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Volatile organic silicon compounds: the most undesirable contaminants in biogases

Aurélie Ohannessian, Valérie Desjardin, Vincent Chatain and Patrick Germain

ABSTRACT

Recently a lot of attention has been focused on volatile organic silicon compounds (VOSiC) present in biogases. They induce costly problems due to silicate formation during biogas combustion in valorisation engine. The cost of converting landfill gas and digester gas into electricity is adversely affected by this undesirable presence. VOSiC in biogases spark off formation of silicate deposits in combustion chambers. They engender abrasion of the inner surfaces leading to serious damage, which causes frequent service interruptions, thus reducing the economic benefit of biogases. It is already known that these VOSiC originate from polydimethylsiloxanes (PDMS) hydrolysis. PDMS (silicones) are used in a wide range of consumer and industrial applications. PDMS are released into the environment through landfills and wastewater treatment plants. There is a lack of knowledge concerning PDMS biodegradation during waste storage. Consequently, understanding PDMS behaviour in landfill cells and in sludge digester is particularly important. In this article, we focused on microbial degradation of PDMS through laboratory experiments. Preliminary test concerning anaerobic biodegradation of various PDMS have been investigated. Results demonstrate that the biotic step has an obvious influence on PDMS biodegradation.

Key words | anaerobic biodegradation, biogas, polydimethylsiloxanes

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INTRODUCTION

Anaerobic digestion is usually practiced in sewage sludge treatment. It also occurs naturally in landfill site. During this process, the formed biogas can be upgraded energetically (either heat production or electricity).

Biogas produced by this way is considered as a form of renewable energy. Because of its methane content (40–75%), biogas is generally used at wastewater treatment plants and landfills for heating, electrical generation or cogeneration. However, as a waste by product, biogas may also include undesirable components including volatile sulfur and volatile organic silicon compounds (VOSiC). Sulphur contaminants are currently treated by activated carbon or other treatments that are very well known. VOSiC are less known and their behaviour is not yet really understood. Moreover, they are one of the most difficult contaminants to remove from biogas.

Nowadays, it is identified that VOSiC originate from silicone presence and their degradation products in solid waste (LF site) and in sludge (WWTP) (Craig 2003). Accurately, silicones wastes present three different outlets according to their physical forms: fluid, elastomer or resin. Silicone used in cosmetics and detergent products generally end up in the wastewater. Other silicones used in packaging, construction, etc … end up in solid waste that generally fate in landfill. Silicone polymers are widely used cause to their really interesting properties compare to other polymers (Tomanek 1991). Silicones refer to a large family of polymeric substances, i.e., macromolecules containing Si-O

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bonds with organic radicals bound to Si and including functional organic groups (methyl, ethyl, etc.). The number of repeating units, "n" can range from one to several thousand. The most common silicone oils encountered are the polydimethylsiloxane (PDMS) oils whose structure is shown below (Figure 1). They are defined by the siloxane unit (Figure 2; Schorsch 1988; Smith 1991).

Combustion of silicon containing gases leads to the accumulation in gas engines (pistons, cylinder heads and valves) of abrasive microcrystalline silica and silicates. These deposits build a surface thickness of several millimetres, very difficult to remove by chemical or mechanical treatments (Figure 3). They also reduce compression and engine efficiency. Additionally, these glassy residues generally initiate the efficiency decrease of the catalyst emission control system (Schorsch 1988; Schweigkofler & Niessner 1999).

According to applied filter technology, an internal combustion generator engine running on 400 standard cubic feet per minute (SFCM) of biogas containing only 1 ppmv of VOSiC, could generate approximately 59 kg of silicon dioxide (SiO_2) per year. Thus, maintenance requirements are multiplied by 5 to 10. Normally designed to run 20,000 to 40,000 hours, many engines require maintenance after 14,000 hours of work and, in severe cases, after only 2,000 to 4,000 hours. These considerable damages increase dramatically the operating cost of the generation equipment.

Due to little knowledge about siloxanes behaviour in landfill cells or in sludge digester, a better understanding of their degradation mechanisms is fundamental from an environmental or/and a financial point of view. The growing consumption of silicones and siloxanes all over the world (5% per year, data from CES, the European Center for Silicone) and the subsequent increase in biogases, has led

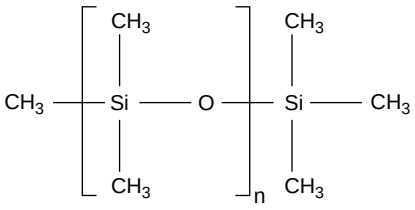

Figure 1 | PDMS chemical structure.

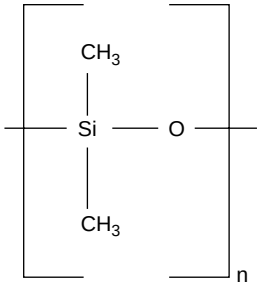

Figure 2 | Siloxane unit.

to significant concern about the presence of VOSiC and the induced problems in gas engines.

During wastes storage (either sludge or solid waste) PDMS and microorganisms are in contact, investigations using biodegradation experiments will thus contribute to a better understanding of biotic degradation. But, performing biodegradation tests on PDMS appears difficult due to their physicochemical properties (low solubility, high vapour pressure…). The fate and the degradation of PDMS in various natural and anthropogenic environments have been discussed controversially in the literature (Heinen 1978; Buch & Ingebrigtson 1979; Watanabe *et al.* 1988; Wasserbauer & Zadak 1990; Lehmann & Miller 1996; Lehmann *et al.* 1998; Griessbach & Lehmann 1999; Grümping *et al.* 1998, 1999; Hagmann *et al.* 1999; Lehmann 1999). For a long time PDMS were thought inert with respect to living organisms. During the last two decades, the possibility of their chemical degradation and biodegradation in the environment was demonstrated. PDMS were found to be degraded in soil (Lehmann *et al.* 1995; Griessbach & Lehmann 1999) through a two-step mechanism.

Hydrolysis reaction is considered as the first predominant step to degrade polymers in nature (Lehmann *et al.* 1994, 1996, 1998, 2000). This abiotic step is faster in dry soil than in wet one. The main hydrolysis product is DiMethylSilaneDiol (DMSD), which is found in soils and sludges (Hobbs *et al.* 1975; Fendinger *et al.* 1996; Sabourin *et al.* 1996; Lehmann *et al.* 1998, 2000).

On the opposite, the second step should be biological (Lehmann *et al.* 1998; Graiver *et al.* 2003). The main degradation product, DMSD, has been described to be potentially biodegraded or evaporated in nature (Buch & Ingebrigtson 1979; Lehmann *et al.* 1994, 1995; Grümping & Hirner 1999; Craig 2003). This molecule seems to be

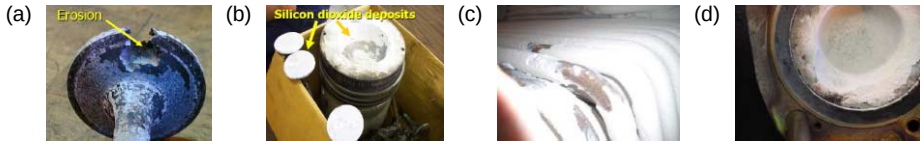

Figure 3 | a) Erosion silicon dioxide deposits b) on pistons c) on boiler tubes d) on piston crown.

biodegraded in priority (compared to PDMS). Two microorganisms isolated from soils (Fusarium oxysporum *Schlechtendahl*, and *Arthrobacter)* were described recently for their ability to co metabolize DMSD (Lehmann *et al.* 1995).

Some authors have shown that long PDMS can also be biodegraded (by *Pseudomonas fluorescens* and *Pseudomonas putida*, for example Wasserbauer & Zadak 1990). Surprisingly, it was concluded that higher molecular weight PDMS were better growth media, which implies that higher molecular weight polymers are more digestible than lower one.

The objective of the research presented here was to investigate the possible biotic degradation of PDMS. Preliminary results concerning microbial effects on PDMS degradation are first presented. Then anaerobic biodegradation has been studied more precisely for three PDMS.

MATERIALS AND METHODS

PDMS

Several polymers were tested. The chosen PDMS present different chemical end groups and viscosities (Table 1). These PDMS have been supplied by BlueStar® silicone.

Silicon (Si) analysis

Si was analysed in aqueous phase after filtration through 0.45-μm-pore-size syringe filters (cellulose). Si measurements have been done with an Inductively Coupled Plasma-Optical Emission spectrometer (ICP-OES) (Jobin–Yvon Longjumeau, France) using the most sensitive emission line (288.158 nm). The standard deviation was less than 10%. An instrumental detection limit of 0.005 mg L^{-1} was achieved.

Table 1 | The different polymers used in the study

PDMS Denomination	End group	Viscosity (cst)
M1	Methyl	1,000
M2	Methyl	3
V1	Vinyl	1,500
H1	Hydroxyl	5,000

Micro-organisms and culture media

Several inocula and strains from our laboratory stocks and from Waste Water Treatment Plant (WWTP) have been used for aerobic and anaerobic tests (Table 2).

Morphological isolate strains were observed by a light microscope with Gram stained cells and a scanning microscope.

DNA extraction, PCR amplification, and sequencing of 16S rDNA have been realized. Bacterial isolates DNA was extracted by a modified procedure of the method described by Pitcher *et al.* (1989). The PCR amplification of 16S ribosomal DNA (rDNA) was performed with using the highly conserved 16S rRNA gene primers pA (AGAGTTTGATCCTGGCTCAG) and pH (AAGGAGGTGATCCAGCCGCA).

PCR amplification conditions were 95°C for 2 min followed by 45 cycles of 94°C for 30 s, 55°C for 30 s, and 72°C for 1 min and a final 10-min extension step at 72°C.

Sequencing was carried out and sequences obtained were matched with sequences from GenBank Databases. The closely related strains were retrieved from this database and the Genbank references are added in the table with the percent of similarities.

The inocula density was estimated by spectrophotometry at 600 nm. All the strains were stored at −20°C in an aqueous glycerol solution (15%) prior to be used.

The preliminary tests were realized in sterile water and in LB (Luria Broth) media. LB was obtained from Roth (Carl Roth Gmbh, Germany). Anaerobic tests were performed in a media consisting in: KH_2PO_4 (0.27 g), $Na_2HPO_4{\cdot}12H_2O$ (1.12 g), NH_4Cl (0.53 g), $CaCl_2{\cdot}2H_2O$

Table 2 | Strains used during the different tests

Tests	Strains/inocula	Genbank references	Isolate by matching	Source
Preliminary test®	JB	AY395016.1	*Staphylococcus xylosus (100%)*	Laboratory stocks
	SG	DQ311007.1	*Agromyces sp (93%)*	
	P	EU430096.1	*Stenotrophomonas maltophilia (100%)*	
	W1	EU874887.1	*Bacillus thuringiensis (99%)*	
Anaerobic test	WWTP2			WWTP Chambery (France)

(0.075 g), $MgCl_2{\cdot}6H_2O$ (0.10 g), $FeCl_2{\cdot}4H_2O$ (0.02 g), $Na_2S{\cdot}9H_2O$ (0.10 g) and 10 ml of a trace solution containing $MnCl_2{\cdot}4H_2O$ (0.050 g), Na_2SeO_3 (0.005 g) H_3BO_3 (0.005 g), $ZnCl_2$ (0.005 g), $CuCl_2$ (0.003 g), $Na_2MoO_4{\cdot}2H_2O$ (0.001 g), $CoCl_2{\cdot}6H_2O$ (0.1 g), $NiCl_2{\cdot}6H_2O$ (0.01 g) dissolved up to one liter of deionised water. All solutions and liquid media were autoclaved at 121°C during 20 minutes.

Biodegradation experiments

Preliminary tests consisted in adding polymer in an aqueous phase (sterile or not). 2 grams of polymer were added to 20 mL of liquid medium inoculated or not in sterile propylene bottles. The mixtures were tumbled in an end-over-end fashion at a speed of 15 ± 2 rpm at room temperature. The objective was to measure Si concentration in the aqueous phase, by ICP-OES, as a tracer of PDMS degradation. Samplings were realized at 5, 15, 25, 35 and 45 days.

The anaerobic tests, called BMP test for Biochemical Methane Potential test, were conducted in penicillin bottles (125 mL) or Schott® bottles (250 mL) with a 50 mL sample (inoculum (20 mL) + liquid medium (20 mL) + silicone oil (10 ml)). Tests were conducted in a temperature-controlled room 35 ± 2°C without agitation. To account for biogas production from residual degradable matter in the inoculum, sludge controls (sludge blanks) containing only media and inoculum were incubated simultaneously to allow subtraction of gas not attributed to the substrate. In addition, positive controls containing only cellulose ($10\ g.L^{-1}$) were also incubated and sampled simultaneously. This was done to ensure that the results are not affected by inoculum, media or sampling procedures.

All the experiments have been carried out in triplicate.

Biogas analysis

The gas produced within the anaerobic reactions contains O_2, N_2, CO_2 and CH_4. The compounds were analysed by gas chromatography (Micro-GC, Agilent Varian). Biogas analysis by micro-GC (micro gas chromatography) pass through two columns, first one is a PoraPLOT U (8m × 0.320 mm ID, 0.5 μ df) and the second one is a Molsieve 5Å 10 m/PPU 3 m. Helium was the carrier gas used. Gas production from all bottles was calculated at incubation temperature ($35° \pm 2$°C) by measuring pressure in the bottles (apparatus Digitron).

RESULTS-DISCUSSION

Preliminary tests

Preliminary tests have been conducted on M1 and H1 polymers. They are the most representative PDMS in terms of industrial production. Their viscosities are respectively 1,000 and 5,000 cts and their end groups are methyl for M1 and hydroxyl for H1. The test consisted in adding the polymer (2 g) to 20 mL of liquid medium (water or LB) inoculated with different strains. Si was followed in the liquid medium during 45 days. Figure 4 illustrates the results obtained after 45 days.

In the case of inoculation, Si concentration in the liquid media is more important than in sterile medium. In every instance, abiotic degradation occurs ($1\ mg.L^{-1}$ in water and $1.55\ mg.L^{-1}$ in LB). Moreover, Si concentration is less important in water than in LB medium, with or without inoculation. The presence of microorganism enhances Si release in aqueous phase up to twice in water and three times in LB media. The presence of nutrients in LB enhances microbial growth and metabolism, compared to

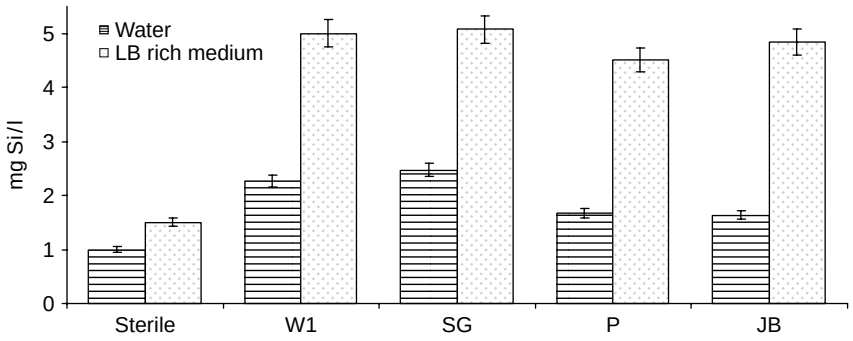

Figure 4 | Si concentration in the aqueous phase after 45 d of incubation (room temperature, 15 rpm). 2 g of M1 polymer with 20 ml of water or LB inoculated or not by W1, SG, P or JB.

experiments in water. Finally, there is no significant differences between the different strains tested.

The inocula concentration influence was tested in order to confirm or not the bacteria influence on PDMS degradation (data not show). These experiments demonstrated that Si release depends on cell concentration in medium. No significant differences have been observed for the three lowest concentrations. For the highest concentration, Si release is 2.5 times greater than with the other ones.

Anaerobic-BMP tests

Anaerobic conditions were especially studied as this step is preponderant during waste storage. The anaerobic-BMP tests were realised in order to determine if a PDMS supplementation would have disturbed cellulose degradation reaction. Biogas kinetic production was followed (Figure 5).

Due to microorganism acclimation in this environment, gas production rate obviously accelerated after a lag period. As can be seen from Figure 2, the acclimation period was around 20 days. Addition of the different polymers was realised at the 25 days. As previous studies have indicated that end groups nature is not important in term of microbial activity, it was decided to test for the same end group methyl (two different viscosities). PDMS supplementation at the 25 d induced an increase in the biogas production (160 ± 7 ml and 125 ± 5 ml for M2 and M1 respectively) compared to blank control (118 ± 5 ml). Biogas production at the last day of the test is represented in Figure 6.

The ratio of CH_4 versus CO_2 was studied in order to determine the efficiency of the methanogenesis reaction. Indeed, biogas interest consists in high methane content. If methanogenesis reactions are well established the ratio is always in favour of CH_4. During the experiments, the methane production was superior to carbon dioxide production. No acidification problem was encountered. Figure 7 illustrates the differences between the blank and the assays.

PDMS supplementation conduces to a better ratio than in the blank. PDMS presence influences a better production

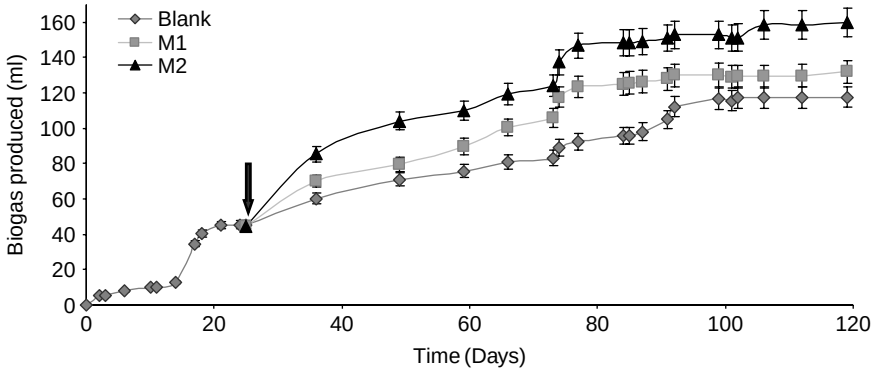

Figure 5 | Biogas kinetics production during 120 d at 35°C without agitation. PDMS addition of M1 and M2 polymers at the 25 d is notified by the black arrow, (BMP assay).

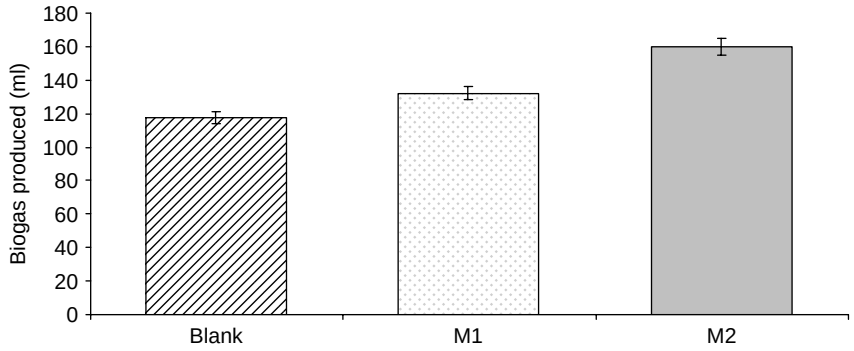

Figure 6 | Biogas production in ml at the 120 d of the BMP assay for the blank and the assay with M2 and M1.

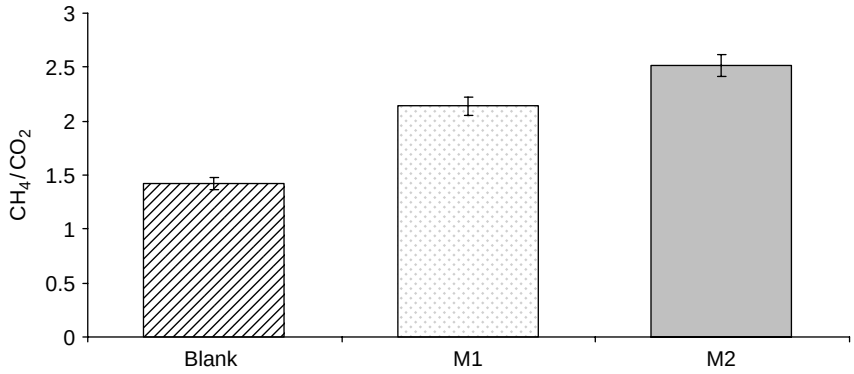

Figure 7 | CH_4/CO_2 ratio after 120 day of incubation at 35°C without agitation (BMP assay), in the presence of M1 and M2 polymers.

of methane versus carbon dioxide. All other tests performed in the laboratory lead to same conclusions.

Previous reports stated that high-molecular-weight [^{14}C] PDMS are not degraded to label CO_2 by anaerobic sewage bacteria (Hobbs *et al.* 1975). During our experiments, the presence of PDMS induced an enhancement of biogas production. Moreover, CH_4/CO_2 ratio was enhanced in their presence. These phenomena might found two origins: either PDMS might have been degraded or it could be due to an enhancement of microorganisms metabolism. Bacteria cells are may be sensitive to PDMS presence. This kind of phenomenon has been demonstrated by others authors with the D4 silicone relatively to the transformation of TMBi in Bi (Michalke *et al.* 2002). For an archaebacteria nammed *Methanosarcina barkeri*, which is strongly present in wastes, D4 seems to trigger the bismuth transformation to its volatile toxic derivative trimethylbismuth. It has been proved that the stimulation of bismuth methylation is possible.

CONCLUSION

PDMS biodegradation is actually investigated for a better understanding on wastes storage phenomenon. The present research and our future developments will give a significant contribution to an issue, which presents very few data available from literature for time being. To our knowledge, it is the first report that demonstrates microorganisms influence on PDMS degradation by following Si release in the aqueous phase. This method gives the advantage of a one step analysis compared to other studies that need complex analyses and consequently more uncertainties. Moreover, it is possible to evaluate PDMS biodegradation in biphasic samples. Our method is not limited by sample solubility in an aqueous phase.

Anaerobic degradation could be considered as the predominant step during waste storage in landfill cell and also in sludge digester. So it was decided to test anaerobic conditions.

Microorganisms influence on the degradation of waste containing silicone stored in landfill cells has been proved. To ensure the results, an interesting way forward could be experiments with radiolabelled PDMS extend, in order to follow more precisely PDMS degradation products.

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