Environmental fate of silicone-based durable water repellents in textile applications

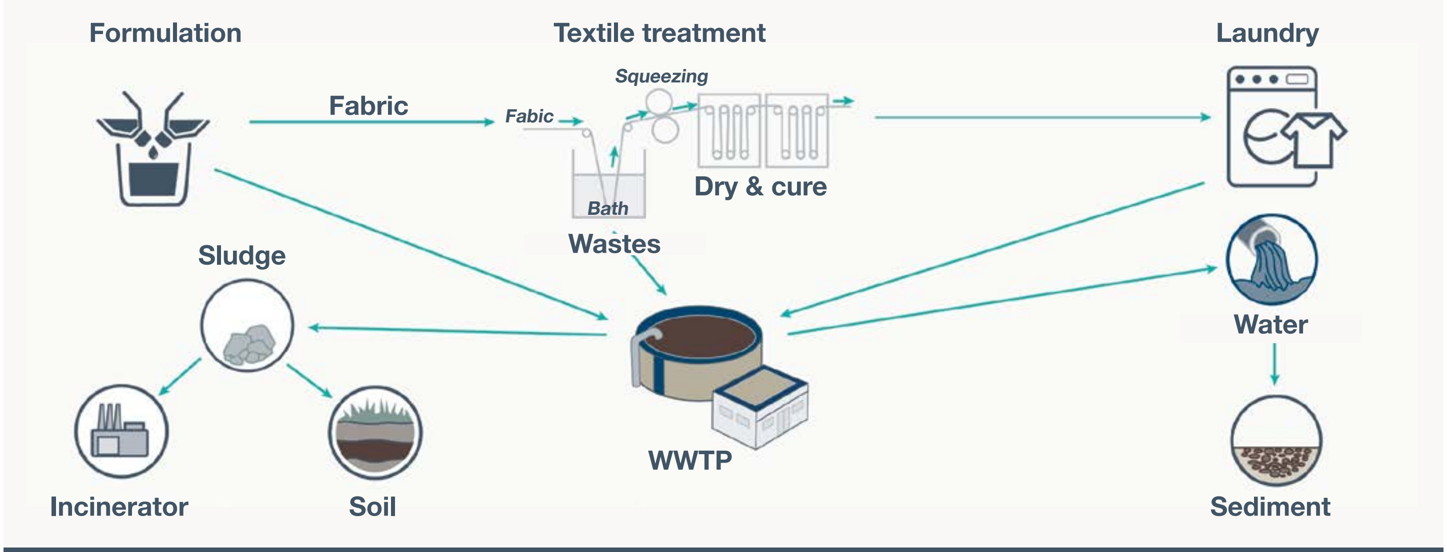
Application background

Silicones have multiple applications in textiles processing, ranging from fiber lubrication to antifoam and finishing applications. Silicones are associated with softening and have recently been the focus among Durable Water Repellents (DWRs) due to the move away from perfluorocarbon (PFC). Dow offers multiple generations of PFC-free DWRs by leveraging our strong experience in silicone and organic technology. Beyond their DWR performance, silicone DWRs are also recognized as one of the best materials for increasing the softness of fabrics and enhancing durability (CES, 2015, Dow, 2012, and Dow, 2020a). They improve water repellency on a variety of fabrics without compromising breathability. Several physical properties, such as tear strength, abrasion, and wrinkle resistance, stretch recovery, and shrinkage reduction can also be addressed, making fabrics more comfortable and more desirable to touch, purchase, and wear.

Description of chemistry

Silicone DWRs are available in a wide range of chemistries to meet a broad range of specific fabric property needs (Dow, 2012). Chemistries may involve various classes of silicones, including both non-reactive polymers and fabric-reactive functional polymers.

- Amino functional polymers are among the most popular textile softeners. The amine functionality readily adheres to textiles and allows for increased deposition of silicone, which in turns yields a durable water repellent soft finish.
- High molecular weight silicones as well as elastomeric polymers may also be leveraged to impart water repellency.
- Other silicone functionalities typically used in fabric finishing formulations include hydroxy, methyl hydrogen, epoxy-polyether, and silicone-hybrid technologies.



Conceptual model for DWRs in textile application

To understand the environmental fate of these silicone DWRs, it is important to develop a conceptual model for use and disposal to identify where these substances will enter or be found in the environment.

Silicone-based durable water repellents are expected to most likely be processed in wastewater treatment plants. Releases are believed to come from three primary sources:

- Manufacturing (formulating the DWR),
- Textile treatment (application of DWR to fabric), and
- Losses of DWR from consumer textiles when laundering.

Generally, all these waste streams enter a wastewater treatment facility. Regardless of the functionality, the silicone DWRs are based on a primary silicone backbone, polydimethylsiloxane (PDMS) which influences the environmental fate of these polymers.

Environmental fate

The fate of PDMS in different compartments has been well described (ECETOC, 2011). PDMS has extremely low water solubility, low volatility, and a high affinity for organic matter. Therefore, PDMS is expected to not be released to or found in the air. During wastewater treatment, PDMS does not affect biological processes and is removed from the aqueous phase (>97%) by sorption to sewage sludge. The remaining minor fraction will partition onto suspended solids/sediment in effluent or receiving waters where it will be transferred to sediment. These trace amounts of PDMS found in sediments will hydrolyze to dimethylsilanediol as it does in soil. The rate is slower, with an initial estimated half-life of several years; however, with the longer half-life, it is important to note that burial of the sediment will also represent a loss process from the sediment (Kim, et al., 2018). Once formed, the dimethylsilanediol is released to the water because of its high water solubility. There is also evidence for potential degradation of dimethylsilanediol in the water phase by indirect photolysis (CES/SEHSC/SIAJ, 2012, Anderson, et al., 1987, and Buch, et al., 1984).

The degradation (or ultimate fate) of PDMS is therefore largely linked to the fate of the sludge (CES/SEHSC/SIAJ, 2012). The subsequent fate of the sewage sludge-bound PDMS depends on local practice and regulations. Much of the sludge is now directed to landfill, incineration, and soil amendment. Laboratory and field studies have demonstrated the potential for PDMS to degrade via mineral-catalyzed hydrolysis in soils and sediments, ultimately to form silicone dioxide (SiO_2), carbon dioxide (CO_2) and water (H_2O). The same degradation products are also formed under incineration. The silicon dioxide in the resulting ash is land filled.

The degradation of PDMS in soil has been well characterized (ECETOC, 2011 and Lehmann et al., 1998). The initial step of PDMS degradation in soil is hydrolysis by clay catalysis which involves a combination of random scission to shorten the polymer chain to small molecular weight water-soluble silanols, in particular, dimethylsilanediol (DMSD). Under laboratory conditions, PDMS in contact with dry soil will undergo abiotic degradation in 1 to 4 weeks depending on soil type. Under field conditions where the soil moisture was maintained at >10% over the entire study period, PDMS had a half-life of 2 to 4 years. When samples of the soil were taken into the laboratory to simulate arid conditions >80%, PDMS degraded within 20 days. Further work demonstrated the potential for DMSD to undergo subsequent biodegradation, in wet soil and loss to the air in dry soil (Xu, 2016 and 2017), where it is predicted to undergo reaction with OH radicals that are generated in the presence of sunlight, ultimately forming silicic acid or silica.

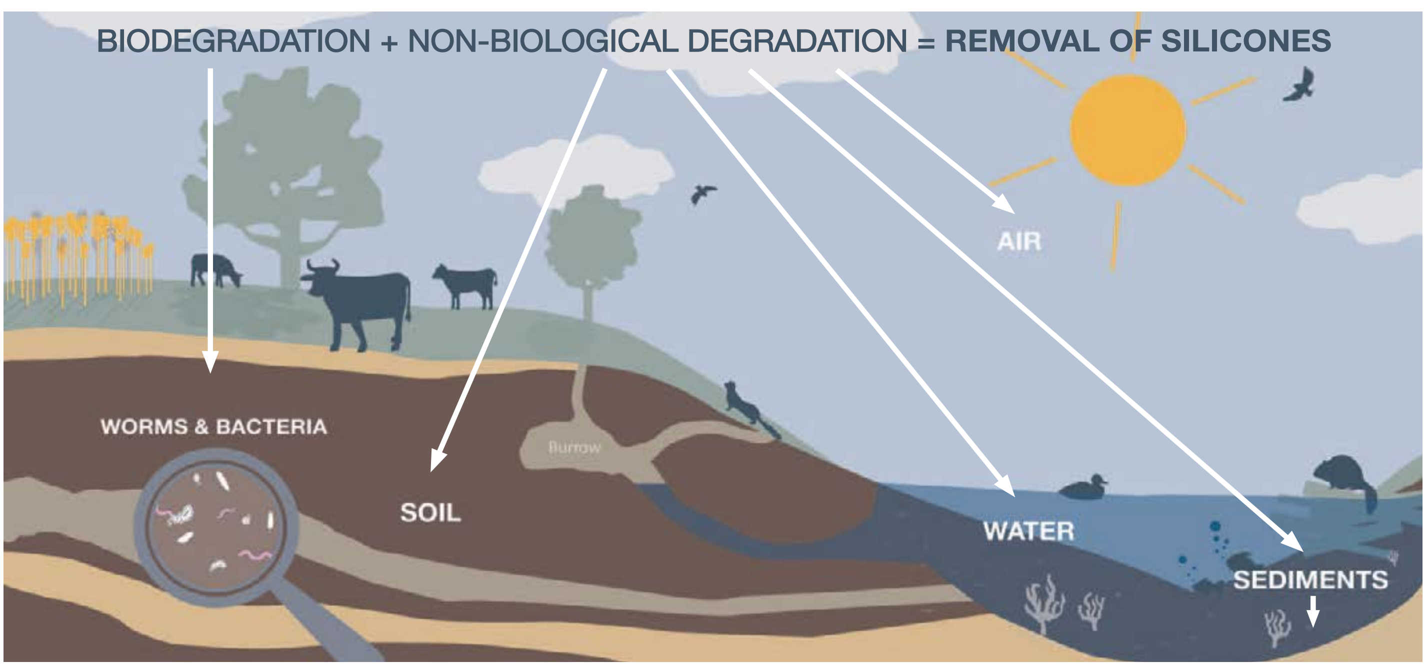
In a study conducted by Singh et al., 2000, the degradation of PDMS was modeled across a variety of soil types and climatic regions (e.g., Los Angeles, San Juan, Athens, Columbus, and St. Paul). The most relevant environmental degradation half-lifes of PDMS in soil water content less than 5% for these regions was less than 1 year.

Therefore, the overall persistence of any residual PDMS in the environment predominantly depends on soil type and climatic conditions, with drier conditions having greater degradation half-lives than wetter conditions.

Regardless of the functionality, silicone DWRs are mostly based on a silicone backbone – polydimethylsiloxane (PDMS) – and therefore will ultimately degrade in the environment, resulting in the formation of compounds such as silicon dioxide, carbon dioxide and water (ECETOC, 2011). The combination of these degradation processes is critical for the removal of silicones and their ultimate conversion to naturally occurring substances.

Dow is committed to continuing our research to better understand these mechanisms that achieve the ultimate degradation of silicones in the environment.

How do silicones degrade in the environment?



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