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A Review of the Environmental Fate and Effects of Silicone Materials in Textile Applications

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Few issues are getting more attention from textile manufacturers and suppliers today than the environmental impact of their products and processes.[1] From fiber production to finished goods and packaging, researchers are studying the fate and effects of traditional materials and processing methods, exploring new technologies that offer environmental advantages.

Silicone is a generic term that refers to a class of man-made polymers based on a framework of alternating silicon and oxygen (siloxane) bonds, with organic substituents attached to the silicon. Methyl groups (Me) are the most important of the organic substituents used in commercial silicones, the vast majority of which are polydimethylsiloxanes (PDMS).[2] Because of their "inorganic-organic" structure and the flexibility of the siloxane bonds, silicones have some unique properties, including thermal/oxidative stability, low temperature flowability, low viscosity change vs. temperature, high compressibility, low surface tension (spreadability), hydrophobicity, good dielectric properties and low fire hazard.[3] Materials based on silicone technology include fluids and greases, emulsions, rubber products and resins. Silicones find application in many diverse markets, such as aerospace, automotive, construction, electrical, electronics, medical materials, performance chemicals and coatings, personal care, paper and textiles.[4]

Silicones have broad utility in textile processing and finishing; most of the products for this industry are based on PDMS technology.[5-9] The applications for silicones vary widely and include antifoams for fabric and carpet dyeing, print paste softeners, fabric finishes and coatings. In fabric processing, silicone antifoams are often used to maximize efficiency of scouring baths, washing/dyeing and bleaching operations. They serve as fiber lubricants for spinning, winding and slashing. Various types of silicones are commonly used as softeners, wetting agents and water repellents. In sewing operations, silicone thread lubricants are essential to meet the demands of high-speed industrial sewing machinery. Silicones also have many uses in nonwoven applications, such as binder additives for wet-laid processes.

Some silicones are supplied as neat fluids, while others are in the form of emulsions or room temperature curing elastomers. PDMS is extremely versatile, and can be modified to formulate a wide range of products with tailored hydrophobicity and durability, used to modify the feel and appearance of fabrics, or to improve processing. Performance-enhancing additives and finishes based on PDMS technology can be either nonreactive (Fig. 1), conventional reactive (Fig. 2) or organofunctional materials (Fig. 3). One of the advantages to processors is the ability to derive more than one benefit from a single product. A feature shared by many silicone materials is effectiveness at very low concentrations. Very small amounts are usually required to achieve the desired properties, which can improve the cost efficiency of textile operations and help ensure a minimum of environmental impact.

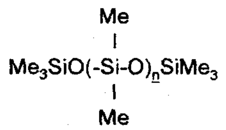


Fig. 1. Example of nonreactive silicone polymer.

ABSTRACT

Silicones have broad utility in the textiles industry, functioning both as process aids (including antifoams and lubricants) and performance enhancers (such as water repellents and softeners). Most of these products are applied to textile substrates as emulsions of polydimethylsiloxane (PDMS) or aminofunctional PDMS. Other types and forms are commonly used as well, including silicone polyethers, elastomers and silane crosslinking agents.

KEY TERMS

Air Quality
Environment
Silicone
Wastewater

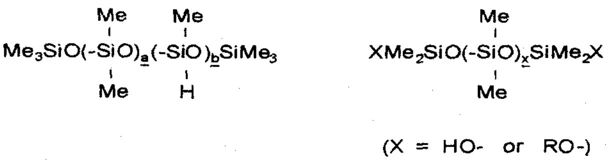


Fig. 2. Example of conventionally reactive silicone polymers.

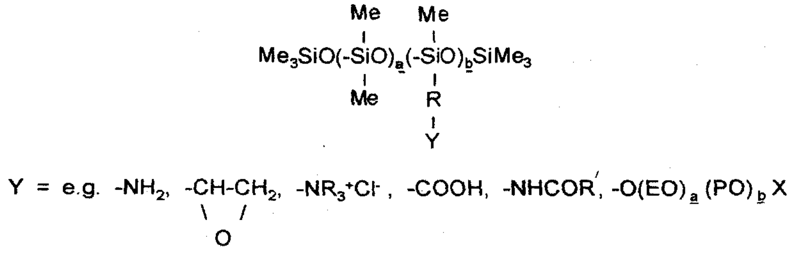


Fig. 3. Example of organofunctional reactive silicone polymer.

Environmental Entry of PDMS

Textile processing operations produce an aqueous waste stream, usually directed to a wastewater treatment plant (WWTP) for processing. Silicones are a minor part of that discharge. PDMS becomes part of a plant's wastewater stream in the form of tiny dispersed droplets and attach to suspended solids. Because nonvolatile PDMS fluid is essentially insoluble in water, these materials become a minor component of the sludge in a treatment plant. The specific route of nonvolatile silicones depends on how the individual WWTP handles its sludge. If the sludge from water treatment is incinerated, the silicone content converts to amorphous silica, water and carbon dioxide. Treated sludge used as fertilizer may introduce PDMS to the soil environment, where it is subject to natural degradation processes. Similar soil-catalyzed degradation is also expected to occur if sludge-bound PDMS is landfilled.

Fate

PDMS materials are highly resistant to biodegradation by microorganisms, but they undergo very effective degradation via natural chemical processes, such as catalyzed-hydrolysis and oxidation.[10-14] PDMS breaks down into lower molecular weight siloxanols and silanols (Fig. 4) during soil contact.[11] These degradation products are susceptible to both biological and abiotic decomposition, eventually oxidizing to natural silica.[12-14] The general nature of this soil-catalyzed degradation has been demonstrated in agricultural soils with varying pH, moisture, sand, silt, organic matter and clay content.[15]

Effects

PDMS is ecologically inert and has been found to have no effect on aerobic or anaerobic bacteria. It does not inhibit the biological process by which wastewater is treated. In laboratory tests using carbon-14 labeling techniques, activated sludge reactors and anaerobic/aerobic digesters have been used to examine PDMS loadings far exceeding any anticipated environmental level (up to 10,000 mg/kg^{-1} dry weight).[16] Data indicates that PDMS has no effect on:

- pH
- Sludge volume index, suspended solids or settling rates
- Specific growth rates
- Endogenous decay
- Cell yield
- Oxygen uptake rates in model activated sludge systems
- Gas generation rates in pilot scale anaerobic digestors
- Half-saturation content for substrate utilization
- Aerobic/anaerobic digester operation

PDMS-loaded samples exhibited no observable differences from control groups. Mass balance measurements demonstrated that essentially all of the PDMS partitioned onto the microbial biomass and remained essentially unchanged. The results strongly support the conclusion that PDMS is an inert component of wastewater systems, with no measurable effect on treatment processes other than the expected benefit of foam control.[16]

Because PDMS molecules are adsorbed onto sludge particulates which may end up as a soil amendment, researchers have used soil-core microcosm techniques to predict the ecological effects of waste materials in an agricultural ecosystem. Recent experiments on the effects of PDMS materials in sludge-amended soil have focused on two crops, spring wheat and soybeans. They were selected primarily for their importance to U.S. agriculture and the tendency to rotate the two in that sequence in the field. Vaying levels of PDMS content have been studied from both aerobic and anaerobic sludge digestion systems.[17]

No adverse effects were seen for seed germination, survival percentages or plant mass of crops. Nitrate-nitrogen loss appears likewise unchanged in the presence of PDMS fluid, which does not induce significant consequences in microorganism populations. Studies found no evidence that PDMS may inhibit the bacteria responsible for nitrogen fixation in some crops. Uptake of carbon-14 labeled species by wheat grains or beans was not observed, and sludge-bound PDMS was shown to degrade in soil.[17,18] The PDMS-loaded samples exhibited no significant differences from control samples.[17] Testing continues on the potential impact of these materials, as researchers further investigate the effects of PDMS on sludge-amended agricultural soils.

If nonvolatile methyl silicones enter an aquatic environment, they do not bioconcentrate. Their molecular size prevents them from passing through the biological membranes of fish or other animals.[19] PDMS fluids attach to particulate matter and are effectively removed by the natural cleansing process of sedimentation; they do not partition back into the water column.[20] PDMS fluids exhibit insignificant biological oxygen demand (BOD).[21] Testing on aquatic plant and animal life revealed no measurable adverse effects, even under highly exaggerated conditions of exposure. No significant change in the growth of algae, plankton or other marine organisms has been found.[22]

PDMS has not been found to pose any threat to insect populations and birds. Even in direct dietary exposure testing, ducks and chickens displayed no significant impact, and egg production and viability remained unchanged.[23]

Volatile Methylsiloxanes

Volatile methylsiloxane (VMS) fluids are low-viscosity, cyclic materials:

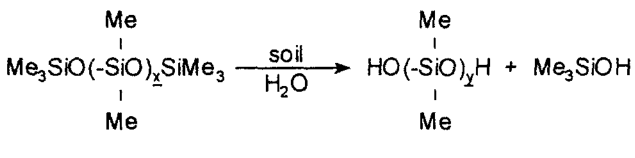
$$(Me_2SiO)_x$$

where x=4-6, or short-chain linear siloxanes:

$$Me_3SiO(SiMe_2O)_nSiMe_3$$

where n=4 or less. Nonvolatile silicones may have some volatile components, and small amounts of VMS can also be released during elevated temperature processing of silicone-treated textiles.

In response to tighter environmental regulations limiting emissions of volatile materials, many processors have added pollution control technologies that capture volatiles and some companies add them to the wastewater stream for processing along with aqueous effluent. Volatile methylsiloxanes are also recovered by these techniques, and eventually partition to the atmosphere during wastewater treatment. When volatile silicones enter the atmosphere, they are broken down by oxidative chemical processes.[24,25] The partially oxidized degradation products are less volatile, and will be scrubbed out of the atmosphere or deposited on the earth's surface by rain, where they are further diluted and degraded. The final products of this oxidation would be naturally-occur-



y = mainly 1

Fig. 4. Degradation of PDMS during soil contact to form siloxanols and silanols.

ring substances—silica, carbon dioxide and water.[13,14]

VMS materials degrade quickly, with an atmospheric lifetime of just 10 to 30 days.[24] They are considered to have no potential to deplete stratospheric ozone. Further, VMS fluids are not a significant contributor to global warming. They make no measurable contribution to ground-level ozone formation.[26] Aerosol formation (visibility reduction) has not been observed under atmospheric conditions likely to be encountered in a typical urban airshed with moderate photochemical activity.[27]

VMS molecules could be small enough to pass through biological membranes such as fish gills, where they might bioconcentrate to produce some effect.[28] However, under real-world conditions, this phenomenon does not occur due to the volatility and extremely low water solubility of VMS fluids.[29,30]

Formaldehyde

One of the prominent issues facing the textile industry is the development of formaldehyde (CH_2O) during processing, and many initiatives are underway to reduce the formation and release of this substance.[31] Formaldehyde may be present in textile finishing resins, biocides or other chemicals as a resident component of the formulation. It can also develop during storage or as a result of exposure to elevated temperatures. In fact, high-temperature oxidation of almost any organic material containing methyl or methylene groups can cause the development of formaldehyde.

Because many silicones are methyl-containing materials, testing has been conducted to measure evolved formaldhyde from more than 70 different silicone materials. Though not required by any legislation or regulatory agency, a number of PDMS materials have been analyzed, including fluids, resins, elastomers, emulsions, greases and sealants.

Evolution rates have been determined at elevated temperatures using a modified thermogravimetric analyzer in conjuction with a hydrazine/polarographic procedure. The testing showed that PDMS materials evolved formaldehyde beginning near 200C. Formaldehyde was not seen above background levels (<5µg/g per hour) when 50 cs PDMS was heated in air at 197C. The evolution of formaldehyde started above 200C and increased to 245 µg/g per hour at 225C.[32]

It was expected that the methyl groups might oxidize at similar rates, whether bonded to silicon or carbon, but testing showed that the evolution rate for polypropylene at 200C was greater than 425 µg/g per hour.[32] These findings indicate that carbon-based materials containing methyl groups pose a significantly greater formaldehyde hazard than PDMS. Potential risk is further minimized in light of the fact that textile processing rarely requires heat in excess of 215C, and average temperatures are generally lower. Dwell time is usually brief, and it is uncommon for the fabric itself to exceed 175-200C. Because PDMS contains no chlorine atoms, there is no risk of developing chlorinated dioxins or furans.

Regulatory Status

PDMS is not classified as hazardous under SARA, RCRA or CERCLA regulations. Silicone fluids are currently excluded by definition and review from the lists of toxic, bioaccumulative water pollutants in the U.S. EPA's National Fish Study, National Contaminated Sediments Strategy and Great Lakes Initiative. Unlike hydrocarbon oils, silicone fluids are not covered by the Oil Pollution Act of 1990.

Recent studies demonstrated that VMS compounds have little or no potential to adversely impact urban air quality.[26] Similar conclusions were drawn when the atmospheric reactivity data was used to calculate the photochemical ozone creation potential of VMS materials by European atmospheric chemistry experts using the Harwell Photochemical Trajectory model.[24,33]

In November of 1994, the U.S. EPA issued a formal ruling that exempts VMS materials from regulations as VOCs.[34] The action was taken in response to a petition and supporting data submitted by Dow Corning, which demonstrates that VMS fluids do not contribute to ground-level ozone formation.[26] Individual states will be petitioned next to request that similar action be taken to coincide with the federal government's VOC definition.

In some applications, VMS fluids have been identified as good candidates to replace CFCs and other organic solvents which can contribute to air quality problems.[35,36]

Conclusions

The benefits of silicone materials based on PDMS technology in textile applications are well documented, with a wide range of advantages at low concentrations. They have been found to make up a minor component of the wastewater stream, becoming attached to particulate matter in wastewater treatment sites. Testing has indicated no adverse effects from PDMS on the sludge treatment processes or the microorganisms necessary for effective sewage degradation. An added benefit of these essentially non-toxic products is their ability to reduce unwanted foam.

Methyl silicones have undergone intensive eco-toxicological testing and have been found to be inert, without significant potential for negative environmental impact. They have a long history of safe use in textiles and nonwovens, at times serving as replacements for organic materials. The advantages of products based on PDMS technology include superior performance and minimal environmental concerns.

PDMS materials do not form significant levels of formaldehyde at typical process temperatures and have no potential to produce hazardous dioxins or furans either during textile processing or waste treatment. Testing of PDMS has shown no evidence of toxicity to aquatic, terrestrial or avian life forms, either plant or animal.

Under realistic conditions, PDMS has been shown to degrade very effectively by natural chemical means. Though not considered biodegradable, the molecules break down via hydrolysis during soil contact. The degradation products are susceptible to both biological and abiotic decomposition, eventually oxidizing to silica, water and carbon dioxide, all of which occur naturally. In textile and nonwovens processing, VMS materials are not typically present in ecologically significant amounts. These fluids readily partition to the atmosphere and degrade via oxidative chemical processes. They have an atmospheric lifespan of just 10-30 days. Studies have shown that VMS materials do not contribute to ground level ozone formation and the U.S. EPA has ruled that VMS fluids are exempt from classification as VOCs.

While manufacturers across the globe continue to seek environmentally friendly alternatives for many of the performance additives and finish chemicals in the textile industry, the inherent eco-safety of silicones and their low usage levels indicate the likelihood of their sustained presence in textile manufacturing.

Dow Corning continues to expand the range and depth of environmental science as it relates to silicone technology. The company is committed to open dialogue with employees, customers, regulatory agencies and the general public, and welcomes partnering relationships to proactively address environmental concerns.

References

1. Second Conference for Executives and Managers on Environmental Issues Affecting the Textile Industry—A National Perspective, Charlotte, N.C. 1994.
2. Noll, W., *Chemistry and Technology of Silicones*, Academic Press, New York, 1986.
3. *Silicones Chemistry and Technology*, Edited by Bayer AG, Th Goldschmidt AG, Wacker Chemie GmbH and Haus der Technik, CRS Press, Boca Raton, Fla., 1991.
4. Smart, M., F. Kalt and N. Takei, "Silicones," in *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1993.
5. Sabia, A. J., *Book of Papers*, AATCC International Conference & Exhibition, Boston, Mass., 1980.
6. Buckingham, A. M., *Nonwovens Industry*, November 1991, p34.
7. Calamari Jr., T. A. et al., *American Dyestuff Reporter*, June 1991, p28.
8. Buckingham, A. M., J. Borkovich and D. J. Avery, *TAPPI Proceedings*, 1993 Nonwovens Conference, Atlanta, Ga., p331.
9. Joyner, M. M., *Textile Chemist and Colorist*, Vol. 18, No. 3, March 1986, p34.
10. Buch, R. R. and D. N. Ingebrigtson, *Environmental Science and Technology*, Vol. 13, 1979, p676.
11. Lehmann, R. G., S. Varaprath and C. L. Frye, *Environmental Toxicology and Chemistry*, Vol. 13, 1994, p1061.
12. Lehmann, R. G., S. Varaprath and C. L. Frye, *Environmental Toxicology and Chemistry*, Vol. 13, 1994, p1753.
13. Buch, R. R. et al., *Environmental Toxicology and Chemistry*, Vol. 3, 1984, p215.
14. Anderson, C. et al., *Chemosphere*, Vol. 16, 1987, p2567.
15. Lehmann, R. G., Final Report from Dow Corning Corp. to the PDMS Environmental Task Force of the Silicones Environmental Health and Safety Council Inc., March 1994.
16. Watts, R. J. et al., submitted to *Water Research*, November 1993.
17. Tolle, D. A. et al., submitted to *The Science of theTotal Environment*, April 1994.
18. Lehmann, R. G. et al., submitted to *Water, Air and Soil Pollution*, May 1994.
19. Annelin, R. B. and C. L. Frye, *The Science of the Total Environment*, Vol. 83, 1989, p1.
20. Gettings, R. L. and T. H. Lane, "The Use of Microecosystems in Determining the Environmental Fate of Polydimethylsiloxanes," Dow Corning Internal Report I-0005-0957, 1982.
21. Calandra, J. C. et al., *Polymer Reprints*, Vol. 17, 1976, p12.
22. Firmin, R., C. L. Frye and A. L. J. Raum, *Ecotoxicological Testing for the Marine Environment*, Vol. 1, 1984, p591.
23. Hobbs, E. J., M. L. Keplinger and J. C. Calandra, *Environmental Research*, Vol. 10, 1975, p397.
24. Atkinson, R., *Environmental Science and Technology*, Vol. 25, 1991, p863.
25. Sommerlade, R. et al., *Environmental Science and Technology*, Vol. 27, 1993, p2435.
26. Carter, W. P. L. et al., Final Report from the University of California, Riverside to Dow Corning Corp., November 1992.
27. Carter, W. P. L. et al., Final Report from the University of California, Riverside to Dow Corning Corp., June 1994.
28. Surprenant, D. C. et al., *Book of Papers*, Annual SETAC Meeting, Cincinnati, Ohio, 1992, p56.
29. HydroQual Inc., Report to the Silicones Environmental Health and Safety Council, Job No. SHC00010, March 1992.
30. HydroQual Inc., Report to the Silicones Environmental Health and Safety Council, Job No. SHC00020, June 1993.
31. Andrews, B. A. K., *Colourage Annual*, 1991, p77.
32. Filsinger, D. H., submitted to *American Industrial Hygiene Association Journal*, June 1994.
33. Jenkins, M. E. and C. E. Johnson, AEA/CS/16411030/001/ Issue 1, August 1993.
34. *Federal Register*, Vol. 59, No. 192, October 1994, p50693.
35. *Federal Register*, Vol. 59, March 1994, p13044.
36. Verbiese, N. BICS International, VOC Conference II, London, December 1993.

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