Post-Curing of Silicone Elastomers: When is it Necessary?

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William Inman has been employed with Dow Corning Corporation for more than 20 years. He is currently an Application Engineer providing technical product assistance for Dow Corning Silicone Elastomers. While Inman had devoted his career to healthcare — working in Bio-Analytical, Application Engineering, Technical Service, and Sales Development — he recently expanded the industries he serves to include electronics, food and beverage, as well as infant care, among others. He has significant experience in chemical and physical characterization of materials, as well as product development, manufacturing and extrusion of silicone elastomers used in medical devices.

Inman earned his bachelor’s degree from Saginaw Valley State University in 2000.
ABSTRACT
The process of post-curing silicone elastomer has been in practice since the inception of silicone rubber materials. Some of the early silicone technology patents describe a secondary post cure cycle, mainly to improve the physical characteristics of the material. In some instances, especially with the newer materials available today, this costly step can be removed from the overall scenario leading to cost savings, safety, and even environmental benefits.

INTRODUCTION
Post-curing, as the name describes, involves a secondary cure of the silicone, typically in a hot air circulating oven at a given temperature for a certain amount of time. The process reduces toxic by-products from some peroxide-cured silicones and generally improves the physical characteristics of both peroxide-cured and platinum-cured silicones. The post curing of silicone elastomers is a costly endeavor, adding time and money to the manufacturing process. While some original equipment manufacturers (OEMs) must post-cure their products to meet certain regulatory requirements and safety standards, others may benefit from recent technology advancements in silicone elastomers. Manufacturers have searched for ways to eliminate the need to post-cure materials after curing. This white paper details the advantages and disadvantages of post-curing, and highlights the situations where the process can be completely eliminated.

SILICONE ELASTOMERS
In the 1800’s, researchers started making synthetic silicones from elemental silicon combined with carbon. Dr. Frederick Kipping spearheaded these development efforts, which eventually would lead to the commercialization of silicone elastomers. Scientists at Corning Glass developed the first commercially used silicone in the 1930’s. Since then, the material has been used in multiple industries because of its many advantages, such as resistance to heat and moisture, low volatility and inertness.

Today, the majority of silicone elastomers fall into two main groups: liquid silicone rubber (LSRs) and high-consistency silicone rubber (HCRs). LSRs, with their inherent low viscosity, are easier to pump and can fill intricate mold cavities making more geometrically complex component parts. HCR is considerably higher in viscosity and, as a result, does not flow as well ultimately making for simpler parts in similar molding processes. HCRs, due to their good green strength (cohesive capability prior to cure) are much better suited for extrusion applications. Extruded silicone tubing is used for diverse applications ranging from fluid transport to electrical insulation (e.g., pacemaker leads). Silicone HCR can also be milled and molded or calendared into sheets.

Silicone elastomers are cured (or “vulcanized”) to turn from thick liquids or semi-solid putties and pastes into solids. The two most common curing processes are peroxide initiated curing and platinum catalyzed curing. Many, but not all, HCRs are cured with organic peroxide initiators, while LSRs typically are platinum-cured.

PEROXIDE-CURED SILICONE
Initially, all silicone elastomers were cured with peroxide-based chemicals. This curing system is also called a free radical cure system or a high-temperature vulcanizing system because the peroxides generate free radicals that decompose at high temperatures and initiate the cross-linking reaction.

While silicone polymer materials have extremely low concentrations of intrinsic siloxane volatiles, the process of curing silicone with peroxide-based chemicals adds lower molecular weight organic by-products to the material. After curing, some of these by-products remain. For example, when 2, 4-dichlorobenzoyl peroxide is used to cure silicone tubing, the main by-product 2, 4-dichlorobenzoic acid starts to accumulate at the surface of the tubing as a white powder (also called “bloom”). Post-curing helps remove the bloom and other by-products — mainly dichlorobenzene and small quantities of polychlorinated biphenyl (PCBs) — reducing levels to a parts-per-billion range.

Post-curing means that the material is heated in an oven at a given temperature for a certain amount of time. While there are many variations in temperature and time, the three most common combinations seem to be 2 hours at 177°C, 2 hours at 200°C and 4 hours at 200°C. Post-curing peroxide-cured silicone removes residue, odor, and toxins; and improves the characteristics of the material. Post-curing is also necessary to prevent acidic-catalyzed decomposition of the rubber.
PLATINUM-CURED SILICONE

Platinum-based curing systems are sometimes called addition cure systems, because there is a silicone hydride polymer that adds across the double bond of a vinyl functional siloxane polymer in the presence of a platinum-based catalyst to create a cross-linking reaction. Platinum-based curing does not create any by-products, and component parts can theoretically be ready for use straight out of the mold. However, when platinum-based curing systems were invented, many manufacturers continued to post-cure their silicone elastomers since silicone elastomers had historically been post-cured. They discovered that post-curing platinum-based silicone can bring some advantages. In a typical molding or extrusion application, curing continues to take place after the article is molded or the tubing is formed. This is because the material is cured sufficiently enough to be de-molded and inspected before it has completely cured. Manufacturers take advantage of this phenomenon to be able to speed up the overall productivity of the process.

The down side to this practice is that the material will continue its cure, until it attains full cure, as it ages. With this additional curing, changes can be observed in the physical properties of the materials; the hardness of the material will increase, ultimate tensile strength will typically improve and the elongation will drop. These changes can be important in specific applications, so this effect needs to be well understood. To account for these changes, a post cure is often implemented to drive the elastomers cure to completion and stabilize the physical characteristics of the material.

Furthermore, volatile siloxane species remain in the cured silicone matrix of the particular component after initial cure. Unlike some by-products of peroxide cure, these lower molecular weight volatile components are generally not considered particularly toxic; however some industries must follow specific regulatory, environmental and safety requirements which limit the amounts of these volatile components that can be found in the cured component. Some examples are:

2. Food and Beverage
   Per 21 CFR 177.2600, silicone elastomer parts for food contact applications can meet regulatory requirements either by formulation or extraction. If the material doesn’t meet formulation specifications, the parts need to meet extraction requirements. If a manufacturer’s products cannot meet these requirements as molded and processed, post-curing becomes necessary.

3. Health Care
   Because of the inherent risks and concomitant regulatory requirements involved with the majority of healthcare applications, healthcare original equipment manufacturers strive to ensure part to part consistency in their molded articles. Post-curing is often implemented because it can stabilize the silicone to help standardize the end products.

Post-curing is also used in the health care industry to prepare samples prior to biocompatibility screening. The majority of biocompatibility requirements for silicone elastomers are assessed based on testing of extracts of the cured material. As mentioned previously, when cured material is post cured, the lower molecular weight species in the material (volatile content) is reduced. By decreasing the overall volatile content of the elastomer, the concentration of volatile components in the extract is lowered as well; that may improve the odds of successfully passing a biocompatibility test of the cured article’s extracts. Attention should be given to the use of a materials supplier’s biocompatibility data in this regard. If the material supplier performed a post cure prior to biocompatibility testing of the material, then the cured article or component should be post cured as well for the data to be considered relevant for the application.

Post-curing of platinum-cured silicone also is carried out in many industries to prepare silicone articles for secondary bonding procedures. The low molecular weight volatile fluids that remain after initial curing have the potential to migrate to the surface of the component, in effect acting as a release agent negatively impacting the ability to adhere the component to another substrate. For example, if you are looking to bond a silicone balloon to an extruded silicone catheter shaft, any low-molecular weight silicones that remain on the surface of the shaft could act as a release, preventing good attachment between the balloon and the catheter shaft. Post-curing both components will drive off the low-
molecular weight fluid and improve the overall adhesion to the balloon.

**COSTS OF POST-CURING SILICONE**

Despite the many advantages of post-curing silicone elastomer, manufacturers continue to look for ways to eliminate this step from silicone processing in order to cut the costs associated with it. Post-curing adds overhead to the manufacturing process in the following ways:

1. **Floor space:**
   Companies must allocate area on the manufacturing floor for the ovens, carts, and trays to perform the task.

2. **Ovens:**
   These ovens add additional costs to the capital budget.

3. **Utilities:**
   The electricity used to operate the ovens adds to a manufacturer’s expenses.

4. **Equipment:**
   Companies also must purchase equipment such as timers, racks, and gloves to run a post-curing process.

5. **People:**
   While post-curing does not require high-skill labor, companies must either hire unskilled laborers whose only job will be to post-cure silicone parts, or pay skilled workers to do it as part of their job.

6. **Time:**
   The time added to the manufacturing process while the silicone parts are sitting in the oven during post-cure delays usually creates a bottleneck in the overall manufacturing flow of the cured article or component. Depending on how it is defined, a suitable post-cure typically will only take a few hours; however, some companies post-cure their silicone for days at lower temperatures, a process that adds significant time to the manufacturing process.

7. **Safety:**
   While post-curing is a relatively safe process, accidents can happen, perhaps with greater severity due to the higher temperatures that can be used in the process. A burn injury could be not only painful and disfiguring, but also quite disruptive and costly. In addition, certain regions in the world require the use of scrubbers or other systems that recapture the volatiles liberated during post-cure so they don’t end up expelled into the environment.

**IS POST-CURING NECESSARY?**

Depending on individual product and process circumstances, post-cure may or may not be necessary. The majority of silicone suppliers (Dow Corning being an exception) require some type of a post-cure for their materials to achieve the physical property profile described in the sales specification or data sheet.

Because of the costs associated with post-curing, OEMs should seriously question if the process step is necessary for their application. In some instances, a higher degree of variability in the cured article is acceptable if the silicone meets minimum physical properties; in these cases, post-curing might be adding unnecessary processing time and costs. But even in industries where stable physical properties over time are required, such as health care, new developments in materials offer promising alternatives to post-curing.

A current development aimed at providing more physically stable as-molded articles and components is the new Dow Corning® brand C6-7XX series of liquid silicone rubber materials. These recently introduced LSRs from Dow Corning exhibit a physical profile that is essentially unaffected by the addition of a post-cure.

**Figure 1: Shore A Durometer Comparison**

![Shore A Durometer Shift with Post Cure](image)

In Figure one, above, the hardness measured for various high and low consistency silicone materials with nominal 50 Shore A hardness are compared as molded, and after a two- and four-hour post-cure at 177°C. The new Dow Corning® C6-750 Liquid Silicone Rubber is the only material that shows no change in hardness after each post-cure cycle when compared against...
Silastic® Q7-4850 BioMedical Grade Liquid Silicone Rubber, Dow Corning® C6-550 Liquid Silicone Rubber, and Dow Corning® C6-150 Elastomer.

**Figure 2: Tensile Strength Comparison**

In Figure 2, a comparison of ultimate tensile strength is shown as molded and after the same two- and four-hour post cure that was described above. Again, the new Dow Corning C6-750 Liquid Silicone Rubber is essentially unchanged after post cure whereas the older silicone materials exhibit a fair amount of variability in the measured property.

**Figure 3: Elongation Comparison**

In the third and final figure, elongation is compared in the same manner as previously described. As in each of the previous figures, the new Dow Corning C6-750 Liquid Silicone Rubber remains essentially unchanged after post cure whereas the older silicone materials continue to exhibit a fair amount of variability in this measured property as well.

**CONCLUSION**

Post-curing of silicone rubber can easily become a requirement when the material has been cured with particular peroxide-based initiators such as 2, 4-dichlorobenzoyl peroxide, because it is an effective way to remove the problematic by-products from the vulcanization process. However, manufacturers that post-cure platinum-cured silicone should evaluate if they can eliminate the post-cure process step.

Innovative material suppliers are continuing to develop new silicone elastomer technology that may enable companies to eliminate the process of post-curing their silicone parts, cutting time and costs from the manufacturing process.

**REFERENCES**


http://www.dowcorning.com/content/discover/discoverinnovate/
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