4]. Methyl and vinyl functional silphenylene-siloxane copolymers have glass transition temperatures $\leq -59^{\circ}\text{C}$ and degradation onset temperatures ranging from $374^{\circ}\text{C} - 462^{\circ}\text{C}$ [2, 3]. The most stable silphenylene-siloxane copolymer is a vinyl-vinyl silphenylene-siloxane with almost 70% residue in air at 900°C [2]. The high residue is the outcome of thermally induced cross-linking of the vinyl groups that result in a resinous structure that is resistant to further degradation. This process is specific to vinyl functional silphenylene-siloxanes and begins at 230°C . This precludes the use of these elastomers in high temperature applications.

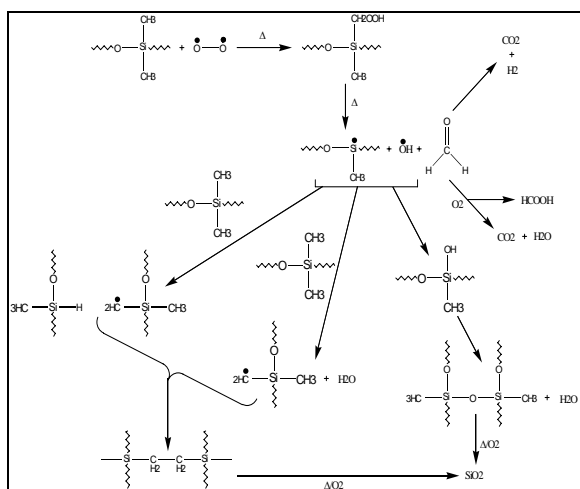


Figure 5: Andrinov mechanism for thermal oxidation of polysiloxanes

Methods for Evaluating Flame Resistance

Flame resistance can be evaluated by numerous test methods. The methods have widely different sample requirements, procedures and criteria. In general, the methods can be loosely divided into two groups based on the presence of a flame source. The first group of flame resistance methods utilizes a flame source to initiate combustion of the sample. FAR 25.853 and FTMS 191A Method 5903.1 orient the sample in the vertical position and initiate combustion with a pilot flame held under the sample for a specific duration [9, 10]. After flame time and char length are measured and used to determine flame resistance of a material. After flame time is the duration of flaming after the ignition source is removed and char length is the distance of material charred during the test. Orientation of the sample in the vertical direction allows heat from the pilot flame and burning material to preheat the flame path.

Preheating the flame path promotes thermal degradation which provides additional fuel to support the combustion process. UL94V is similar to FAR 25.853 and FTMS 191A Method 5903.1 except that it ignites the sample twice and accounts for material that may drip or fall away from the sample [11]. The second ignition gives insight into the resilience of the flame retardant. Materials with flame retardant that is rapidly consumed may show extended after flame times during the second ignition. Additionally, materials that drip or break up during combustion are likely to ignite surrounding materials in a real world scenario. UL94V ranks materials in decreasing order of flame resistance as V-0, V-1 or V-2. The ranking is based on the after flame times, after glow, and whether or not dripping material ignites a material placed under the sample. UL94HB orients the sample horizontally to measure the burning rate of the material [11]. Orientation of the sample horizontally does not allow either the pilot flame or burning material to preheat the sample and will tend to produce slower burning rates than if the sample was oriented vertically. Lastly, FAR 25.856 utilizes a radiant panel and a pilot flame to better replicate a real world flame scenario. The sample is oriented horizontally and impinged with a pilot flame for 15 seconds. The radiant panel remains on for the entire test. The radiant panel increases the heat input into the sample. This heat input creates a situation as if there are materials burning in the vicinity of the sample.. The heat input promotes thermal decomposition and produces flammable by-products that fuel combustion. The after flame time and flame propagation distance are used to determine acceptance.

The second group of flame resistance test methods does not utilize a flame source to initiate combustion of the sample. ASTM E 1354 and thermogravimetric analysis (TGA) utilizes a radiant heat source to impart heat to the sample being tested [12, 13]. ASTM E 1354 radiates a horizontally oriented sample with a constant heat flux to initiate thermal decomposition. A sparker oriented above the sample fires continuously until a sufficient buildup of decomposition products ignites. Time to ignition is determined and then mass loss and heat release are all measured and plotted against time. TGA imposes an isothermal or controlled temperature ramp to thermally decompose a sample. Mass loss as a function of temperature or time is used to determine the thermal stability of a material. Additional analytical equipment such as gas chromatographs, infrared spectrometers or mass spectrometers can be attached to the effluent of the TGA to identify by-products of decomposition. Neither ASTM E 1354

nor TGA measure flame resistance directly. Instead, they measure thermal degradation which is a process during combustion and directly related to flame resistance. ASTM E 1354 measures heat release from the sample, which differentiates it from other methods, and can be used to determine how much heat will buildup in an area as a result of material combustion. This can be used to predict how a material may influence combustion of other materials within the vicinity.

Arlon's Flame Resistant Silicone Rubber Materials

Arlon Silicone Technologies Division offers high consistency silicone rubber compounds capable of satisfying the flame resistant requirements of most applications. The silicone rubber compounds listed below can be provided as bulk compounds as well as calendered sheet goods for a variety of applications. Calendered products with thicknesses from 0.002 – 0.060 in. are available and may be unsupported or supported on a wide variety of substrates. Woven fabric substrate options include fiberglass, aramid, liquid crystal polymer, polyester, and nylon. Film substrate options include polyester, polyimide, and various fluoropolymers. The silicone rubber compounds can be applied as single or multiple layers to one or both sides of the substrate.

Compound Number	Flame Resistance*	Application
510C	1,3,4	Flexible heaters
414C	1,3,4	Flexible heaters
427C	1,3,4	Flexible heaters
493C	1 – 4	Flexible heaters
595CX	1 – 4	Electronic adhesive
594CX	1 – 4	Electronic adhesive
336CX	1 – 5	Hose & duct
RC-3771	1 – 5	Hose & duct

Table 1: Flame resistant silicone rubber compounds offered by Arlon.

* 1: FTMS 191A Method 5903.1. 2: UL 94 V0. 3: UL 94 HB. 4: FAR 25.853. 5: FAR 25.856

Conclusion

The flame resistance of silicone rubber compounds can be modified to meet a variety of flame resistance specifications. Modification is most often performed by admixing the compound with various chemicals that disrupt the combustion cycle or by improving thermal stability. Flame resistance of the final part is dependant on composition, construction and test environment. It is critical to verify flame resistance

on the final product because it can vary significantly from the individual parts.

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