Rethinking silicone coatings: Using polymer architecture to eliminate VOCs

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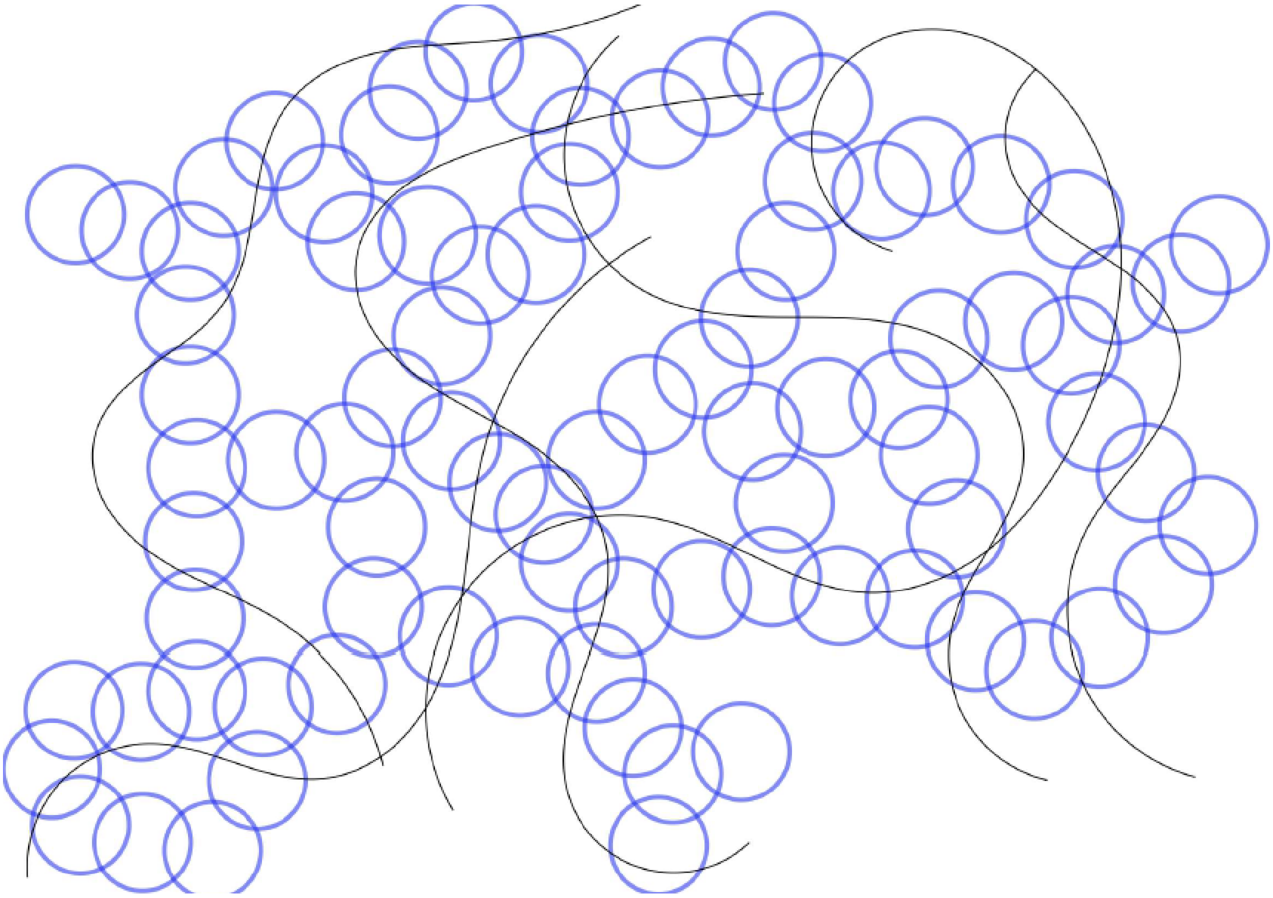

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Ring polysiloxanes offer a promising route to VOC-free silicone coatings without compromising performance; Anne Ladegaard Skov and Cody Brian Gale from the Technical University of Denmark explain

Silicone coatings: An important class of materials

Silicone coatings account for approximately one-third of the global coatings market. This market share can be attributed to the desirable properties exhibited by silicone coatings, including water repellency, chemical, thermal, and UV stability, as well as flexibility even at low temperatures. This combination of unique properties enables silicone coatings to be utilized across multiple industries, including construction, defence, marine, and aerospace. They have become deeply embedded in modern life, protecting critical infrastructure, electronics, and offshore structures. However, like many classes of coatings, silicones face increased scrutiny regarding their environmental impact.

Solvent utilization: A key hurdle

Most current-generation silicone coating formulations are solvent-based. Solvents, also referred to as volatile organic compounds (VOCs), provide a means for coating formulators to control critical parameters for application and curing of the coating and thus are an essential component of silicone coatings. While currently strictly necessary for proper use, solvent utilization is a key environmental and health concern. From an environmental standpoint, the release of VOCs produces air pollutants that contribute to reduced air quality and increased global temperatures. Additionally, evaporation of solvents during curing can lead to the development of residual stress in the coating. Internal stress can impact the longevity of the coating, necessitating coating removal and reapplication, which in turn further increases the environmental impact of the coating. VOC use has also been shown to cause acute and chronic respiratory and neurological conditions in humans, further growing concern over their use.

These are not new issues. Governments worldwide have implemented legislation limiting VOC content in coatings, including several EU and North American directives. Legislative efforts have encouraged companies to respond, resulting in formulations with lower VOC content. Despite remarkable efforts, VOCs in silicone coatings continue to be an issue that must be addressed. This is especially relevant as many countries are placing greater emphasis on environmental protection and sustainability. Given the environmental impact of VOCs, it is reasonable to anticipate that future regulations may become more stringent. To support long-term environmental goals, it may be beneficial to shift the focus from merely reducing VOC content in coatings to developing solutions that eliminate them.

A paradigm shift is required

Obtaining VOC-free silicone coatings requires fundamentally reevaluating the status quo in silicone formulations. Currently, most silicone formulations utilize commercial linear silicone polymers, which are available in a range of molecular weights. The molecular weight of the polymer influences multiple parameters, including the barrier performance of the coating, mechanical integrity, drying time, and viscosity. Balancing these parameters can be challenging. For example, using a low molecular weight silicone to achieve a desired viscosity can be detrimental, as it impacts the mechanical properties and causes sagging during application. Conversely, a higher molecular weight polymer may prove beneficial for the mechanical integrity of the coating but could result in poor substrate coverage or a less appealing coating appearance. Solvents provide formulators with a means to modulate these properties independent of the molecular weight. This is why they remain essential to current polymers. Overcoming these limitations requires moving past the commonly used linear silicones.

The Danish Polymer Centre (DPC) explored the potential of different polysiloxane architectures in coating applications and identified ring polysiloxanes as a promising architecture for coating development. It is believed that ring polymers offer an alternative means to balance properties through a process known as threading. Threading refers to a phenomenon in which linear polymers penetrate through cyclic polymers, enhancing viscosity and mechanical integrity.

If linear polymers react to form rings while threading ring molecules, concatenations are formed. Adjusting the ratio of rings to linear enables control over viscosity and other properties, eliminating the need for VOCs, as all reactants are low-molecular-weight. Researchers at DPC were able to synthesize ring silicones reliably, but when mixed with linear polymers, threading did not occur. However, it was observed that when the precursors to the ring polymers were mixed and exposed to a catalyst, a strong and flexible network possessing the desired mechanical properties for coatings was formed. It is believed that these networks form due to the concatenation, or linking, of the silicone rings, forming what are commonly referred to as Olympic ring networks. These networks have the potential to redefine how silicone coatings are manufactured and improve the environmental impact. Not only are they solvent-free, but they are also durable, reducing the need for reapplication and the associated environmental impacts. Ultimately, these materials employ a straightforward and robust chemistry that is compatible with current industrial processes.

Next steps

The development of solvent-free coatings using ring silicones represents a significant shift in coating development. Recognizing the potential of these materials is an ongoing process, and further research is necessary. Key areas of future research include:

- Developing specific characterization techniques for concatenated networks to better understand and model their behaviour;
- Incorporating other components of coatings, such as pigments, into existing networks;
- Scaling up synthesis without compromising on quality; and
- Integrating functional properties such as self-healing and anti-fouling.

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