Adding color to medical devices using pigment masterbatch

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WHITE PAPER

ABSTRACT

The use of silicone materials in medical devices is ubiquitous. Silicones have good physical properties, can be processed into a multitude of forms, and are largely considered bio-inert. Adding color to silicone materials that are extruded, molded or calendared for medical devices is common. Medical device companies continue to aid the healthcare community by differentiating models and sizes by color and/or improving the aesthetics of the device with the addition of a corporate color. The incorporation of pigments is often a challenge to the medical device industry both from a processing , consistency, and regulatory perspective.. Processing with pigments are discussed at length and include various methods for adding pigments and the pros and cons of each method.Regulatory support of materials used in medical devices is a mandate in the medical device industry and this paper will outline basic requirements and the relevance to the device engineer.

SILICONES IN MEDICAL DEVICES

Many applications such as pacemaker leads, hydrocephalus shunts, heart valves, finger joints and intraocular lenses utilize silicone materials. Silicones expanded into healthcare and medical applications in the 1950's after extensive use in the aerospace industry in the previous decade and have had a steady growth in use and importance ever since. Over the last twenty years, a considerable body of work had established that silicone oils and crosslinked siloxane systems did not give rise to harmful consequences and have been characterized as biologically and toxologically inert. Several reviews of silicones as biomedical and healthcare materials have been published that provide comprehensive surveys of the chemistry and applications.1-6

Silicones used as medical devices including for long term implants consist of elastomers, gels, adhesives, oils, and lubricants all of which are based on silicone polymers. The polymeric structure of silicones allows it to be designed and formulated to create a variety of material types with specific properties.

SILICONE CHEMISTRY

Silicone elastomers fall into several categories: high consistency rubbers, liquid silicone rubbers, low consistency elastomers and adhesives.

High consistency elastomers are typically composed of high viscosity polymers, high levels of reinforcing silica, and some contain crosslinking polymers. These materials are clay like in an uncured consistency and offer good physical properties. High consistency materials can be molded into parts by compression molding or extruded into tubing configurations.

Liquid silicone rubbers or LSR's are elastomers that contain medium viscosity polymers and moderate amounts of silica. The cured elastomers have good physical properties. They tend to have an uncured consistency like that of Vaseline. These materials can be molded into parts and require the use of liquid injection molding equipment.

Low consistency silicones are pourable systems that are composed of lower viscosity polymers and reinforcing fillers such as silica and resin. These systems have lower physical properties than high consistency or LSR formulations but can easily be processed and molded by hand. These materials can be molded into parts by compression molding or can be used as cured in place seals or gaskets.

Adhesives are low consistency elastomers that contain lower viscosity polymers, reinforcing silica and adhesion promoters. Silicone adhesives are designed to adhere silicones to various substrate surfaces including metals, glass and certain plastics.

POLYMERIZATION

All silicones are inorganic polymers, having no carbon atoms in the backbone, and are named polysiloxane polymers. The diagram below shows their typical structure:

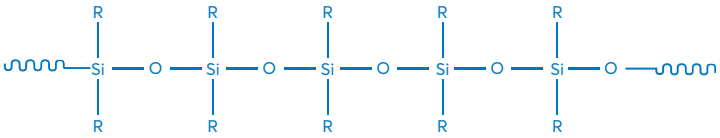

FIGURE 1: Structure of polyorganosiloxane; R= -CH3, -C6H6, -CH2CH2CF3

The silioxane backbone can be formulated with different types of constituent groups be incorporated onto the polymer backbone. Typical constituent groups include dimethyl, methylphenyl, diphenyl, and trifluoropropylmethyl functionality. This chemical flexibility allows polysiloxanes to be used in a wide array of applications.

A silicone elastomer is manufactured in several steps. Initially a silicone polymer is produced in a Ring Opening Polymerization (ROP). The process begins with polyorganosiloxane cyclics reacting with a chain terminating species, or "end blockers," in the presence of an acid or base initiator as shown in Figure 2.

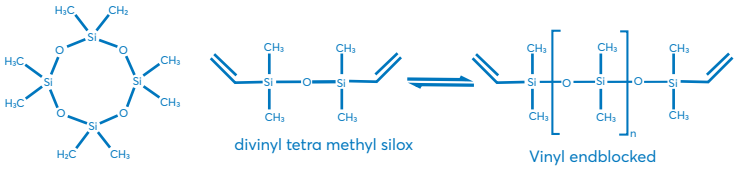

FIGURE 2: Basic Ring Opening Polymerization (ROP) reaction for a vinyl terminated polydimethylsiloxane.

The product of this polymerization reaction is a mixture of various molecular weights of cyclics, short chained linear molecules and higher molecular weight polymers where the concentrations of each species is based on its thermodynamic equilibrium, Figure 4.

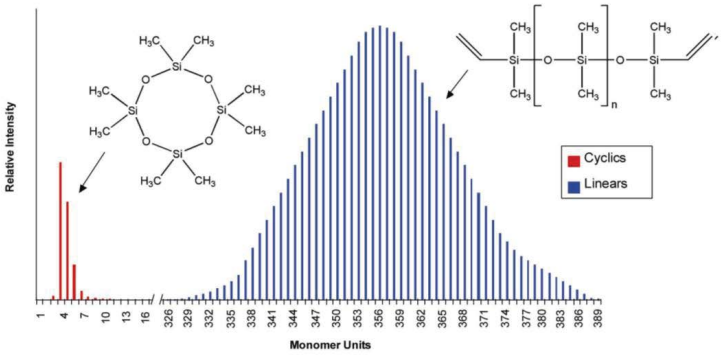

FIGURE 3: Molecular weight distribution of final ROP reaction products of PDMS.

Once the polymer is produced and stripped, it can be reinforced with fillers, pigments and special additives to improve and vary physical properties. At this stage the polymer is called a base. For a 2-part, crosslinker and inhibitor are added to half of the base to create Part B. Catalyst is added to the remaining half of the base creating Part A.

Cure Chemistry:

Silicone systems can be cured by platinum catalyzed addition cured systems, tin condensation cure systems, peroxide cure systems and oxime cure systems. Some of the oldest cure chemistry in silicones is acetoxy tin condensation cure system such as those used in household bathroom caulk. These systems yield a vinegar smell as acetic acid is a byproduct of the reaction. For the purposes of our discussion, the focus will be on platinum systems, as they are the most prevalent in medical device type applications.

Platinum catalyzed silicones utilize a platinum complex to participate in a reaction between a hydride functional siloxane polymer and a vinyl functional siloxane polymer. The result is an ethyl bridge between the two polymers. The reaction mechanism is pictured below:

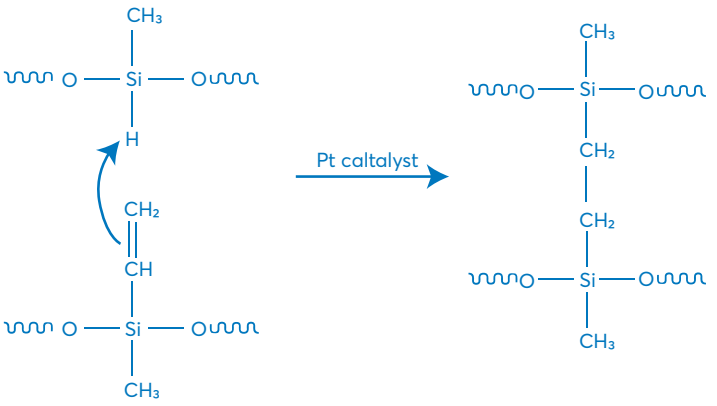

FIGURE 4: Platinum Cure Mechanism.

Platinum systems are often cured quickly with heat but can be formulated to cure at low temperatures and room temperature if necessary. The advantages of these systems include fast cure and no volatile byproducts. Cure inhibition is a disadvantage of this cure system. Inhibition is defined as either temporarily or permanently preventing the system from curing. Some types of inhibitors are added to these systems to control the rate of cure but contact with tin, sulfur, and some amine containing compounds may permanently inhibit cure. Compounds that inhibit cure can be identified easily by attempting to cure a platinum catalyzed system in contact with the compound. Inhibition results in uncatalyzed regions of elastomer systems or inconsistency in cure over time.

INCORPORATING COLOR INTO SILICONE MASTERBATCH

As mentioned above, color in medical devices offer a number of benefits in marketing the device to end use. Color certainly offers a differentiating factor to a device in a competitive marketplace and the addition of corporate colors can create a strong tie to the corporate brand. Color coding of medical devices offers users, such as hospital workers, an efficient means to identify the appropriate device size. Another factor to consider is the migration of medical devices to home use, emphasizing the need for aesthetics to improve use compliance and other factors.(Medical Design Article)

Coloring of silicone materials involves the use of powdered pigments. For a medical device manufacturer powdered pigments often a challenge and can create several problems in processing and color variations. Typically the colored powdered pigment is directly incorporated into an uncured elastomer via milling or mixing procedures. Particulate contamination, handling, and additional cleaning of equipment considerably slows down the production time and adds costly maintenance. A more effective alternative incorporates a color masterbatch prior to the curing stage of the molding or extruding process. Masterbatches are offered in a palette of colors that can be customized to fit a variety of device needs, see Figure 5. Several types of materbatches have been developed for coloring LSR and HCR silicones.

FIGURE 5: Palette of standard colors developed for silicone pigment masterbatches.

Masterbatches consist of pigments dispersed in functional silicone polymers that participate in the elastomer's curing process. Using masterbatch dispersion eliminates particulate contamination in clean rooms and reduces the costly cleaning time involved in using powder pigments.

For coloring LSRs used in the injection molding of silicone parts, a low viscosity masterbatch can be introduced via a third line prior to the dynamic mixing stage. A translucent color palette is also available for coloring LSRs used in the injection molding of silicone parts. However, thickness of the device will affect the color of the device as shown in Figure 6. For HCRs used in tubing extrusion, calendaring, and transfer molding, a high viscosity gum polymer masterbatch can be added directly to the elastomer on two-roll mill during the softening/mixing step.

(a) (b)

FIGURE 6: (a) Translucent palette of colored silicone. (b) The influence of thickness on color.

Consistency is a key consideration facing the device manufacturer. The key to color consistency is the accurate edition of pigment(s) to the elastomer and the homogeneous dispersion of those pigments in the elastomer system. Pigments used in silicones are different than those used in other mediums and because they are not soluble in silicone they must be dispersed. Typical masterbatches are simply powders wet out to be non-dusting materials while in a dispersion pigments are broken down, wet out, and homogenously distributed in the polymer. The addition of powder pigments to a silicone polymer takes expertise and high-quality mixing equipment. An ideal dispersion breaks down the pigments into their primary particle size using high shear mixing and then homogenously dispersing the particles throughout the silicone polymer.

Additional considerations must be taken into account when adding the color masterbatch since colorability can be affected by highly filled systems. Highly filled elastomers tend to be more opaque as shown in Figure 7. Temperature and catalyst may also affect the appearance of color.

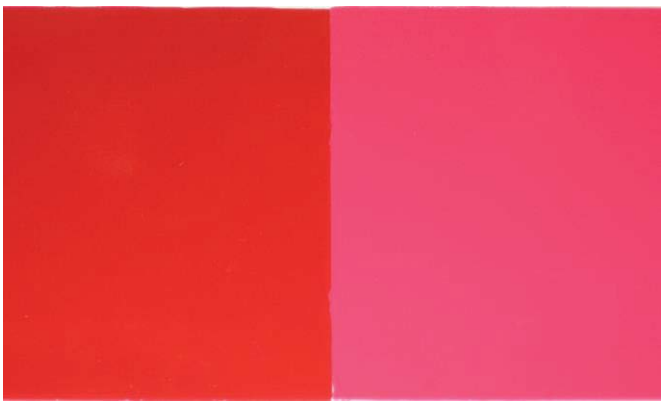

FIGURE 7: The effects of filler concentration on color in an HCR silicone.

REGULATORY CONSIDERATIONS FOR COLOR IN MEDICAL DEVICES

Pigment masterbatches require regulatory support comparable to that provided for the elastomers into which they are incorporated. Support should include a comprehensive masterfile (MAF) submitted by the manufacturer of the masterbatch to the United States Food and Drug Administration (FDA), or other international regulatory authorities responsible for regulating the safety and efficacy of healthcare devices and products in the respective countries into which the finished product is to be marketed. Selection of a pigment with an established healthcare application history, such as those listed on the FDA GRAS 21 CFR § 178.3297 (Generally Recognized as Safe) list, is recommended. The manufacturer of the masterbatch should have a documented quality system certified as conforming to ISO 9001 and cGMP 21 CFR § 820 (current Good Manufacturing Practice).

CONCLUSIONS

The benefits of adding color to medical devices for marketing and/or use are obvious. Several considerations must be taken into account when adding color to silicone materials used in the a device. Processing, more specifically concentration accuracy and clean up are important initial factors to consider. Color consistency in the cured part depends on the optimal filler concentration, material thickness, and cure conditions. , Regulatory requirements, as they relate to materials used in medical devices should be a concern throughout the whole process. Keeping these factors in mind when adding color to a material and ultimately a device will serve to smooth an already complicated process.

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