Biodegradation of polyorganosiloxanes

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SUMMARY. Biodegradation of various polyorganosiloxanes (about 30 substances) under the influence of several biotype bacteria strain (16 types) were studied. A special procedure of biodegradation and analytical methods of evaluation the degree of degradation were applied.
It was found that nearly all polysiloxanes tested are biodegradable but the degree of degradation depends on their composition and structure, as well as on the type of bacteria strain chosen.

Polyorganosiloxanes belong to a spacious class of macromolecular synthetic compounds having backbone skeleton with silicon atoms bonded through oxygen (similar as in case of quarz or inorganic silicates) and additionally substituted with variable organic groups, mainly with carbon and hydrogen atoms. Polyorganosiloxanes with organic radicals bonded directly with Si-C bond are called „silicones" and those bonded through oxygen atoms Si-O-C are called „alkylsilicates".
Silicones are characterised by many special properties: excellent thermal resistance (from -70 to +250°C), good oxidation and chemical resistance, special surface properties like water repellency, low surface tension and others. High molecular polyorganosiloxanes and especially polydimethylsiloxanes (PDMS) have been classified as physiologically inert compounds [1-6].
No biodegradation of 15% aqueous emulsion of methylsilicone fluid after 70 days action of activated sewage sludge was observed in 1976[7]. For this reason, polydimethylsiloxane fluids and rubbers have been widely applied as nontoxic and physiologically inert materials in the food industry, pharmacy and medicine [2,8,9,10]. However, during our preliminary investigations in 1993 on the action of some biotype bacteria on a polydimethylsiloxane fluid and two samples of poly(butylmethyl)siloxanes we have found that these polyorganosiloxanes can be partially biodegradable [11]. Also scientists from teh Massachusetts General Hospital and Harvard Medical School observed in 1993 degradation in vivo of polydimethylsiloxanes [12].
We decided in 1993 to study the influence of structure of polyorganosiloxanes on their biodegradability using various heterotropic bacteria strains. Recently some information about degradation of PDMS in soil determined using ^{14}C method was published [13].

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PRELIMINARY STUDIES

Materials: Three types of polyorganosiloxanes were synthesised, or chosen from commercial samples for these investigations (tab.1)

Type	I	II	II
Chemical name	Poly(alkylaryl)cyclosiloxanes	Poly(alkylaryl)siloxanes - linear	Polyorganosiloxanes branched or crosslinked
Schematic formula	R R CH_3-Si-O-Si-CH_3 O O CH_3-Si-O-Si-CH_3 R R	XO-[CH_3RSiO-]$_n$ X n> 15,	HO-[R_2SiO-]$_a$-[RSiO$_{1,5}$-]$_b$ a+b>10, a:b = 05 -0,7
Radicals	R= CH_3 or $CH_3(CH_2)_3$, $CH_3(C_2H_5)CH$, C_6H_5, $Cl(CH_2)_3$	X= H or $Si(CH_3)_3$; R= CH_3, $CH_3(CH_2)_3$, $CH_3(C_2H_5)CH$, C_6H_5, $Cl(CH_2)_3$, $F_3CCH_2CH_2$, $C_6H_2Cl_3$	R=CH_3, $CH_3(CH_2)_3$, $CH_3(C_2H_5)CH$

Various of all types polysiloxanes were prepared and used in the biodegradation tests (Tab.2)

Tab.2. Polyalkylsiloxanes tested for biodegradation

Comp.symbol		Type	R	Composition count.%			Mol.weight		-HO %
				Si	CH_3	R	M_R	M_N	
B11	D_4	I	Me	37,8	40,5	-	296		-
B21	D_3	I	„	„	„	-	222		-
B12	BMC/7D	I	Bu	24,1	12,9	49,0	465		-
B18	BMC/8D	I	„	„	„	„	„	480	-
B14	MCPC/1	I	ClPr	20,6	10,9	56,2	544		-
B19	MCP/2	I	„	„	„	„	„	540	-
B33	MCP20/I	I	„	26,7	21,4	37,1	630	600	0,5
B20	FMC1/II	I	Ph	20,6	10,9	56,2	544	520	-
B1	OM 300	II	Me	37,8	40,5	-	$[74]_n$		-
B2	BM200/4	II	Bu	24,1	12,9	~49	$[116]_n$		-
B17	BM200/7	II	„	„	„	„	„	~20000	-
B23	MCP02/1	II	ClPr	32,4	30,2	17,1	$[83]_n$		0,42
B24	MCP02/2	II	„	„	„	„	„	~2600	0,2
B29	MCP15/2	II	„	„	31,2	18,3	$[81]_n$		
B36	MCP12/1	II	„	29,6	26,4	27,5	$[95]_n$	~9260	0,3
B37	MCP12/2	II	„	30,5	28,0	24,3	$[92]_n$	~7260	-
B32	MO12/1	II	Oct	26,3	23,4	35,3	$[160]_n$		-
B26	MS710	II	Ph	~29	~19	~44	$[105]_n$		-
B27	DC560	II	$PhCl_3$				$[156]_n$		
B28	FS1256	II	F_3Pr				$[115]_n$		
B3	BBM20/2	III	Bu	25,0	2,7	51,6	$[102]_n$	2550	1,25
B22	BBM20/3	III	„	„	„	„	„	1000	~6,0
B8	BM70/3	III	„	33,1	24,8	20,2	$[85]_n$	950	2,05

*) estimated from VPO and/or GPC method

Procedure of biodegradation

To 5 ml of a nutrient broth spiked with an addition of 1% glucose, 0,2-0,5 ml of a polyorganosiloxane was added together with 0,02 ml of chosen bacterial strain. At least 12 samples for each polysiloxane and each bacteria strain chosen were prepared under aseptic conditions. Zero samples: without polysiloxane (broth+bacteria) and control samples (without bacteria) were prepared for comparision. All samples in glass test tubes were placed in water thermostat at 37°C and incubated for a definite number of days. Every 24 hours all samples were shaken to increase the interphase surface.

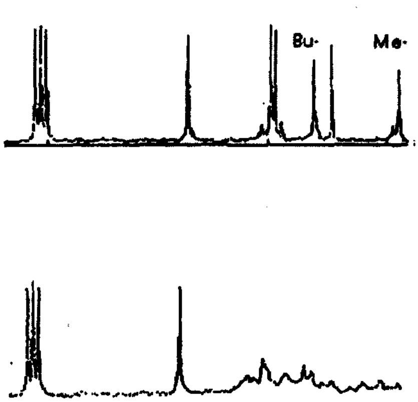
The following biotype bacteria were tested primarily:

a) *Bacilius subtilis,* b) *Proteus species,* c) *Pseudomonas aeruginosa,* d) *Staphylococcus aureus,*
e) *Staphylococcus epidermitis,* f) *Staphylococcus saprophyticus,* g) *Streptococcus faecalis,*
h) *Streptococcus (group A),* i) *Streptococcus (group B),* j) *Streptococcus viridans,*
k) *Haemolysing streptococcus,* l) *Escherichia coli,* m)*Klebsiella pnaemonia* n) *Shigella sonnei,*
o) *Salmonella enteritidis,* p) *Yersinia species,* r) *Clostridium species (aneorobic).*

Selected samples, after a definite period of incubation time were extracted with 5 ml of carbon tetrachloride and analysed using IR, ^{1}H NMR and ^{13}C NMR spectrometry. Comparing spectra of control samples with those incubated -with bacteria, the "degree of biodegradation" as a decrease of concentration polyorganosiloxanes extractable in CCl_4 was calculated. Some changes in spectra were also observed. Silicon content in CCl_4 extracts and in water phase after extraction was also determined by atomic spectrography of some samples.

Results.

The evident changes in ^{13}C NMR spectra of two kinds of poly(butylmethyl)siloxanes of linear (BM200/4) and branched (BBM20/2) structure, and some changes in the spectra of polydimethylsiloxane fluid (OM300) after 30 days of incubation with various strains of bacteria were observed (Fig.1, 2). The biodegradability of some polyalkylcyclosiloxanes under influence of the same 3 types of biotype bacteria was determined by comparing IR spectra of CCl_4 extracts at characteristic wave numbers after14 days incubation of tetra(butylmethyl)cyclotetrasiloxane (BMC-7D) and of octamethylcyclotetrasiloxane (D_4) (Fig.3).



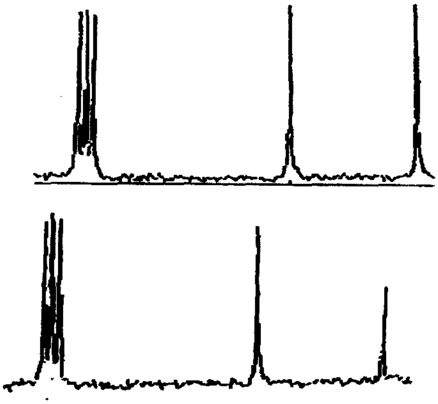


Fig.1. Changes in ^{13}C NMR spectra of poly(butylmethyl)silicone fluid (BM200/2) before and after 30 days incubation with *Escherichia coli*

Fig. 2. Changes in ^{13}C NMR spectra of polydimethylsilicone fluid (OM300) before and after 30 days incubation with *Klebsiella pneumoniae*

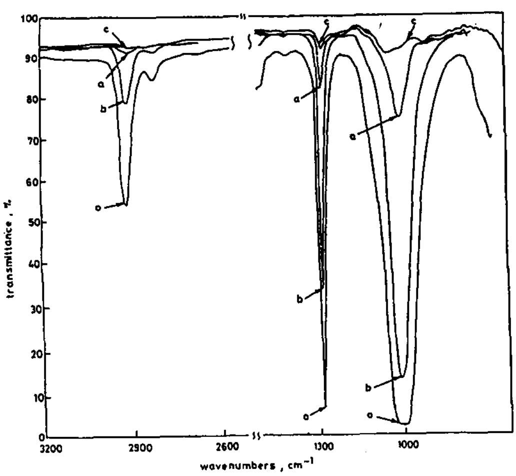


Fig 3. Changes in IR spectra of CCl_4 extracts of octamethylcyclotetrasiloxane (BMC7/D):
o- before testing, a- after 14 days incubation with *Bacillus subtilis*, b- after 14 days with *Proteus species*, c- after 14 days with *Pseudomonas aeruginosa*

Results of silicon content determination by AAS spectroscopy in CCl_4 extracts and in water phase after 14 days of incubation of the same polyalkylcyclosiloxanes with 3 bacteria strains are summarised in Tab.3.

Tab. 3. Changes of silicon content (mg/l) after 14 days incubation of octamethylcyclotetrasiloxane (B11) and tetra(butylmethyl)cyclotetrasiloxane (B12)

Bacteria strain	B11 (D_4)		B12 (BMC7)	
	in CCl_4 extract	in water phase	in CCl_4 extract	in water phase
without	14 100	10	8 600	12
Bacillus subtilis	9 100	16	6 800	16
Proteus species	8 200	12	6 700	25
Pseudomonas aeruginosa	5 000	98	5 000	124

Degree of biodegradation of various poly(butylmethyl)siloxanes and polydimethylsiloxanes varied from 20 to 50%, as calculated from their reduced concentration in CCl_4 extracts after definite time of incubation with various bacteria strains (Fig.4). No evident biodegradation was observed in the case of poly(methyl-3-chloropropyl)cyclosiloxanes (MCPC-1, MCPC-2) and of poly(methyl-3-chloropropyl)silicone fluid (B 24). A summary of a preliminary biodegradability tests of 20 silicone products tested by us with various bacteria till the end of 1994 is given in Tab.4 [14,15].

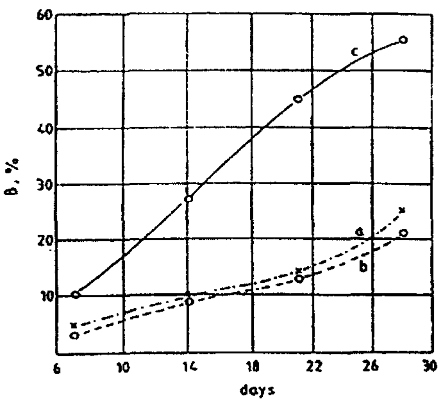


Fig.4. Increasing biodegradation degree B% of polybutylmethylsilicone fluid (BM200/7C) during incubation with 3 bacteria: a) *Bacillus subtilis*, b) *Proteus species*, c) *Psudomonas aeruginosa*

Tabl. 4. Biodegradability of polyalkylsiloxanes

Sig	Results of tests with various bacteria strains																
	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	r
B11	+	+	+														
B12	+	+	+														
B18			+														
B21			+														
B14	-	-	-														-
B19	-	-	-	+									+	+			-
B20	-	-	-														
B1	+	-	+	-	+	-	+	-	-	-		+	+	-	-	-	
B2	+	-	-	+	+	-	+	-	+	+		+	+	-	+	-	
B17	+	+	+														
B23	+	-	+	-							-	-					
B24	+	-	-	-							-	-					
B29	+	+	+	+	+	+	+					+	+		+		
B26	+	+	+	+							+	+					
B27	+	+	+	+							+	+					
B28	+	+	+	+								+	+				
B32	+	+	+									+	+				
B3	+	+	+	+	+	+	+	+	+		+	+	+	+	+	+	
B22	+	+	+								+						
B8				+	-	+	+	+	+		+						

note: + degradable, - non degradable

FURTHER SYSTEMATIC STUDIES

For the last cycle of our studies 11 organosilicone compounds were chosen [16] :

1. Octamethylcyclotetrasiloxane (D_4),
2. Tetra(n-butylmethyl)cyclotetrasiloxane (BMC7/D),
3. Tetra(iso-butylmethyl)cyclotetrasiloxane (BMC8/D),
4. Tetra(methylphenyl)cyclotetrasiloxane (PMC1/II),
5. Methylsilicone fluid (OM300),
6. Butylmethylsilicone fluid (BM200/4),
7. Butylmethylsilicone resin (BBM20/3),
8. Methyloctylsilicone fluid (MO200/1),
9. Methyl-3-chloropropylsilicone fluid (B23),
10. Polyethoxysilicate (Silbond 40)
11. Espumisan (pharmaceutical form of PDMS),

The most active standard bacteria strains were applied in this cycle:
a.*Esherichia coli-* ATCC 25922, b. *Klebsiella pneumoniae* - K 28,
c.*Pseudomonas aeruginosa*-ATCC 27853, d.*Proteus mirabilis* -14a,
e. *Bacillus subtilis* - a stndard strain for didactic purposes.

Procedure of biodegradation has been modyfied additionally, two methods of increasing interphase surface were applied:

- emulsifying of organosiloxane compound in water,
- coating the surfaces of test tubes with a solution of organosiloxane compound and evaporating solvent in a centrifuge,

Growth of bacteria during incubation was controlled and new batches were added, if needed.

RESULTS AND DISCUSSION

The most active bacteria in biodegradation of organosilicone compouds were: *Pseudomonas aeruginosa, Proteus mirabilis and Klebsiella pneumoniae.*

Interphase surface has an evident effect on the degree of biodegradation of some organosilicone compounds tested (Fig.5).

A high concentration of enzymes during the whole period of incubation, depending on the amount of active bacteria strain present is indispensable for proper biodegradation process.

Polyorganocyclosiloxanes are variably biodegradable under the applied conditions.The most biodegradable compounds tested in this cycle were polyethoxysiloxane (Silbond 40) amethyloctylsilicone fluid (Fig.6). In the case of Silbond 40 a simple hydrolysis of Si-OC bond increases under the influence of enzymes (Fig. 7).

Polyorganosiloxanes with long chain linear alkyl substituents are easier biodegradable then those with branched structure of substituens, and especially these with small methyl radicals.

Polydimethylsiloxanes (PDMS) are less biodegradable as the other polyalkylsiloxanes.

Polyalkylsiloxanes with 3-chloropropyl substutients at Si atoms and especially of cyclic structure were not biodegradable under these conditions (Fig. 8).

Molecular structure of siloxanes influences the biodegradability of polymers, eg. branched or crosslinked polyorganosiloxanes are easier biodegradable than those of long chain siloxane structure.

Our studies on biodegradation of various polyorganosiloxanes will be continued.

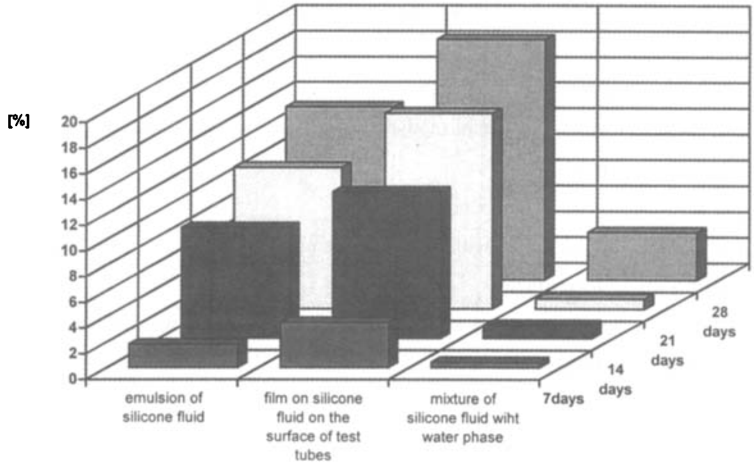


Fig. 5. Influence of interphase contact on degree of biodegradation of butylmethylsilicone fluid with *Pseudomonas aeruginosa*

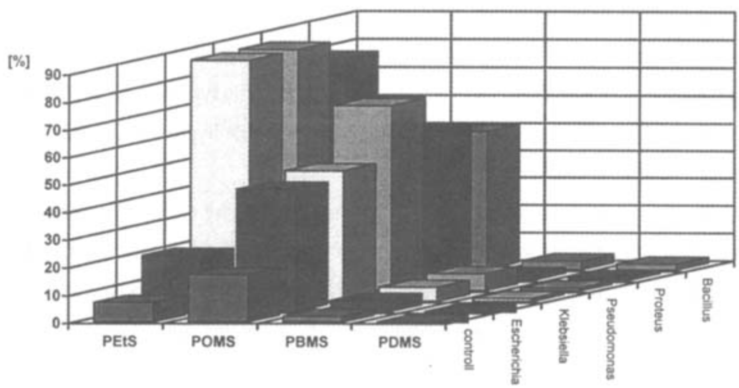


Fig. 6. Influence of the structure of polyorganosiloxanes on their biodegradability

PBMS: poly(butylmethyl)siloxane, PDMS:polydimethylsiloxane

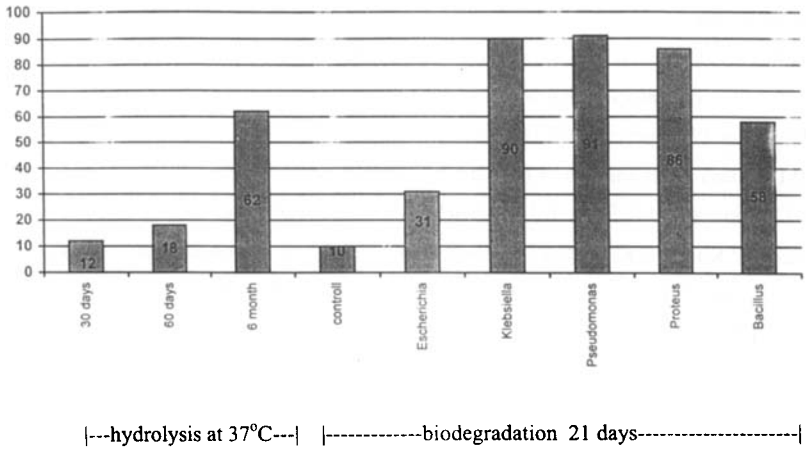


Fig. 7. Degree of degradation of polyethoxysiloxane (PEtS) during hydrolysis and biodegradation

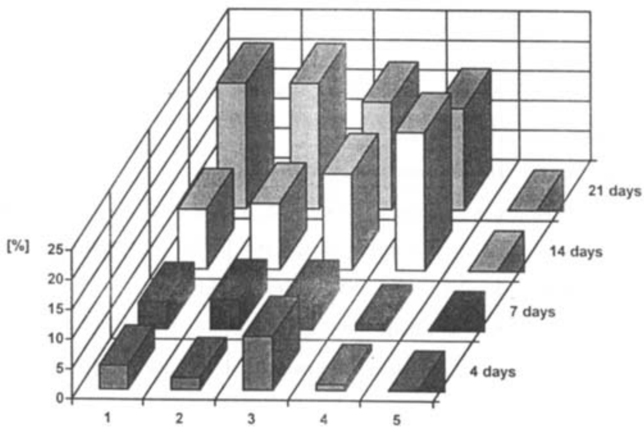


Fig.8. Degree of biodegradation of polysiloxanes after various time of incubation with *Psudomonas aeruginosa* :

1. octamethylcyclotetrasiloxane, 2. tetra(n-butylmethyl)cyclotetrasiloxane

3. tetra(i-butylmethyl)cyclotetrasiloxane, 4. tetra(methylphenyl)cyclotetrasiloxane

5. tetra (3-chlorpropylmethyl)cyclotetrasiloxane

REFERENCES

[1] V.K.Rove, H.C.Spencer, S.L.Bass, *J.Ind.Toxicol.* **30**,332 (1948)

[2] L.Levin,*"The Pharmacy of Silicones and their uses in Medicine"*, London 1958

[3] E.Bien, *Die Pharmacie* **26**,577 (1971)

[4] A.B.Davidov, *Plast.Massy* **6**,71 (1972)

[5] M.G.Voronkov, G.J.Zelchan, E.J.Lukievich, *"Kremnij i zhizn"*, Riga 1978, p.349-355

[6] P.Huber, P.Kochs,.G.Kreis, H.Krohberger, E.Luis, *Int.Ztschr.Lebensmitt.Verf.techn.* **1**,(1984)

[7] J.C.Callandra, M.L.Keplinger, E.J.Hobbs, L.J.Tyler, *Polym.Prep.Am.Chem.Soc.,Div.Polym.Chem.*, **17**, No.1, 12 (1976)

[8] R.N.Meals, F.M.Lewis, *"Silicones"*, Reinhold Publ.Corp.New York 1959

[9] W.Noll, *"Chemie und Technologie der Silicone"*, Verlag Chemie, Weinheim 1960,1968

10) M.V.Sobolevskij, O.A.Musovskaja, G.S.Popieleva, *"Svoistva i oblasti primienienija kremnijorganicheskich produktov"*, Moskwa,1975

11) J.Łukasiak, P.Rościszewski, M.Zielecka, J.Galiński, A.Dorosz, *Abstr.of X^th^ Int.Symp. on Organosilicon.Chem.*,Poznań 1993,p.211-2,

[12] L.Garrido, B.Pfleiderer, M.Popisov, J.L.Ackerman, *Repr.of Massachusetts Gen.Hospital &Harvard Med.School*,1993,p.839-43

[13] R.G.Lehman et al.,*Env.Tox.& Chem.***13**,(7),1061-4, (1994)

[14] P.Rościszewski, S.Iwańska, J.Łukasiak, J.Galiński, A.Dorosz, K.Wiśniewska, M.Szponar, *Industrial Chemistry Research Institute,Annual Report* **'94**, 59 (1994)

[15] P.Rościszewski, S.Iwańska, J.Sołtysiak, M.Cholińska, J.Łukasiak, *„Silicone Containing Polymers"*, The Royal Soc. of Chem. 1995, Spec.Publ. No.166, p.185

[16] A.Dorosz, *Doctors Dissertation,* Medical University of Gdańsk, June 1997 (unpublished)