

Radiation-Cured Silicone Polymers for Use in Release Liners

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Introduction

Silicone-based coatings for papers and films used as adhesive carrier release liners have been on the market for over 60 years. Initial technology utilized solvent-borne, organometallic-catalyzed, thermally-cured systems. In the 1980s, so-called “cold cure” technology was developed, which utilizes free radical or cationic curing reactions initiated by radiation, without the need for added heat¹. Sources for radiation used in these cure chemistries are an electron accelerator (E-beam) and ultraviolet light (UV). We will present an overview of radiation-cured silicone chemistry, use of these systems in release liner applications, as well as advantages that radiation-cured coatings have to offer over traditional thermally-cured systems.

Silicone Chemistry

Siloxane polymers have many attractive attributes including low surface energy, low glass transition temperature, thermal stability, and a low viscosity at relatively high molecular weights². Silicone polymers used for release liner coatings start with polydimethylsiloxane (PDMS) backbone base polymers. Base polymers have pendant or end-blocked functionalities. In thermally-cured systems, hydroxyl groups (condensation reaction, Figure 1) or vinyl groups (addition reaction, Figure 2) react with silane functionalized PDMS in the presence of heat and an organometallic catalyst (Sn, Pt, or Rh). These reactions may take place in the presence or absence of solvents. In solvent-based systems, common solvents include heptane, methyl ethyl ketone, toluene, and isopropanol. Full cure is achieved in a few seconds up to a few days.

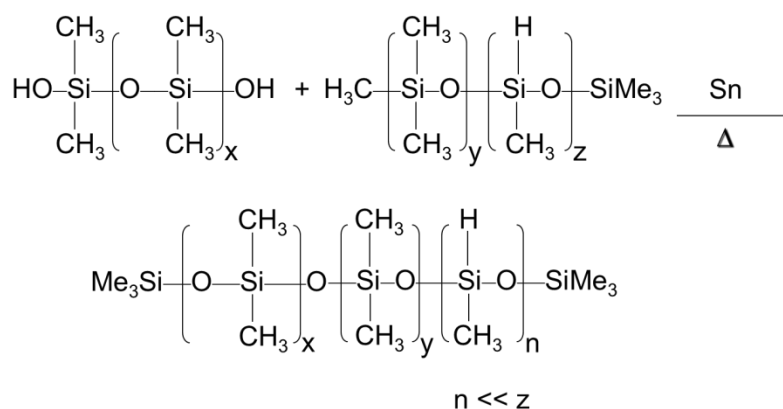


Figure 1. Tin-Cured Condensation Reaction

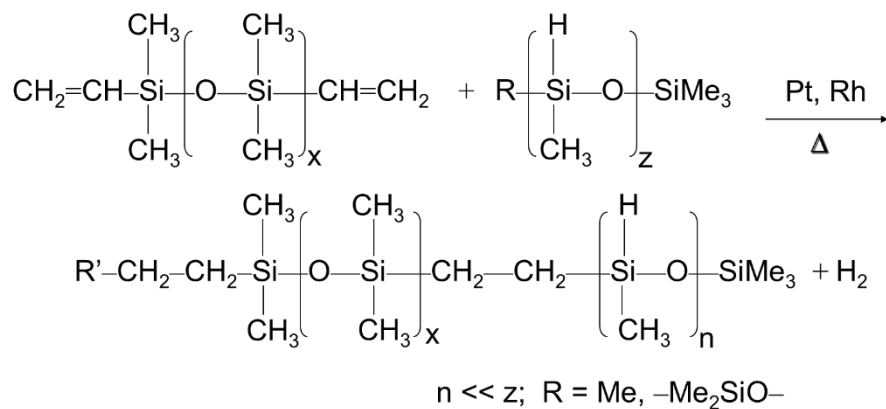


Figure 2. Platinum-Cured Addition Reaction

Radiation-cured silicones incorporate two basic systems: epoxy chemistry with a cationic curing mechanism (Figure 3) and acrylate chemistry with a free radical curing mechanism (Figure 4). Both reaction types occur without the need for a heat source. UV light can be used as an energy source for both types of chemistry, while e-beam is restricted to free radical chemistry.

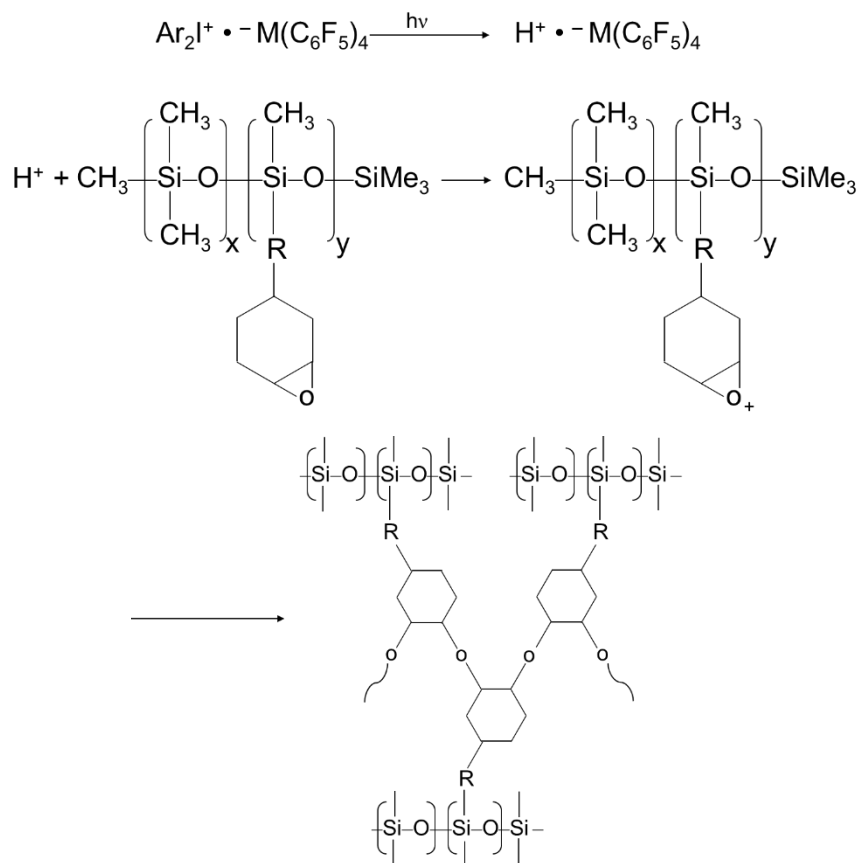


Figure 3. Cationic Epoxide Reaction (UV)

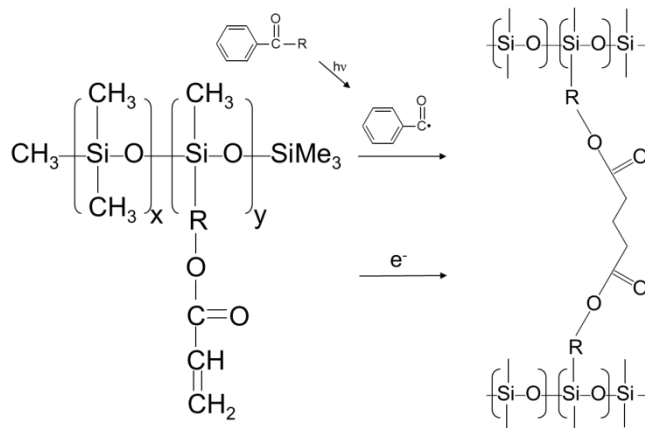


Figure 4. Free Radical Acrylate Reaction (UV and E-beam)

UV-cured systems with cationic chemistry involve a cycloaliphatic epoxide functionalized PDMS and require a photoinitiator. Upon irradiation, the cationic photoinitiator reveals a strong acid which in turn initiates a ring opening reaction for polymerization of the epoxides to polyethers. A diaryliodonium salt with a metal halide counterion is typically used as a photoinitiator³.

UV light may also be used as an energy source for free radical polymerization. This system involves acrylate functionalized PDMS and also requires the use of a photoinitiator. UV light irradiates the photoinitiator to generate free radicals and curing proceeds via free radical polymerization of the acrylates.

E-beam cured systems involve acrylate functionalized PDMS and proceed via a free radical polymerization reaction. E-beam systems provide a higher amount of energy than UV and initiate the free radical reaction without the need for a radical initiator.

In free radical polymerization of acrylates, the intermediate free radicals may be quenched by oxygen, so an inert atmosphere is required to ensure the reaction drives to completion. Cationic polymerization does not require inerting. However, in cationic polymerization systems cure can be inhibited by moisture, so direct coating onto paper is a limitation. Direct-coated applications utilizing cationic chemistry are sometimes possible with prior treatment of the paper to reduce or eliminate the availability of water².

Why Radiation Instead of Thermal?

The most significant advantage of the use of radiation-cured silicone coatings for release liners is that complete cure is achieved quickly without the use of heat. From a liner manufacturer's perspective, this means that a radiation curing coating machine may be constructed with a much smaller footprint due to the absence of lengthy ovens needed to provide enough heat for thermally-cured liner coatings.

Thermally-cured silicone systems also impose limitations and complications in the use of certain substrates. The heat required for thermally-cured coatings is more than many filmic substrates can withstand while maintaining dimensional stability. Substrates for thermal systems are generally limited to papers, polyester, and some polypropylenes. There are some tin-cured systems on polyethylene, although low oven temperatures and slow line speeds are required. The use of radiation-curable coatings opens the door for the use of a much larger variety of substrates. These coatings may be applied to nearly any temperature sensitive substrate such as lower gauge polyester, all polypropylenes, polyethylene, polystyrene, polyvinyl chloride, nylon, in addition to the substrates mentioned above.

The heat required in thermal systems also drives moisture out of paper. Moisture control in direct-coated papers is crucial for lay-flat and dimensional stability. A certain amount of moisture is required for control of liner curl and cockling or the development of bagginess over time due to uneven adsorption of moisture in water-starved sheets. Implementation of remoisturization units and careful tuning of process parameters are often required where these properties are critical to the end use application of the liner, adding cost and complexity.

Radiation-curable coatings are notably fast and complete cure can be achieved at very fast line speeds without the need of a catalyst. Line speeds are typically limited by machine constraints or misting at the coater head, instead of minimum oven dwell times, as with thermally-cured coatings. Tin-catalyzed thermally-cured systems sometimes suffer from post cure of several days resulting in dramatic shifts in release force at the point of use compared to that measured directly off the coater. Platinum-cured systems typically do not suffer from the post cure seen with tin systems, but may be subject to catalyst poisoning from plastic additives and cross contamination, which can prevent complete cure. Because of the absence of a catalyst, UV acrylate systems are far less sensitive to contamination.

Electron beam vs Ultraviolet Radiation

E-beam

Radiation curing technology for silicone coatings began with E-beam as an energy source, starting in the 1980s¹. E-beam curable silicone systems consist of an acrylate functionalized siloxane polymer backbone cured by free radical polymerization (Figure 4). Energy needed for this reaction is provided from an electron accelerator. Free radical polymerization proceeds extremely fast and does not require the addition of a photoinitiator because of the amount of energy provided by the electron beam. E-beam cured coatings can provide a wide range of release force, and very tight release forces can be achieved (400+ g/in-width, measured with rubber-based Tesa 4651 test tape). One disadvantage of E-beam coatings is their propensity to develop increasing adhesion to some aggressive acrylic adhesives over time². For this reason, E-beam coatings are generally recommended for rubber-based adhesives and should be evaluated on a case-by-case basis for acrylic adhesives.

Ultraviolet

Since the inception of radiation curable coatings, UV has gradually taken a strong lead as the go-to method of commercialized silicone coating liners cured without heat¹. Because UV light can be used as

the energy source for both types of curing chemistries (Figure 3 and Figure 4), UV curable systems can realize most of the benefits of e-beam cured coatings with few disadvantages. The notable difference in these 2 systems is the requirement of a photoinitiator when UV light is used. However, a strong advantage of UV-cured coatings is that they are compatible with a wide variety of adhesives and are not restricted from use with acrylic adhesives.

Traditionally, mercury vapor lamps have been used as a UV light source. Mercury lamps emit a broad spectrum of light without the ability for tuning to narrower wavelength bands. For the purposes of free radical initiation, mercury lamps yield 70-75% of radiation in non-useful wavelengths, including enough high energy infrared light to produce a significant amount of heat⁴. Recent work has resulted in the development of light emitting diodes as UV light sources. LED light sources benefit from the ability to fine tune their emission spectrum; typically in a 20-40 nm range. This concentration of energy output allows for more efficient machine operation by delivering a sufficient dose of radiation at the target wavelength without the emission of radiation at wavelengths not needed, which in turn requires less power input. A notable benefit of this is the much cooler operating temperatures. LEDs also benefit from a much longer lifetime than mercury vapor lamps (20,000 h vs. 2,000 h)⁴.

Summary

Radiation-cured silicone coatings offer several advantages over their thermally-cured counterparts. These types of chemistry provide efficient, fast cure and allow for the use of many substrates not available with the use of traditional thermally-cured coatings.

References

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