Application note

Mixing and de-airing addition cure silicones-common methods for bench top and small scale production

Sometimes choosing what silicone is best for your intended application is so distracting that how it will be properly mixed and de-aired during processing is overlooked. Mixing is one of the most common ways air is introduced into a material, and this ultimately causes bubbles in the cured silicone. Thorough mixing is extremely important to ensure the material has the desired cure rate and cured mechanical properties (as reported on the material certification). Silicone and air mixtures are very complex and dynamic systems, however this article's purpose is not to discuss fluid dynamics and laminar flow, but rather the basics of how air can be introduced into a system, common methods of mixing and de-airing, and packaging options when specialized mixing and dispensing equipment is not available. These common techniques can help increase yields and reduce scrap in the long run.

HOW DOES AIR GET IN THERE?

First, vigorous hand mixing or propeller-type mixing equipment can introduce air into silicone. Silicones are also permeable to gasses in the atmosphere, and the amount of dissolved gas within a silicone is dependent on laws that combine physics and chemistry, such as Henry's Law. The temperature, pressure, and solubility of gas in the silicone determine the concentration of any gas species in the silicone. Additionally, applying the silicone onto complex geometries where the silicone does not evenly wet out all the surfaces creates voids and subsequently entraps air.

Don't worry, because most applications don't require getting the solubility constant of each gas to ensure there is little remaining air. There are many techniques to ensure air is sufficiently removed to reduce the formation of bubbles, and there are processing techniques that prevent bubbles from remaining or forming in the cured silicone.

FUNDAMENTALS OF SILICONE POLYMER ADDITION CURE CHEMISTRY

In order to understand why vigorous mixing is so important and how to plan your process, it helps to understand the basics of how addition-cure systems work. Addition-cure systems typically consist of two parts, generally referred to as a Part A and Part B. When the two parts are mixed together, the silicone begins to undergo crosslinking via vinyl hydrosilation and cure into a solid rubber material (see Figure 1). This curing mechanism, also known as "Platinum Cure," is widely used since it has no curing by-products, minimal shrinkage, and can cure at various temperatures. The general concept is fairly simple: one of the parts contains vinyl functional siloxane polymers and a platinum catalyst, and the other part contains vinyl functional polymers, hydride functional crosslinker, and a chemical known as an inhibitor to control the cure reaction. The inhibitor slows down the cure reaction so you have "working time" or "pot life." The type of inhibitor used will determine the pot life and minimum cure temperature. Inhibitors for adhesives and silicones used in applications where the cure must take place at room or low temperature are known as "competitive" inhibitors. They are part of the crosslinking reaction, and thus also part of the cured silicone. Silicones traditionally molded or extruded will use "fugitive" inhibitors. They have relatively high vapor pressures and interact with the platinum catalyst, consequently slowing the cure rate until heat is applied. Silicones using fugitive type inhibitors generally have a long pot life, however if vacuum is applied for extended periods of time, the inhibitor can be removed resulting in a shorter pot life and possibly shorter scorch times.

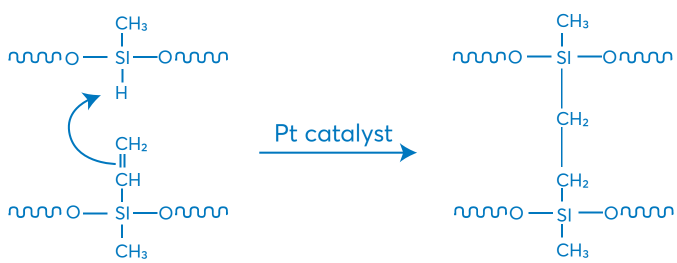

Figure 1. Cross-linking by vinyl hydrosilation

"MIXOLOGY" 101

Mixing silicones is very dependent on two key factors: VISCOSITY and POT LIFE. The viscosity not only dictates how the silicone is processed, but also what processes can be used to remove free and dissolved gasses. One of the key fundamentals when preparing a silicone is to check the pot life (a.k.a. work time) before mixing. For silicones designed to cure at room temperature, the viscosity will begin to increase soon after mixing. Be sure to allow sufficient time to de-air the silicone shortly after mixing it, and do not de-air so long that the silicone becomes too thick. Another key factor when getting started is to ensure that containers, solvents, and mixing materials will not interfere with the addition-cure crosslinking reaction. Please see Avoiding Inhibition When Working with Platinum Catalyzed Silicones for more details.

While mixing by hand may seem intuitive, NuSil Technology strongly recommends having at least 2-3 years of professional baking and/or cooking experience prior to mixing silicone by hand. In all seriousness, mixing by hand does require scraping the container's sides and corners and mixing long enough to ensure the Part A and B are thoroughly mixed. NuSil recommends weighing out a minimum amount of material depending on the viscosity of the silicone and how it is mixed. Silicones are almost exclusively optimized to meet cure times and properties by adding ingredients by weight, and therefore weighing in the proper mix ratio will guarantee the silicone will perform as designed. A common mistake when working at lab bench scale is to weigh very small portions of silicone (i.e. 1 gram Part A and 1 gram Part B). Issues with consistent properties and cure rates can be the result of mixing small quantities because the accuracy of the mix ratio is difficult to control, which can cause the component concentrations to be incorrect. In some cases, unused mixed silicone can be frozen and reused within a certain time of mixing.

Mixing by mechanical means such as using a propeller-type mixer is also common, but typically requires a minimum quantity to achieve a good vortex. Scraping the sides and corners intermittently is also recommended. Cooking equipment such as common stand mixers with a dough hook or flat panel blade are also excellent for bench top or small scale mixing. The curved bowls require minimal intermittent scraping of its sides. However, the air mixed into the silicone when mixing by hand or when using a propeller or stand mixer requires a separate de-airing step.

Planetary and Dual Asymmetric Centrifuge mixers (or "centrifugal mixers") are also growing in popularity as a means to mix viscous materials rapidly and thoroughly. The mixing cup is placed in a sample holder connected to an arm. The arm is revolving while the sample cup is rotated rapidly in the opposite direction. The revolution rates of the mixing cup can be optimized so the material is mixed thoroughly and de-aired in less than 60 seconds. The rotation speeds, mixing time, and sample quantity can be adjusted to reduce heat created from shear, making these types of mixers excellent for silicones containing dense fillers.

GETTING THE AIR OUT

For bench level or small production there are generally 3 main methods used for de-airing: vacuum chamber, centrifuge, or centrifugal mixer. It is virtually impossible to remove all of the dissolved gasses, so the techniques listed below are techniques that will remove enough of the dissolved gasses to reduce the formation of bubbles in the final application. See Table 1 for a summary of the advantages and disadvantages of each.

Vacuum chambers and vacuum pumps (oil or oil-less) are an industry standard and one of the most common methods to remove free and dissolved gasses. De-airing time is dependent on the quantity of silicone, surface to volume ratio, rheology, and effective drop in pressure in the chamber (how much air volume the pump can remove). When working with a vacuum chamber, it is helpful to have additional venting so the silicone will not boil over the container. When working with equipment at reduced pressures, ensure the container and chamber are rated to withstand the supplier's recommended operational pressure. Reference the Standard Material Certification for "Work Time" or other pot life parameters to determine time between mixing and application. Place mixed material into appropriate containers and fill approximately one quarter of the container's total volume to allow the material to rise. It is recommended to slowly apply vacuum up to approximately 28 inches of Mercury (0.95 Barr). Hold vacuum until bubbles are no longer observed. Periodically break the seal while pulling vacuum to allow bubbles to burst and subsequently expedite the de-airing process.

A standard centrifuge is adequate for removing air in low viscosity materials and when transferring from one container to another (i.e. packing into 10 cc syringes); however, its usefulness is very limited when trying to remove dissolved gasses. This is because a centrifuge rotates only in one direction and therefore applies one downward G Force, whereas the centrifugal mixer applies 2 rotational forces (down and side-to-side). Centrifugal mixers can remove free and some dissolved gasses quite effectively while mixing the material. Many have a vacuum function to remove dissolved gasses to very low levels. These can also be used for dispersing powders.

PROCESSING CAN HELP

Not only can processing silicones introduce air, it can also play a critical role in removing air and/or reducing bubble formation. The higher the viscosity of the silicone, the more difficult it is to remove air. Adhesives designed to easily flow will be much easier to de-air than Liquid Silicone Rubbers (LSRs), which are very thick and can have viscosities up to millions of cPs. The solubility of any gas in silicone is dependent on the pressure and the temperature of the system. This allows us to optimize these parameters to cure the silicone in a manner that minimizes the formation of bubbles.

Higher temperatures and lower pressures reduce the solubility of gasses in the silicone. If the silicone is cured open to the environment, trapped air can evaporate while the silicone is still liquid. A "step cure" or "ramp cure" is commonly used when the silicone is cured in place. The goal here is to apply heat in increments so air will evaporate at slightly higher temperatures when the silicone is still uncured and low in viscosity. High heat can be applied at the end to finalize the cure. A common step cure regime used is 24 hrs at room temperature, 1 hour at 70° C, and then 1 hour at 150° C, however this can be modified. NuSil always recommends validation of a step cure regime to ensure it results in a completely cured silicone.

For Liquid Injection Molding (LIM or Transfer) applications where the silicones are almost exclusively cured at elevated temperatures in a closed mold, increasing the pressure by increasing injection speed will reduce the ability of the air to expand. More vents can also be added to the mold cavity to allow air to escape. Many people ask if curing under vacuum can help reduce bubbles. This can help, but once the silicone comes back to ambient pressure, it will also begin coming back into equilibrium with the air. The solubility of some gasses can be high enough such that the cured silicone will expand or swell.[1]

High Consistency Rubbers (HCRs) and silicones dispersed in solvents present challenges when trying to remove air from them. HCRs are very thick and designed to process like wax in the uncured state to maintain "Green Strength" when extruded for tubing. They are typically mixed on a 2 roll mill. This can introduce air, but bubble formation can be controlled by mold pressure and cure time if transfer or compression molding. If pressure cannot be applied, such as in the case of extruding and curing by Hot Air Vulcanization (HAV), high cure temperatures (>150°C) can cure the silicone so rapidly that it is cured before dissolved air and gasses can expand and form visible bubbles.

On the other hand, dispersions are silicones dispersed in solvents, typically to between 15-35% solids. These are usually applied in thin layers by dipping or spraying, so air can escape once applied as long as curing does not occur too rapidly. The dispersion should be de-aired prior to use with vacuum pump able to pump down the head space volume quickly. Dispersions typically de-air quickly, as indicated when bubbles are no longer seen

forming. However, if dispersions remain under vacuum too long, solvent and inhibitor can be removed, resulting in non-uniform layers and bubbles.

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PACKAGING

We have discussed several ways to mix and de-air 2-part Addition-Cure Silicones for bench top and small scale production above. There are multiple reasons when working in a smaller scale that additional equipment to mix and de-air may not be an option. For thicker materials such as LSRs and many adhesives, dual cartridge side-by-side kits (SxS kits) are a convenient option for building prototypes or manually applying silicone in production. The dual cartridge kit may be the only option when working with adhesives or elastomers with limited pot life.

There are several dual cartridge kit sizes available, the most common being 50 ml, 200 ml and 400 ml. These all require the use of a dispensing gun, and the larger sizes often work most effectively using a pneumatic compressed air gun. The smaller sizes such as the 50 ml and 37 ml (for 10:1 mix ratio) can be used with a standard caulking gun with the use of an adapter (see Two-Part, Side by Side Kit Adapter Instructions)

Table 2 summarizes the processing and de-airing techniques based mainly on the silicone's rheology. Many of these methods can be scaled up for larger scale production. Large scale production may require specific packaging to accommodate turnkey solutions for shipping to processing such as straight sided 55 gallon drums that can be placed directly on pumping systems for LIM. By following these simple guidelines, mixing and de-airing does not have to be as painful of a learning experience, and your cooking skills may even improve.

TABLE 1: Techniques to remove air

Type	Advantages	Disadvantages
Vacuum Vacuum pumps and chambers. Recommend 28 in Hg (0.95 Barr)	Drop in pressure removes dissolved gasses.	Can be time consuming if the material is thick. May remove inhibitor, altering pot life and cure profile.
Centrifuge Only	Fast. Recommend when transferring de-aired material from one container to another.	Removes "free", trapped air only. Limited to bench scale but larger centrifuges are available.
Centrifugal Mixer Dual Planetary Mixer, Putty Mixer, etc. (Examples: Flackteck and Thinky)	Fast and removes free and dissolved gases.	Can create heat resulting in premature cure.

TABLE 2: Processing Summary Based on Rheology

How we define rheology for products	Viscosity	Processing	De-gassing
LCE (Low Consistency Elastomer) Pourable, flexible cure schedules and cure chemistry. Include clear (resin reinforced) and silica filled silicones.	Low to medium	Adhesives, potting and coatings	Use of SxS packaging is recommended when silica filled. Resin (clear materials) can be de- aired easily with vacuum chamber
LSR (Liquid Silicone Rubber) Silica filled med to high viscosity polymers. "Pumpable"; mainly HTV	High viscosity and are non- slump	Molded by compression, LIM, Transfer	Use of SxS packaging is highly recommended
HCR (High Consistency Rubber) Silica filled VERY high viscosity polymer. Waxy, retains shape before cure.	Very high and can not be dispensed	"Initially mixed by 2 roll mill. Cured by extrusion (HAV), transfer or compression molding. Commonly calendared"	HAV - Cure at high temperatures (>150 °C). High pressure molded. Sheeting is cured under pressure
Dispersions Most of NuSil's dispersions are made from very thick silicones (>LSRs).	Viscosity dependent on % solids/solvent	Dipping, spraying, knife coating.	Recommended to have very good vacuum. Beware: Do not over de-air and remove solvent and inhibitor.
Electrically and/or Thermally Conductive VERY highly filled with conductive fillers.	Typically self leveling once mixed and can be dispensed but are limited to larger gauge sizes	Poured and cured in place	Centrifuging is not recommend due to potential separation, but is used in some circumstances. Vacuum or centrifugal mixer is more common

References

[1] Kamiya, Y.; Naito, Y.; Terada K.; Mizoguchi K.; Tsuboi A.; Volumetric Properties and Interaction Parameters of Dissolved Gases in Poly(dimethylsiloxane) and Polyethylene. Macromolecules 2000, 33, 3111-3119.

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