materials

MDPI

*Supplementary Information*

# Where ppm Quantities of Silsesquioxanes Make a Difference—Silanes and Cage Siloxanes as $TiO_2$ Dispersants and Stabilizers for Pigmented Epoxy Resins

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## Table of contents

## 1. Pictures of the equipment and samples

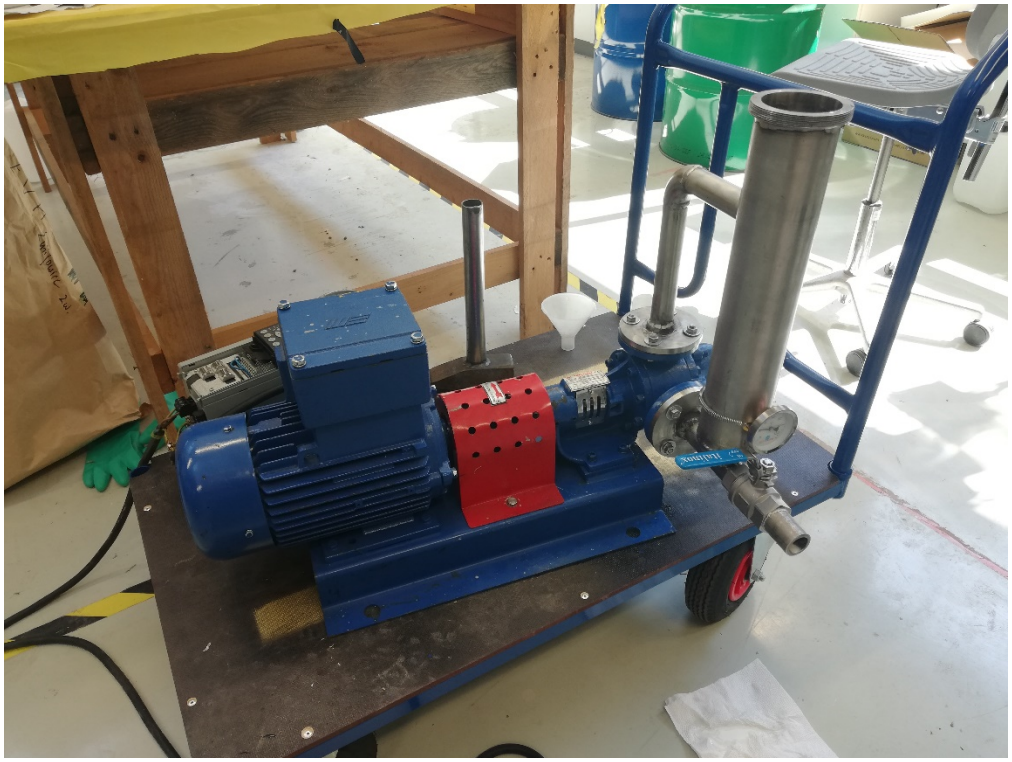


**Figure S1.** Internal gear pump setup used for preparation of $TiO_2$/epoxy dispersions

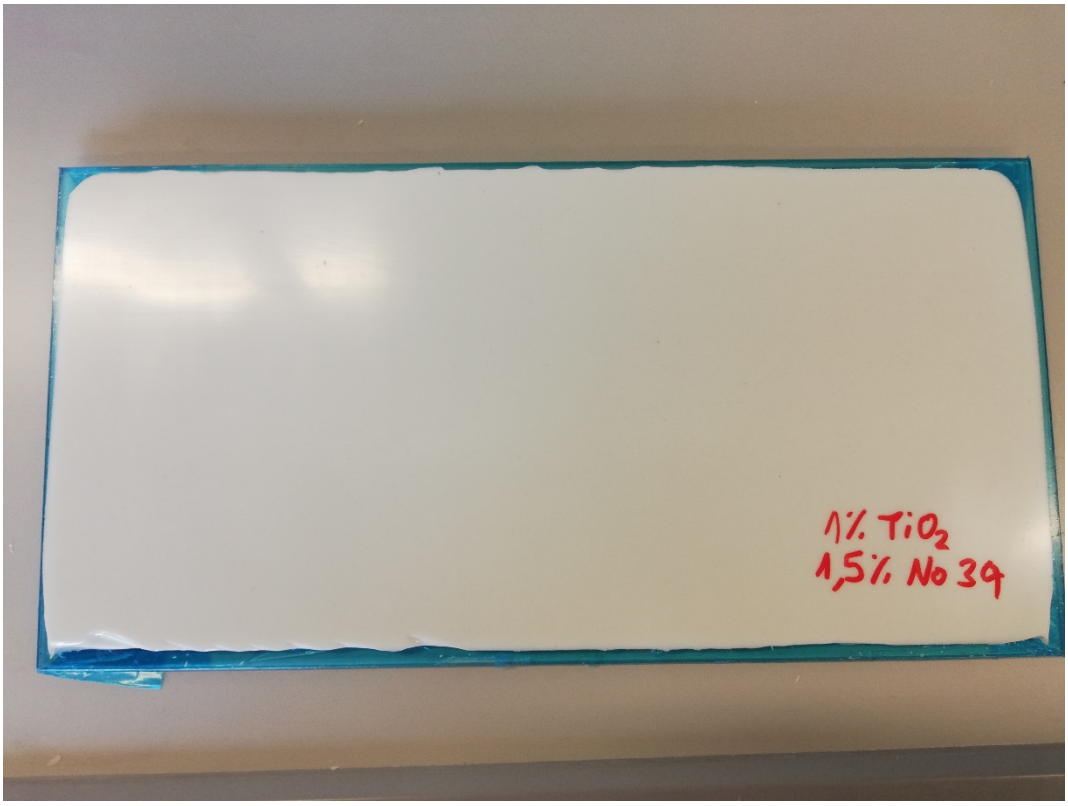
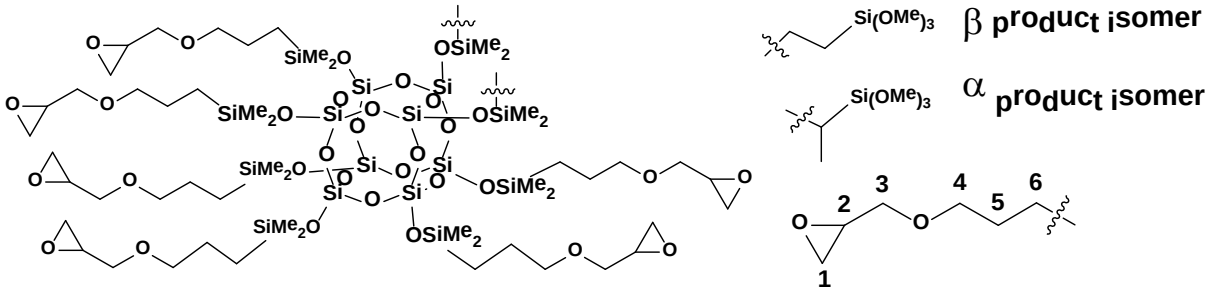



**Figure S2.** A sample of cured $TiO_2$/epoxy composite prepared

## 2. NMR spectroscopy of the obtained compounds

**1,3,5,7,9,11,13,15-hexa((3-glycidoxypropyl)dimethylsiloxy)-di((trimethoxysilyl)dimethylsilloxy) pentacyclo[9.5.1.1$^{3,9}$.1$^{5,15}$.1$^{7,13}$]octasiloxane (SS-6GP-2TMOS)**

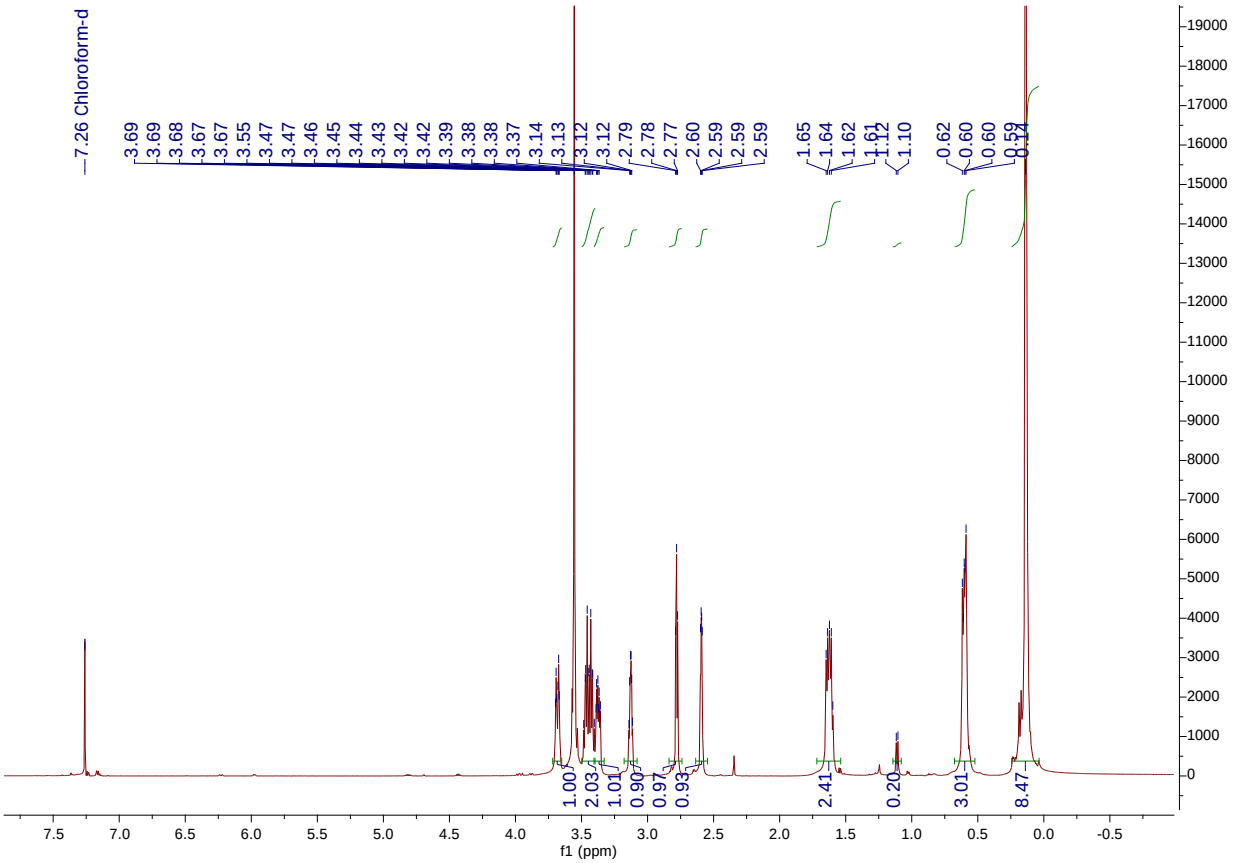



**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.70-3.67 (m, 6H position 3), 3.55 (s, 18H, OMe), 3.48-3.40 (m, 12H, position 4), 3.39-3.36 (m, 6H, position 3), 3.14-3.11 (m, 6H, position 2), 2.79-2.77 (m, 6H, position 1), 2.60-2.59 (m, 6H, position 1), 1.65-1.60 (m, 12H, position 5), 1.11 (d, alpha product -$CH_3$), 0.62-0.59 (m, 20H, Si$CH_2CH_2$Si, position 6), 0.14 (s, 48H, $SiMe_2$); ***α*** and **β** isomers were obseved in 8 : 92 ratio;

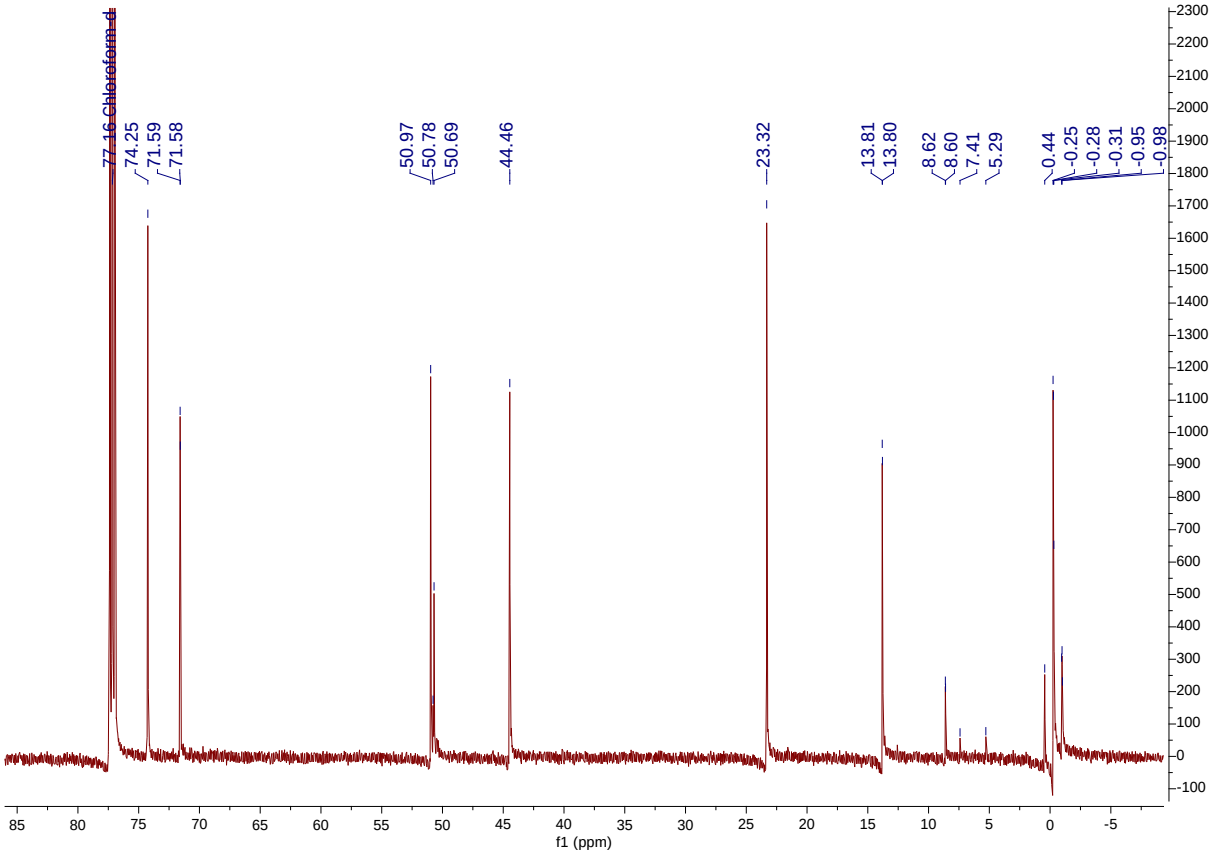
**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 74.25, 71.59, 71.58 (glycidoxy group), 50.97, 50.78, 50.69 (OMe), 44.46 (propyl-3-$CH_2$), 23.32, 13.81, 13.80 (propyl-1 and propyl-2-$CH_2$), 8.62, 8.60 (Si-$CH_2CH_2$-Si), 7.41, 5.29 (Si$CH(CH_3)$Si), 0.44 (Si-$CH_2CH_2$-Si), -0.25, -0.28, -0.31 (glycidoxypropyl $SiMe_2$), -0.95, -0.98, -1.01 (trimethoxysilylethyl $SiMe_2$);

**$^{29}$Si NMR** (79,5 MHz, $CDCl_3$): δ (ppm) = 13.23-13.18 (Si-trimethoxysilylethyl), 12.97-12.91 (Si-glycidyloxypropyl), -41.67 ($Si(OMe)_3$), -109.09 (core).

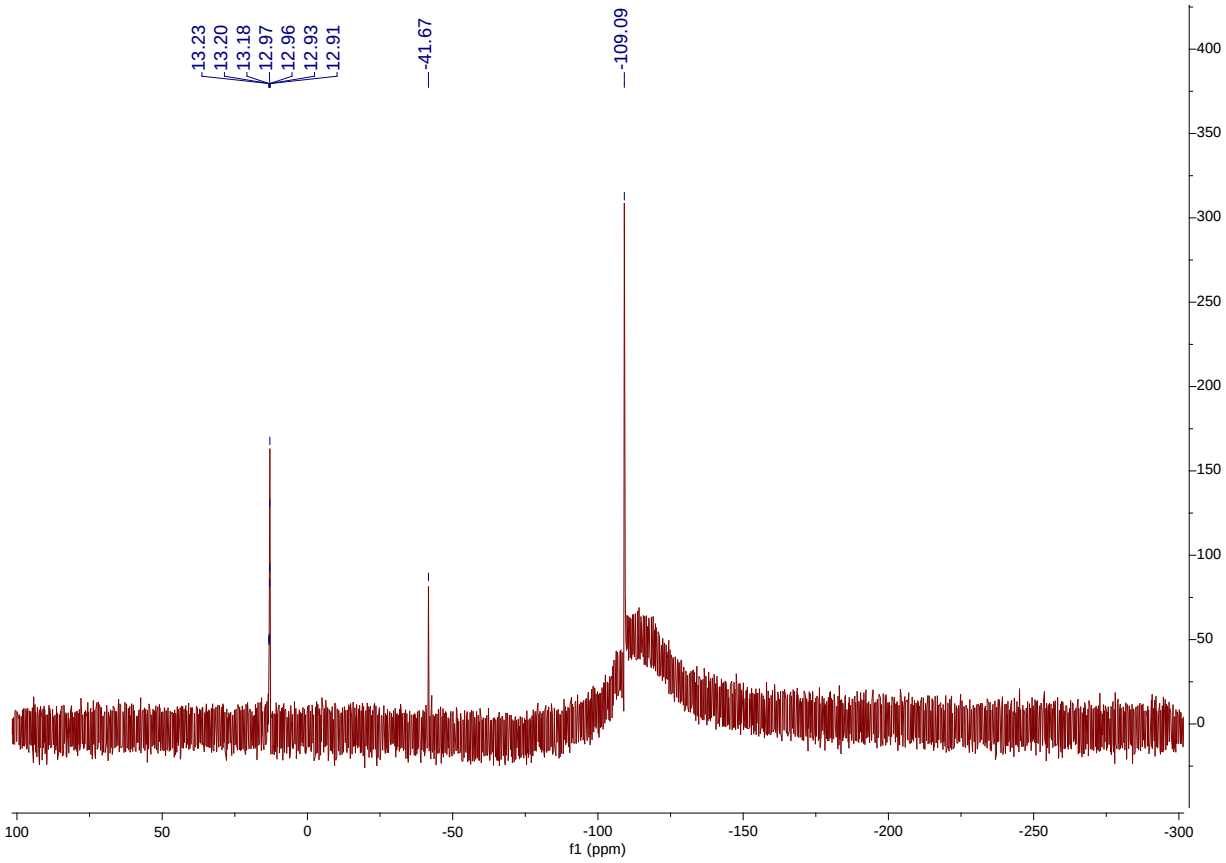
**$^{1}$H NMR**



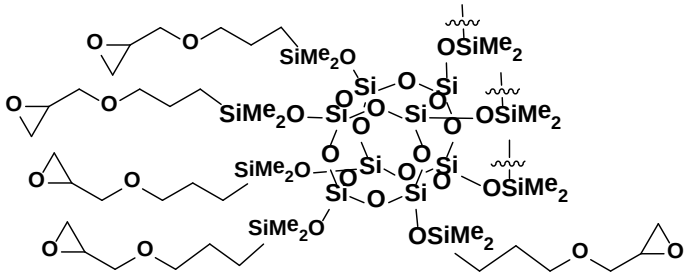
**$^{13}$C NMR**

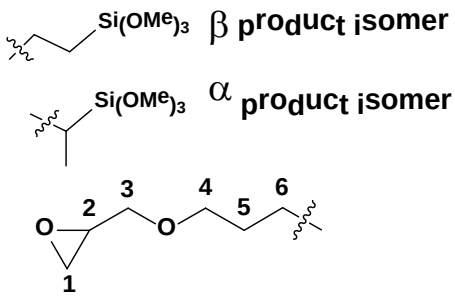



**$^{29}$Si NMR**




**1,3,5,7,9,11,13,15-penta((3-glycidoxypropyl)dimethylsiloxy)-tri((trimethoxysilyl)dimethylsilloxy) pentacyclo[9.5.1.1$^{3,9}$.1$^{5,15}$.1$^{7,13}$]octasiloxane (SS-5GP-3TMOS)**



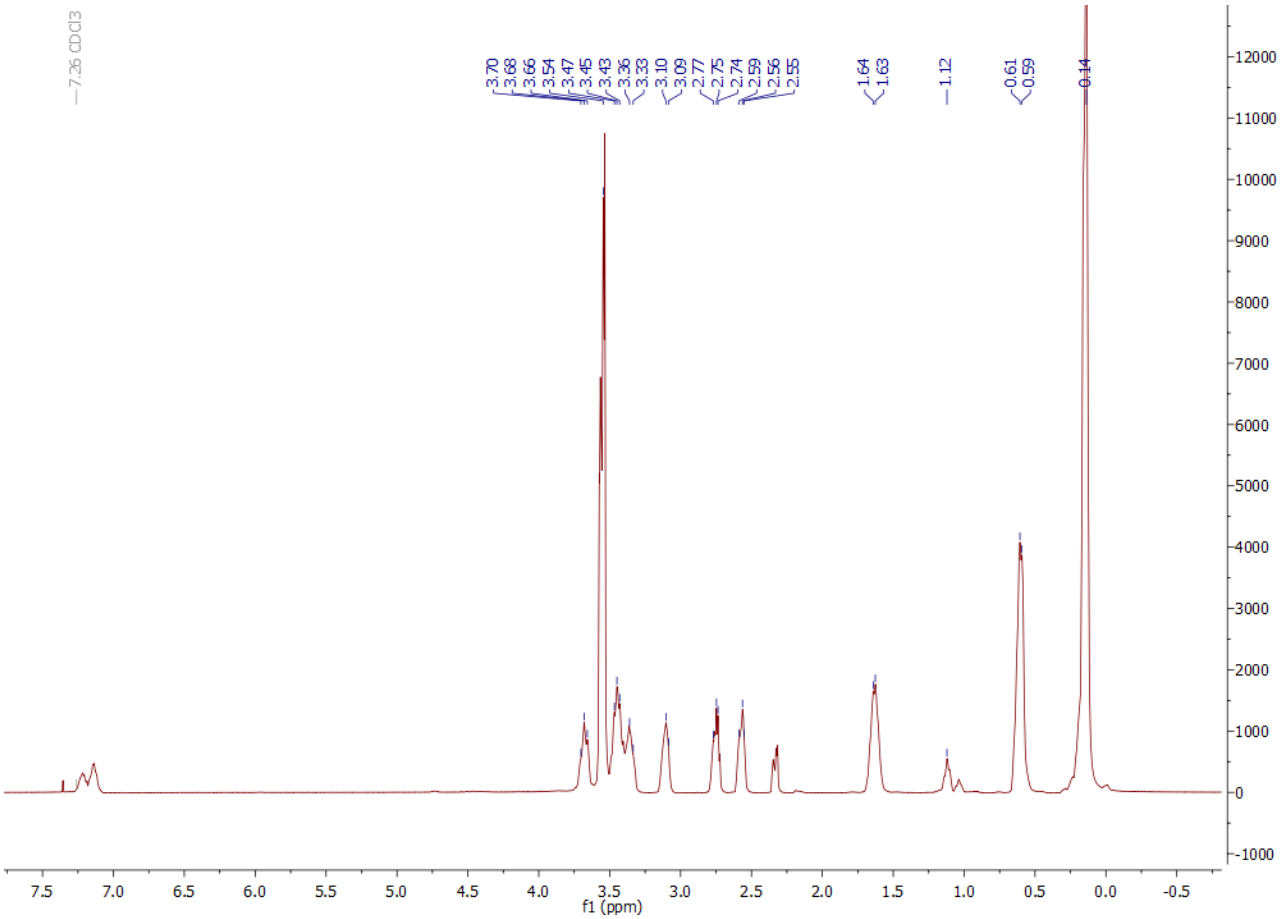




**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.70-3.66 (m, 5H position 3), 3.54 (s, 27H, OMe), 3.47-3.43 (m, 10H, position 4), 3.39-3.33 (m, 5H, position 3), 3.14-3.09 (m, 5H, position 2), 2.77-2.74 (m, 5H, position 1), 2.59-2.55 (m, 5H, position 1), 1.64-1.63 (m, 10H, position 5), 1.12 (d, alpha product -$CH_3$), 0.61-0.59 (m, 22H, Si$CH_2CH_2$Si, position 6), 0.14 (s, 48H, $SiMe_2$); ***α*** and **β** isomers were obseved in 10 : 90 ratio;

**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 73.87, 71.31 (glycidoxy group), 50.61, 50.32 (OMe), 43.99 (propyl-3-$CH_2$), 23.06, 13.55 (propyl-1 and propyl-2-$CH_2$), 8.36 (Si-$CH_2CH_2$-Si), 7.14, 5.01 (Si$CH(CH_3)$Si), 0.17 (Si-$CH_2CH_2$-Si), -0.54, -0.57, -0.61 (glycidoxypropyl $SiMe_2$), -1.24, -1.27 (trimethoxysilylethyl $SiMe_2$);

**$^{29}$Si NMR** (79,5 MHz, $CDCl_3$): δ (ppm) = 13.17-13.13 (Si-trimethoxysilylethyl), 12.92-12.87 (Si-glycidyloxypropyl), -41.87 ($Si(OMe)_3$), -109.12 (core).

**$^{1}$H NMR**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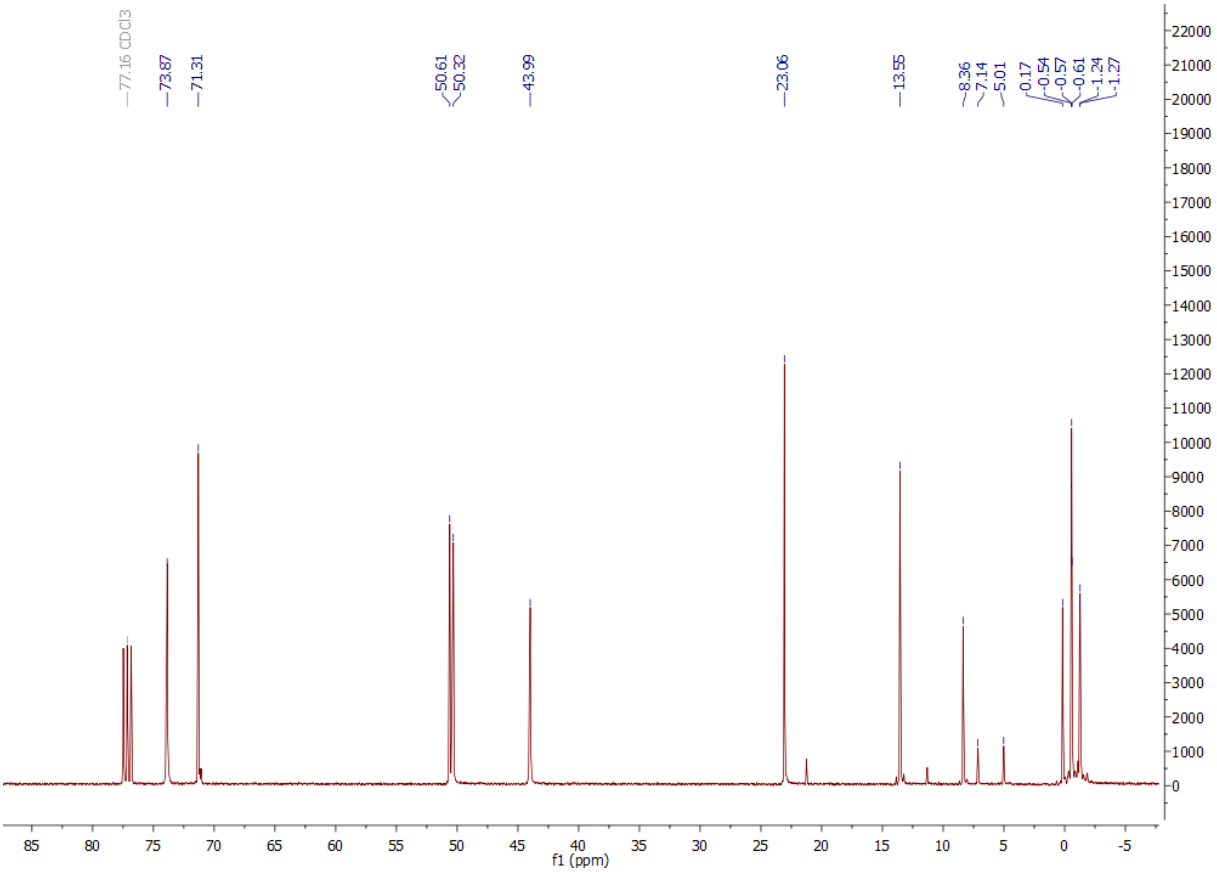
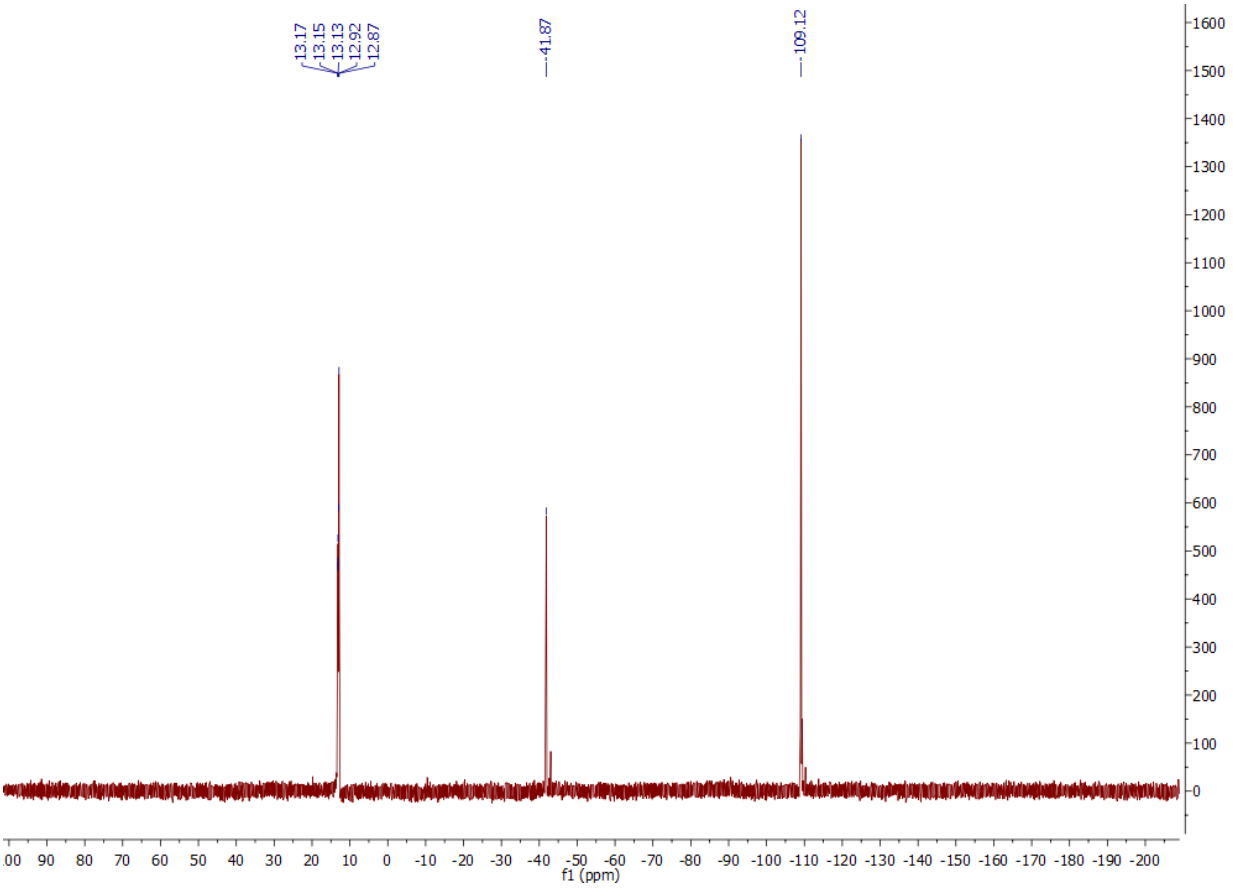
3.66
3.54
3.47
3.45
3.43
3.36
3.33
3.10
3.09
2.77
2.75
2.74
2.59
2.56
2.55
1.64
1.63
1.12
0.61
0.59
0.14
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

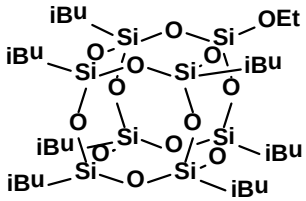
**$^{13}$C NMR**


77.16 CDCl3
73.87
71.31
50.61
50.32
43.99
23.06
13.55
8.36
7.14
5.01
0.17
-0.54
-0.57
-0.61
-1.24
-1.27
f1 (ppm)

**$^{29}$Si NMR**


13.17
13.15
13.13
12.92
12.87
41.87
-109.12
f1 (ppm)

**1-ethoxy-3,5,7,9,11,13,15-heptaisobutylpentacyclo[9.5.1.1$^{3,9}$.1$^{5,15}$.1$^{7,13}$]octasiloxane (iBu$_7$SSQ-OEt)**

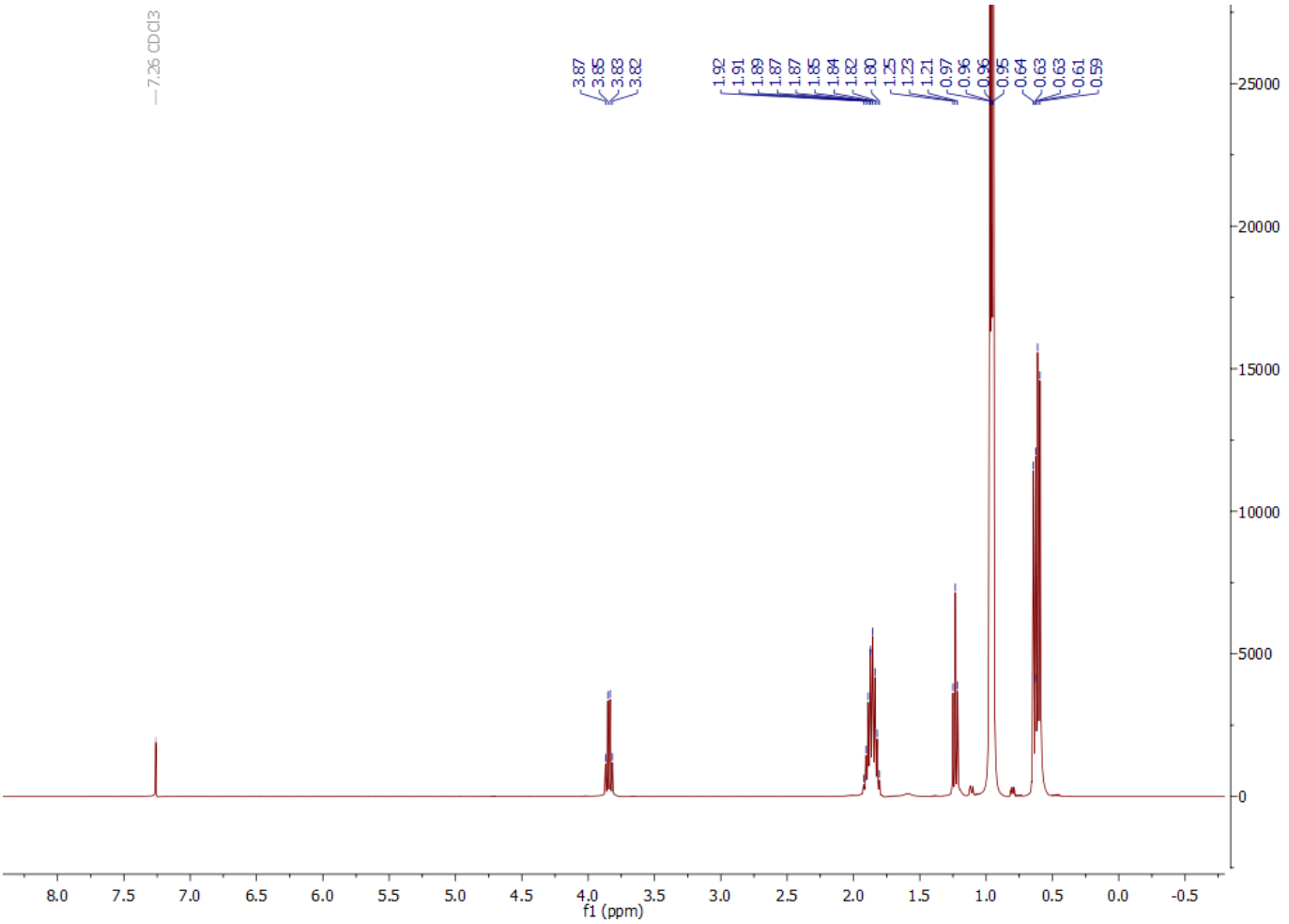



**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.84 (q, J = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$), 1.92-1.80 (m, 7H, iBu), 1.23 (t, J = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 0.97-0.95 (m, 42H, iBu), 0.64-0.59 (m, 14H, iBu);

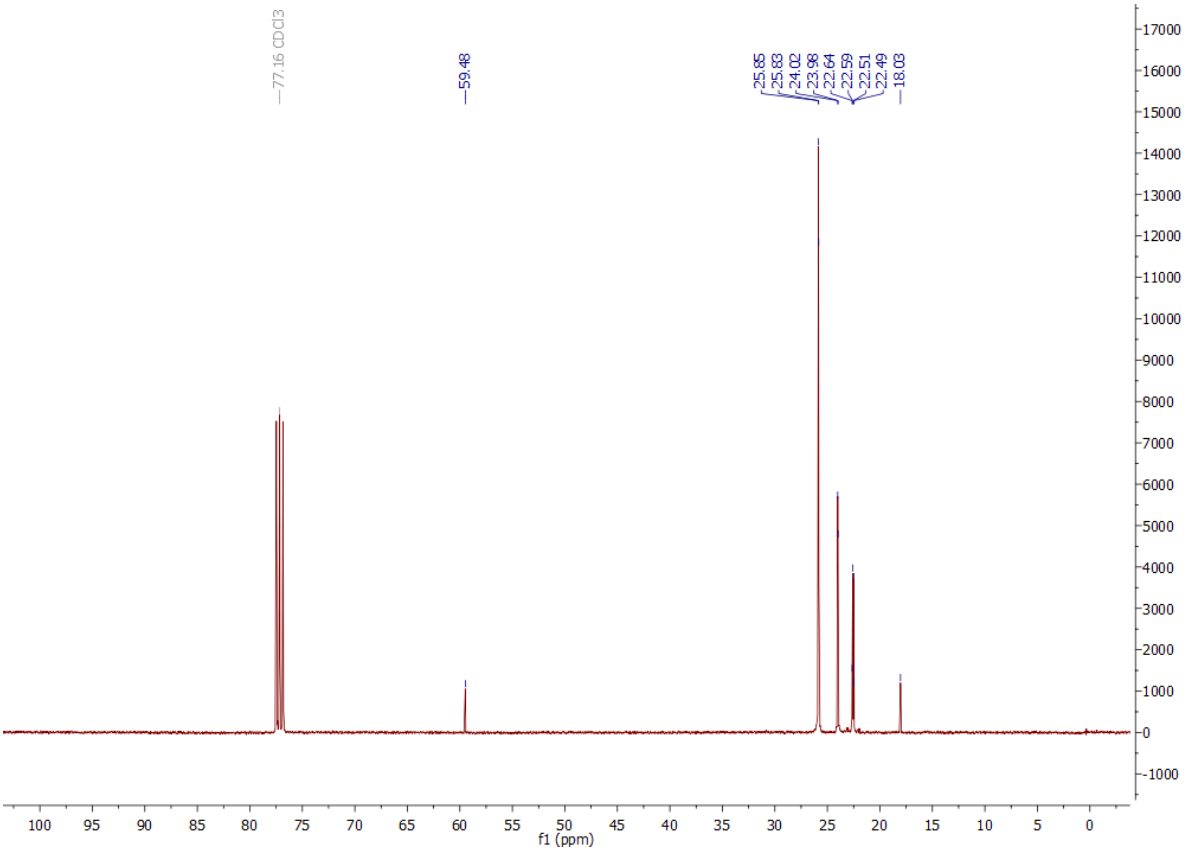
**$^{13}$C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 59.48 ($O\underline{C}H_2CH_3$), 25.85, 25.83, 24.02, 23.98, 22.64, 22.59, 22.51, 22.49 (iBu), 18.03 ($OCH_2\underline{C}H_3$);

**$^{29}$Si NMR** (79,5 MHz, $CDCl_3$): δ (ppm) = -66.71, -66.94, -67.87 (cage), -103.22 (SiOEt).

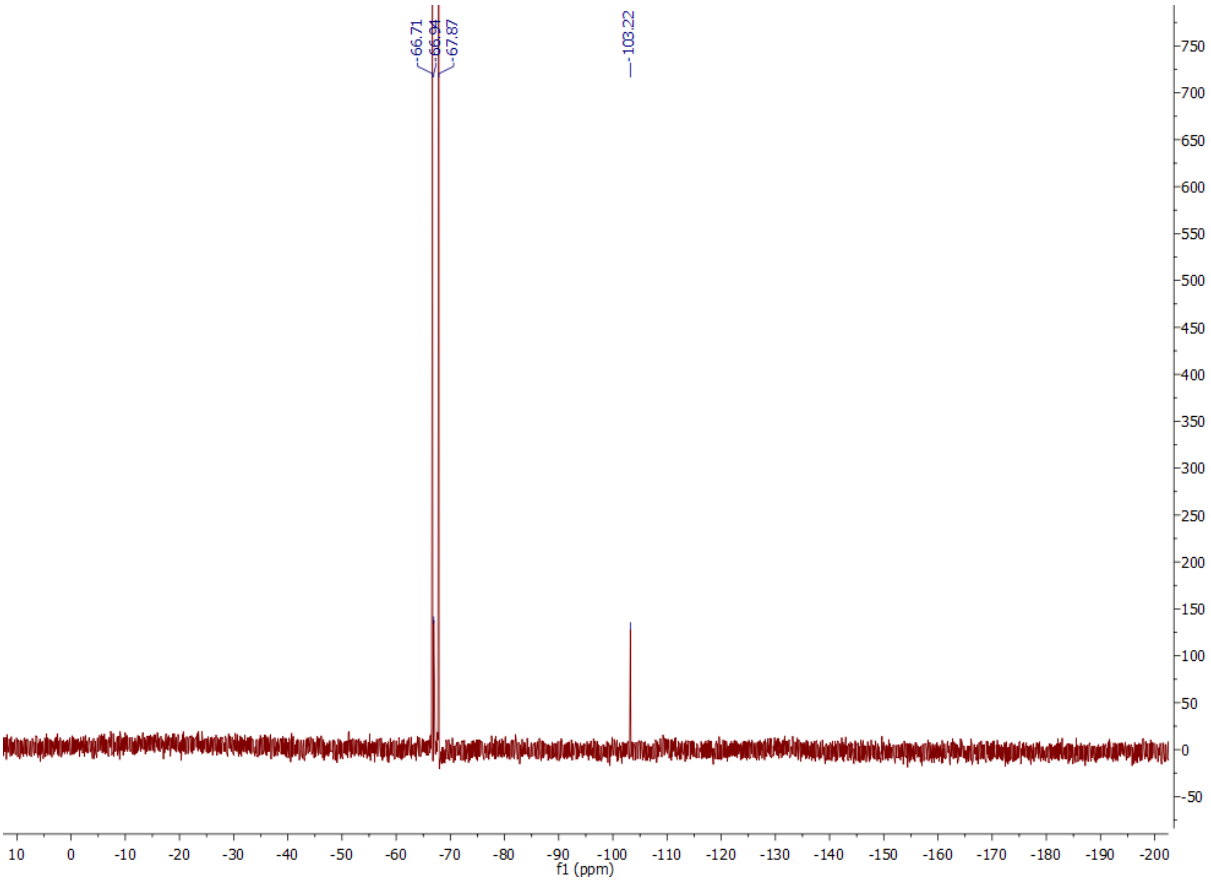
**$^1$H NMR**



**$^{13}$C NMR**

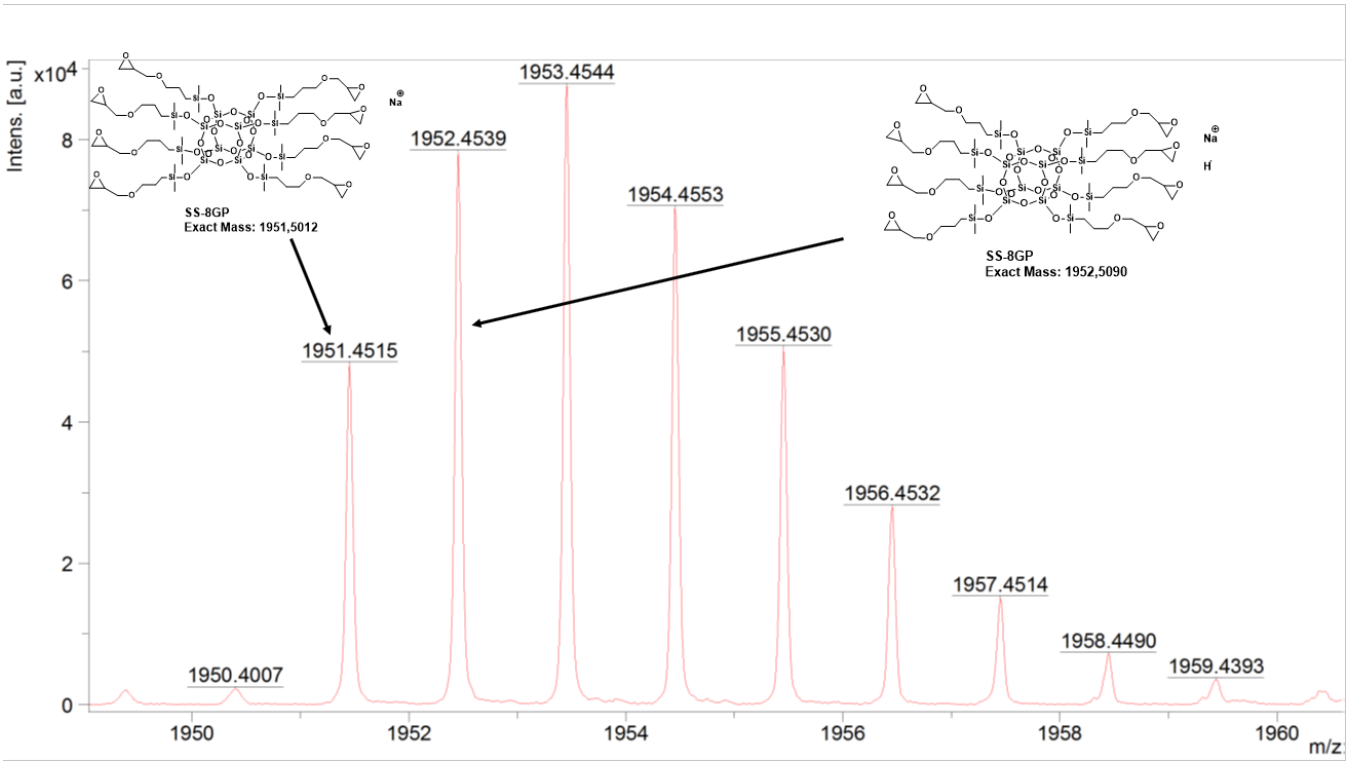


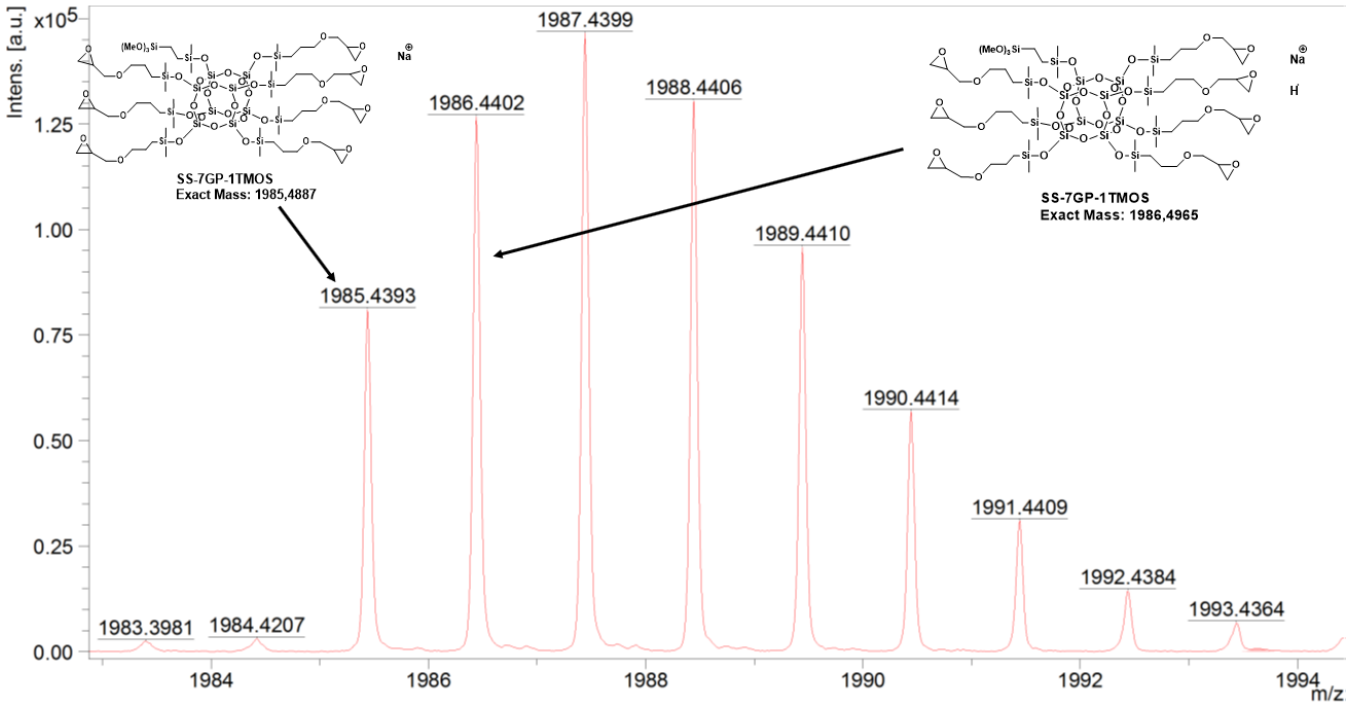

**$^{29}$Si NMR**

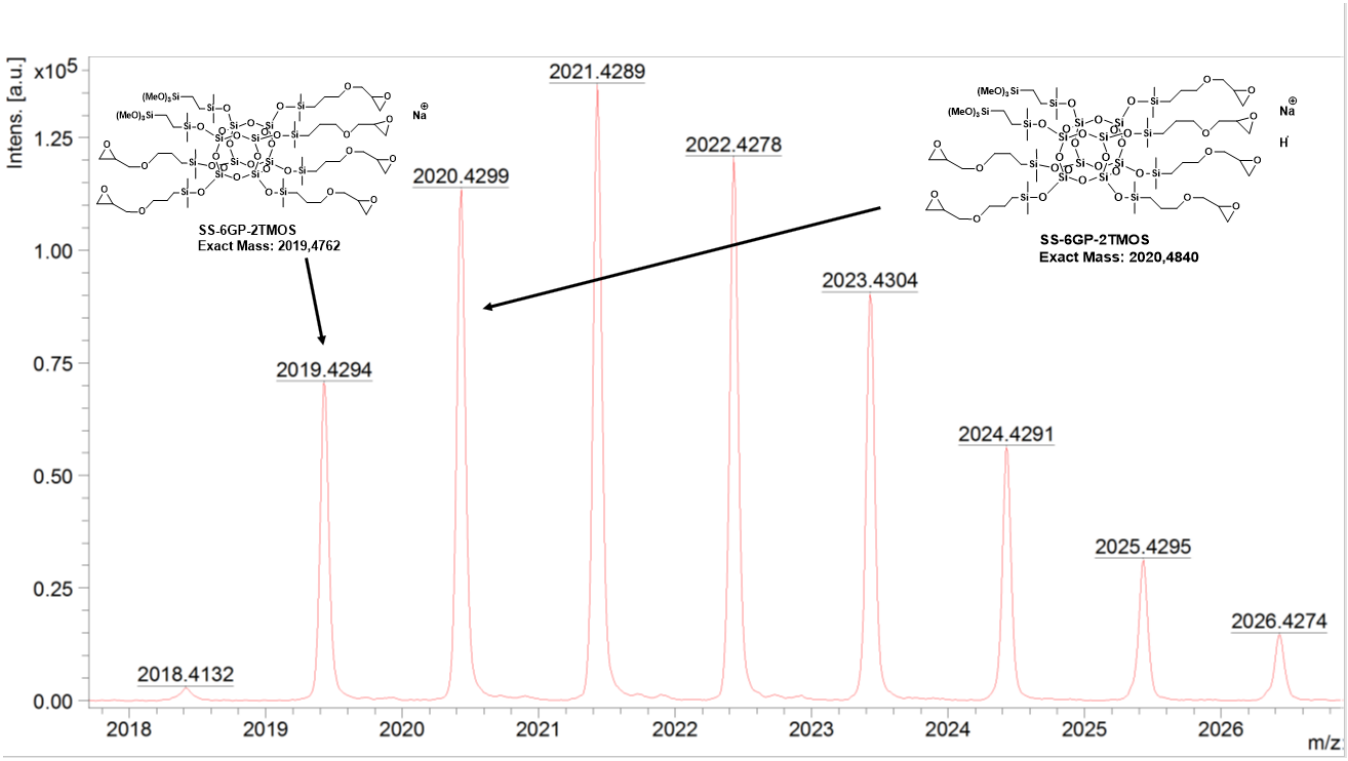


## 3. MALDI-TOF mass spectra of obtained spherosilicate compounds

### SS-6GP-2TMOS

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0.75
0.50
0.25
0.00
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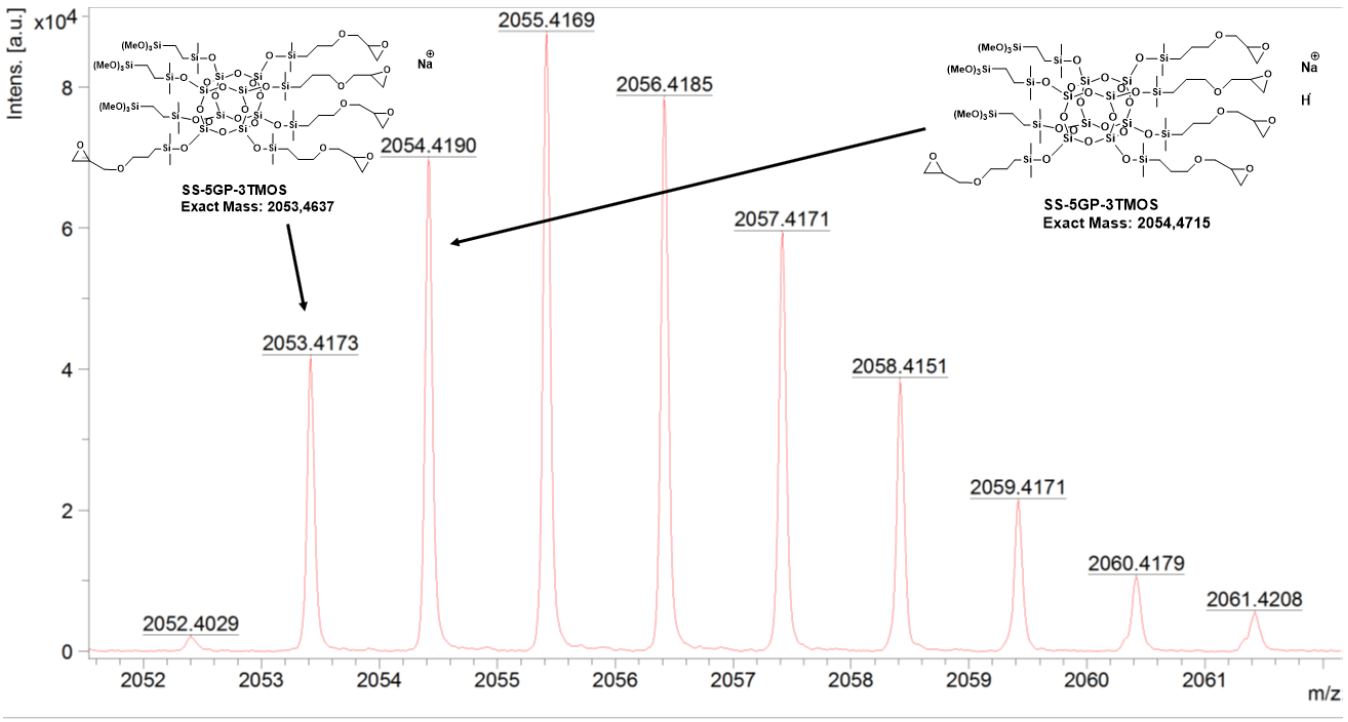
2020.4299
2021.4289
2022.4278
2023.4304
2024.4291
2025.4295
2026.4274
2018
2019
2020
2021
2022
2023
2024
2025
2026
m/z
SS-6GP-2TMOS
Exact Mass: 2019,4762
SS-6GP-2TMOS
Exact Mass: 2020,4840
Na
H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6
4
2
0
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2057.4171
2058.4151
2059.4171
2060.4179
2061.4208
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
m/z
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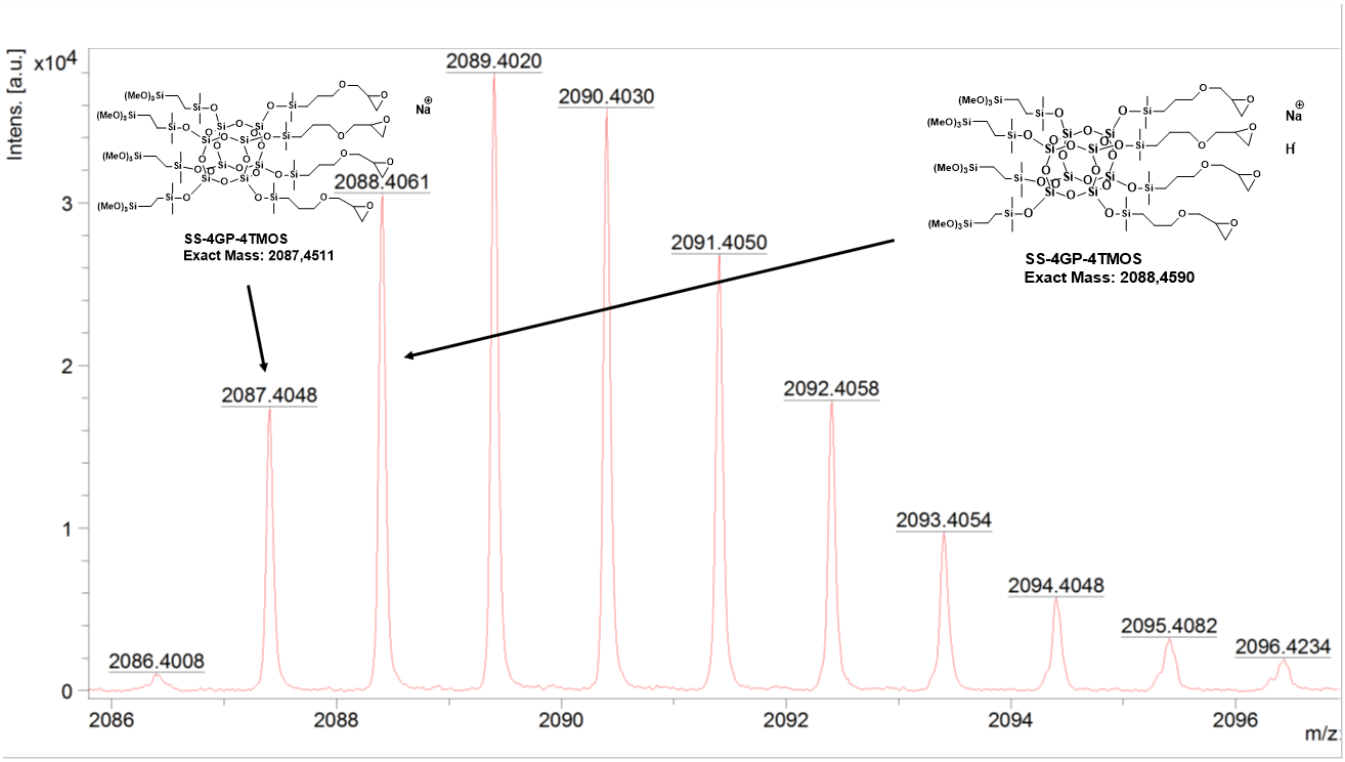
Exact Mass: 2053,4637
SS-5GP-3TMOS
Exact Mass: 2054,4715
Na
H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0
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2092.4058
2093.4054
2094.4048
2095.4082
2096.4234
2086.4008
2086
2088
2090
2092
2094
2096
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Exact Mass: 2088,4590
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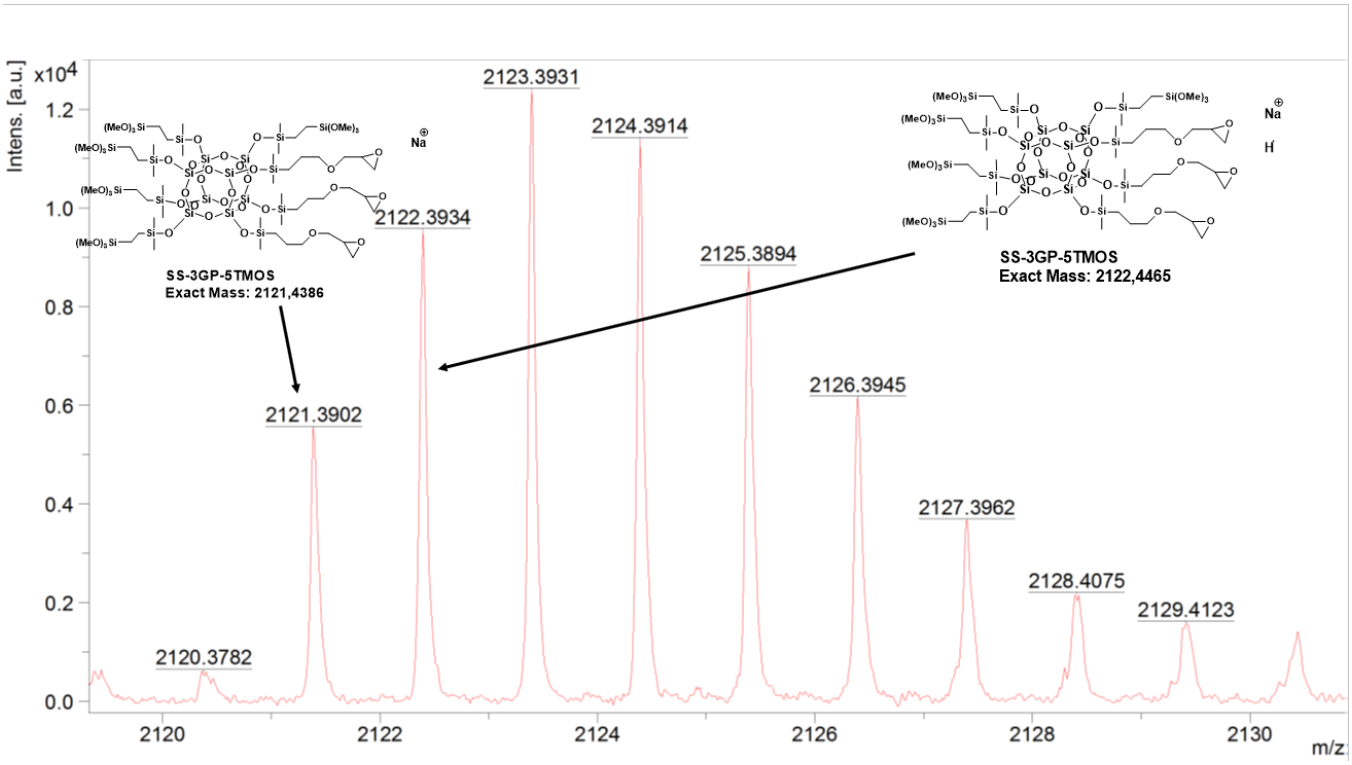
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2122.3934
2125.3894
2126.3945
2121.3902
2127.3962
2128.4075
2129.4123
2120.3782
2120
2122
2124
2126
2128
2130
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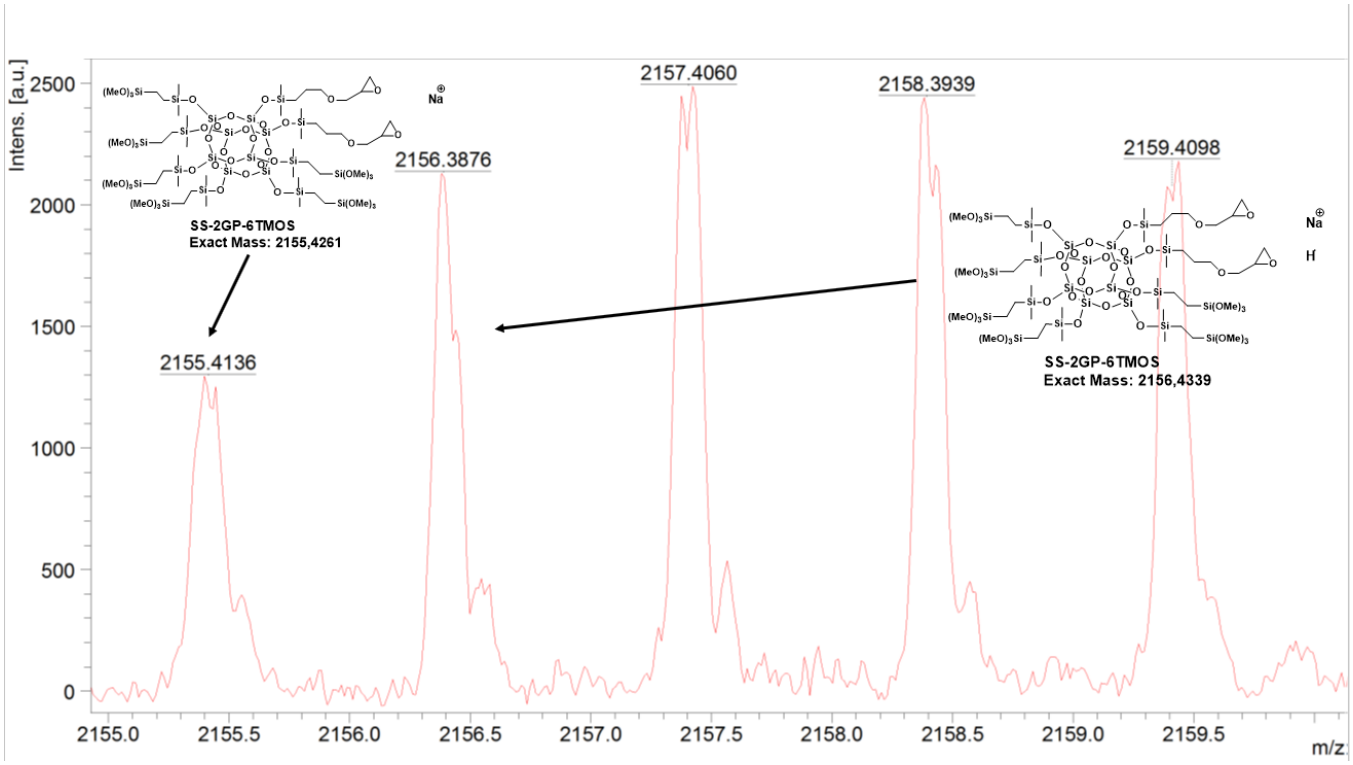
Na
H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1000
500
0
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2156.0
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2157.0
2157.5
2158.0
2158.5
2159.0
2159.5
m/z
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2158.3939
2159.4098
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H
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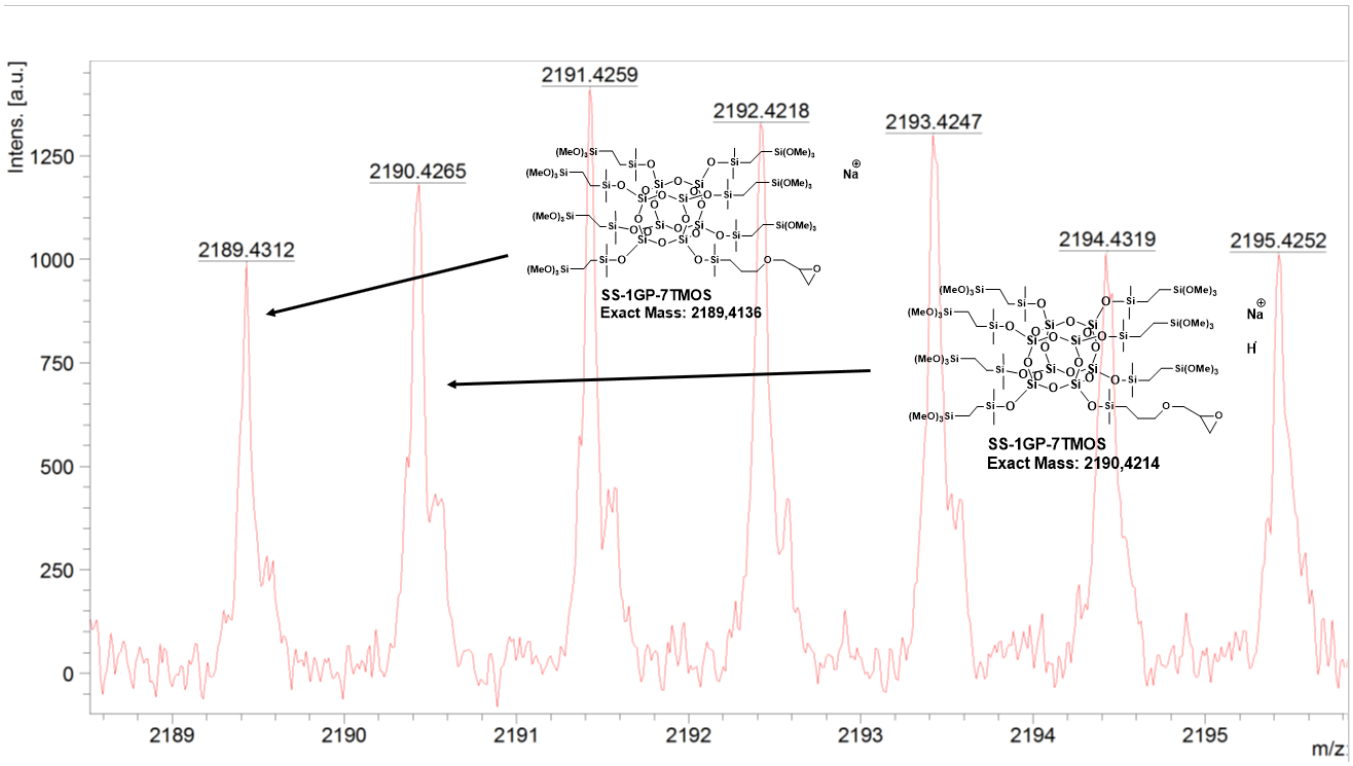
Exact Mass: 2155,4261
SS-2GP-6TMOS
Exact Mass: 2156,4339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m/z
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2190.4265
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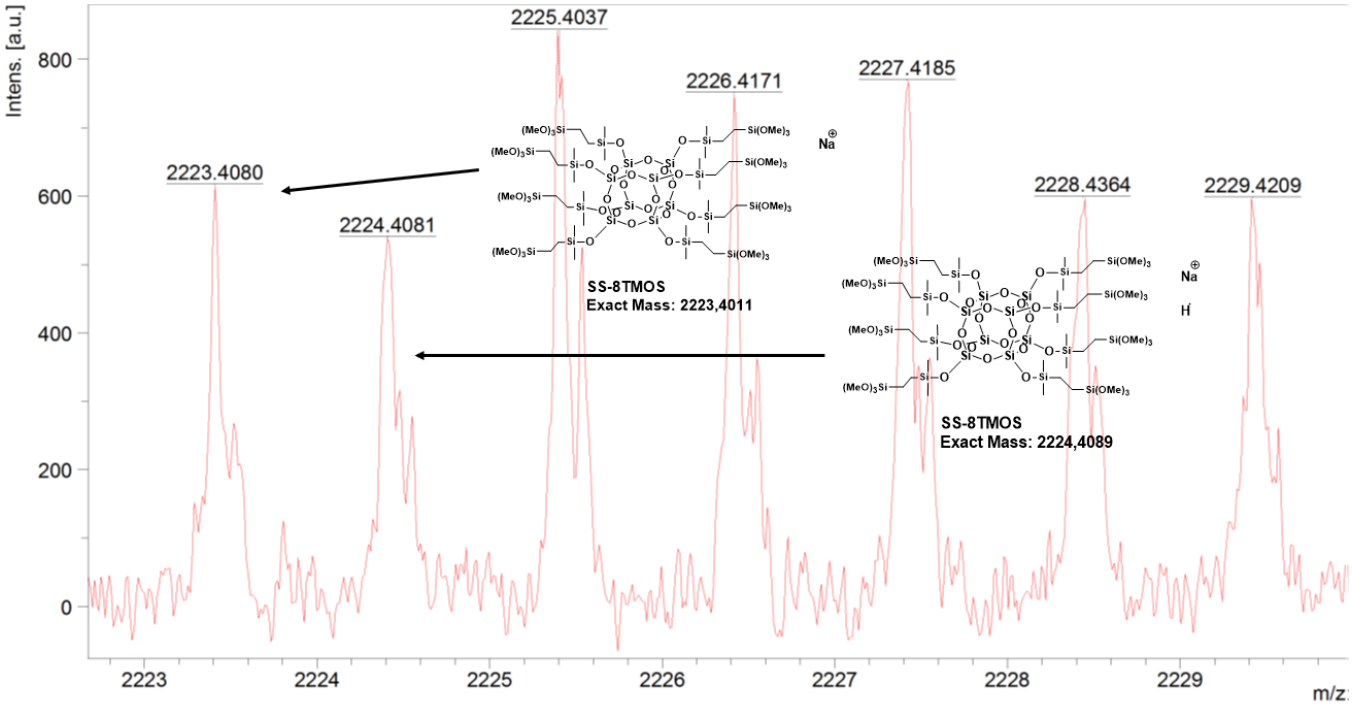
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400
200
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2228.4364
2229.4209
SS-8TMOS
Exact Mass: 2223,4011
SS-8TMOS
Exact Mass: 2224,4089
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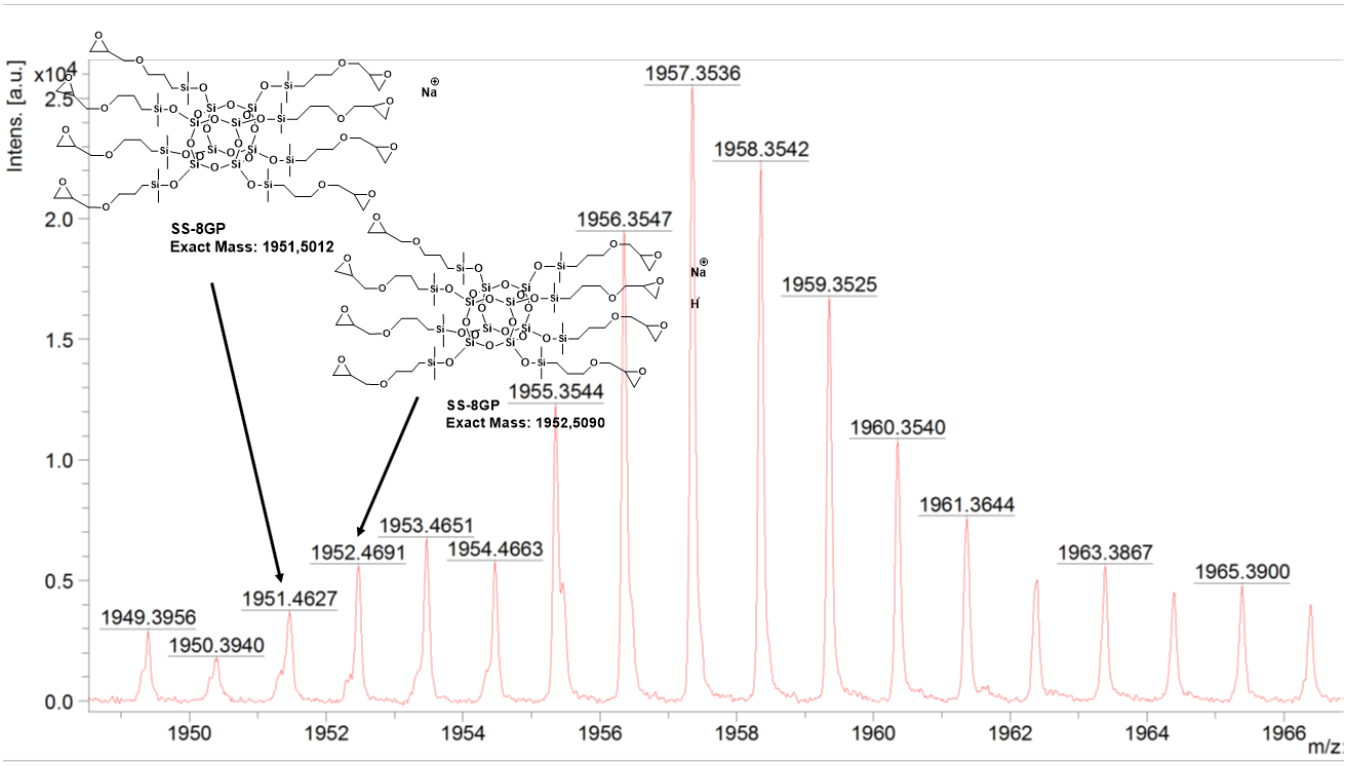
2223
2224
2225
2226
2227
2228
2229
m/z

**SS-5GP-3TMOS**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1.5
1.0
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0.0
SS-8GP
Exact Mass: 1951,5012
SS-8GP
Exact Mass: 1952,5090
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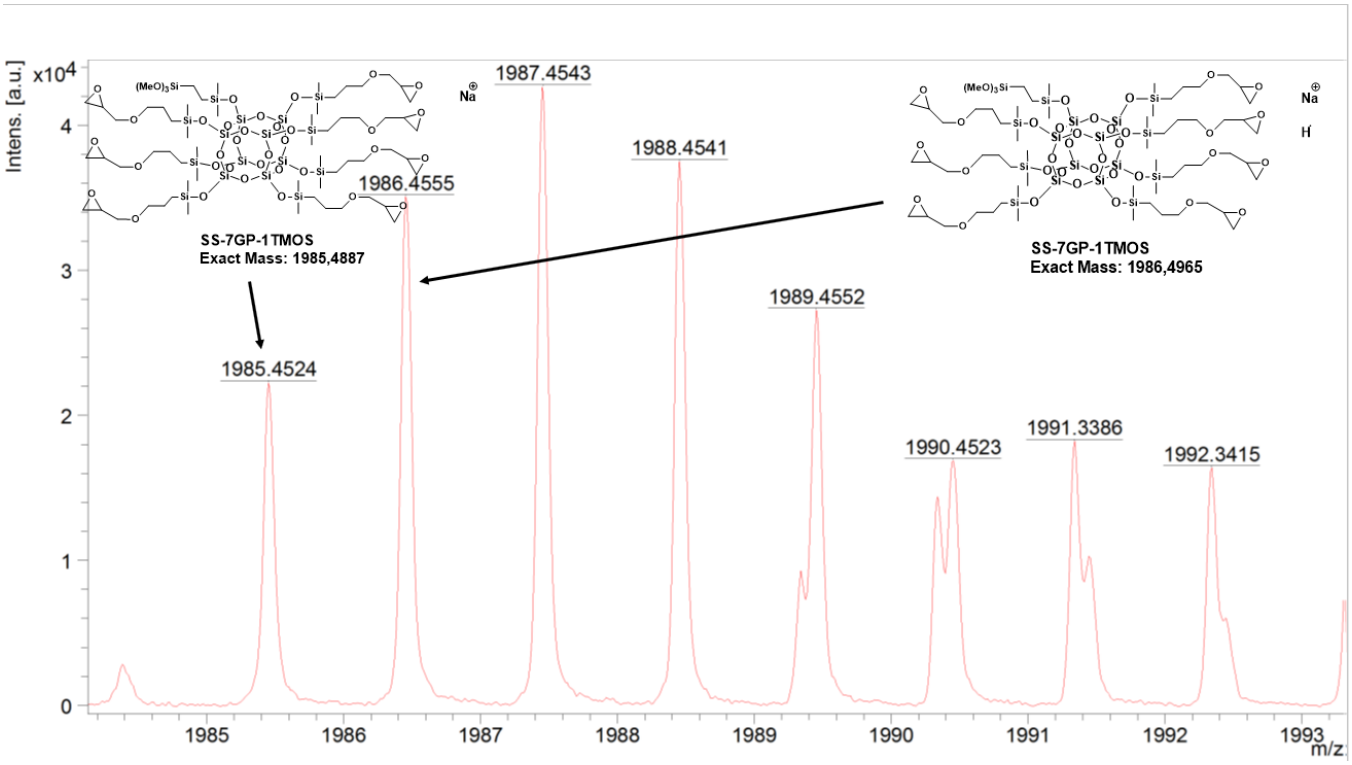
1958.3542
1956.3547
1959.3525
1955.3544
1960.3540
1961.3644
1953.4651
1952.4691
1954.4663
1963.3867
1965.3900
1951.4627
1949.3956
1950.3940
1950
1952
1954
1956
1958
1960
1962
1964
1966
m/z


Intens. [a.u.]
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3
2
1
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SS-7GP-1TMOS
Exact Mass: 1985,4887
SS-7GP-1TMOS
Exact Mass: 1986,4965
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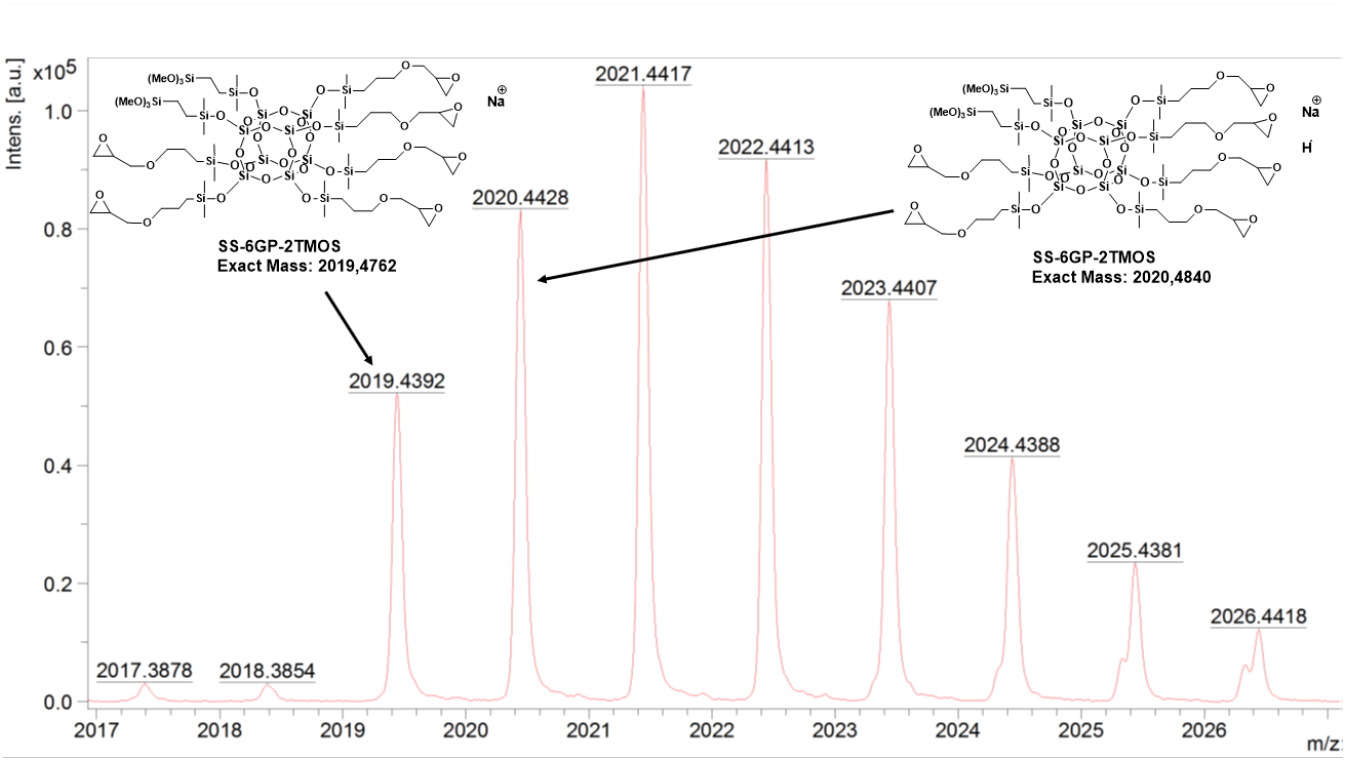
1988.4541
1986.4555
1989.4552
1985.4524
1990.4523
1991.3386
1992.3415
1985
1986
1987
1988
1989
1990
1991
1992
1993
m/z


Intens. [a.u.]
x10^5
1.0
0.8
0.6
0.4
0.2
0.0
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
m/z
2017.3878
2018.3854
2019.4392
2020.4428
2021.4417
2022.4413
2023.4407
2024.4388
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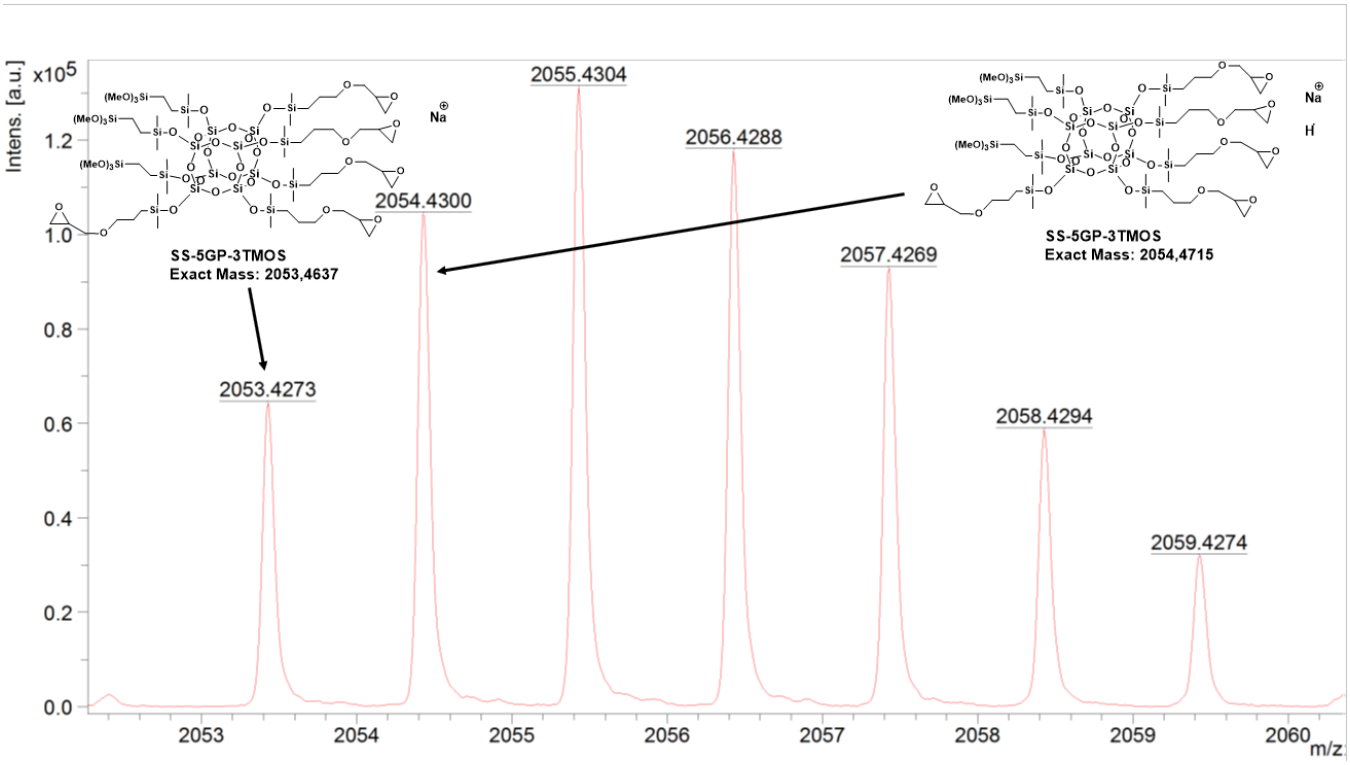
SS-6GP-2TMOS
Exact Mass: 2019,4762
SS-6GP-2TMOS
Exact Mass: 2020,4840
Na
H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1.2
1.0
0.8
0.6
0.4
0.2
0.0
2053
2054
2055
2056
2057
2058
2059
2060
m/z
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SS-5GP-3TMOS
Exact Mass: 2053,4637
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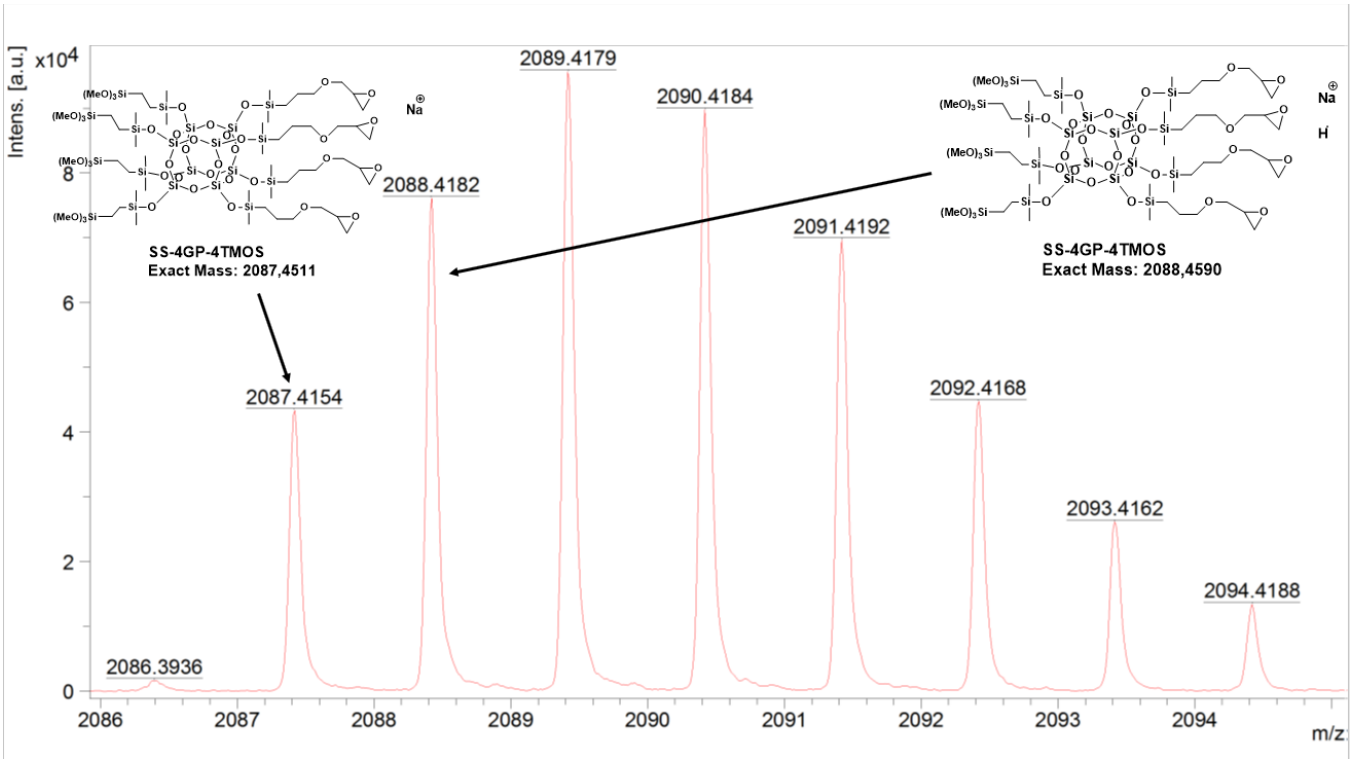
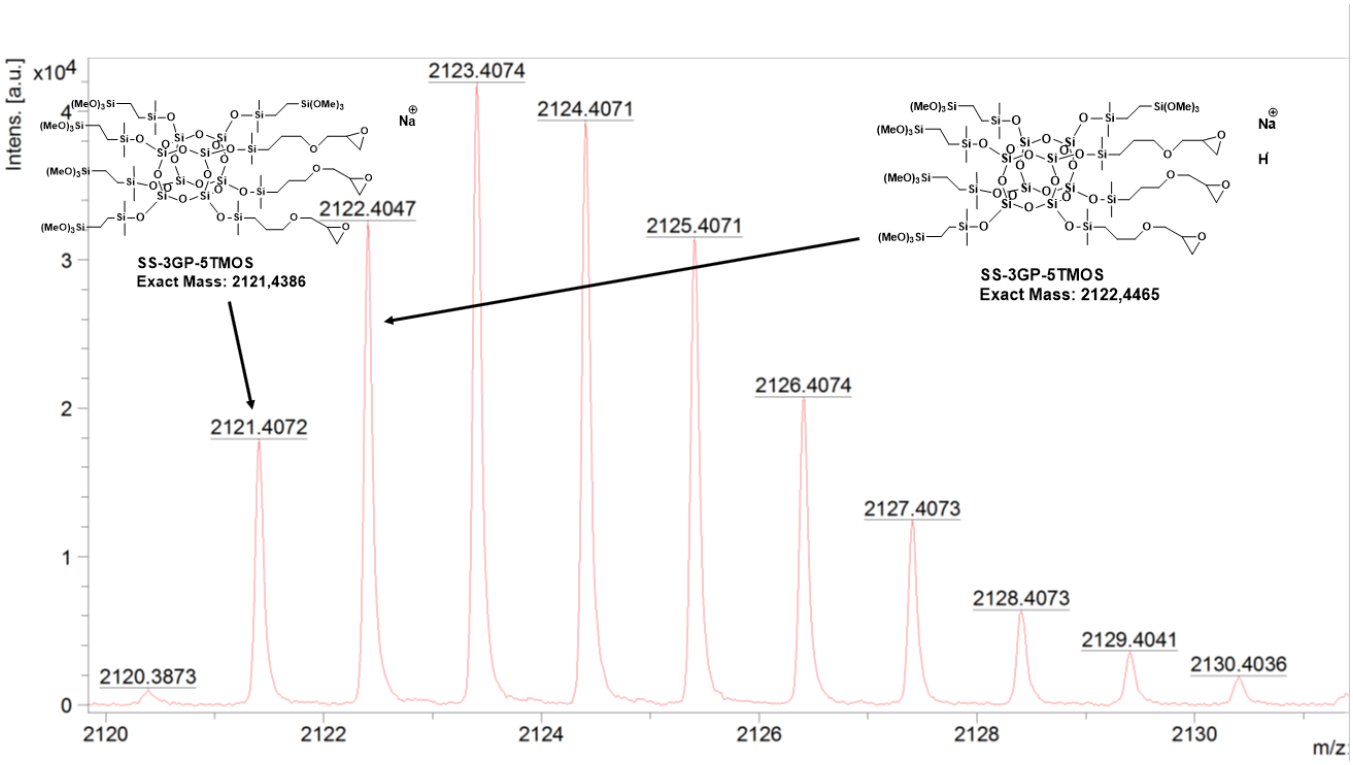
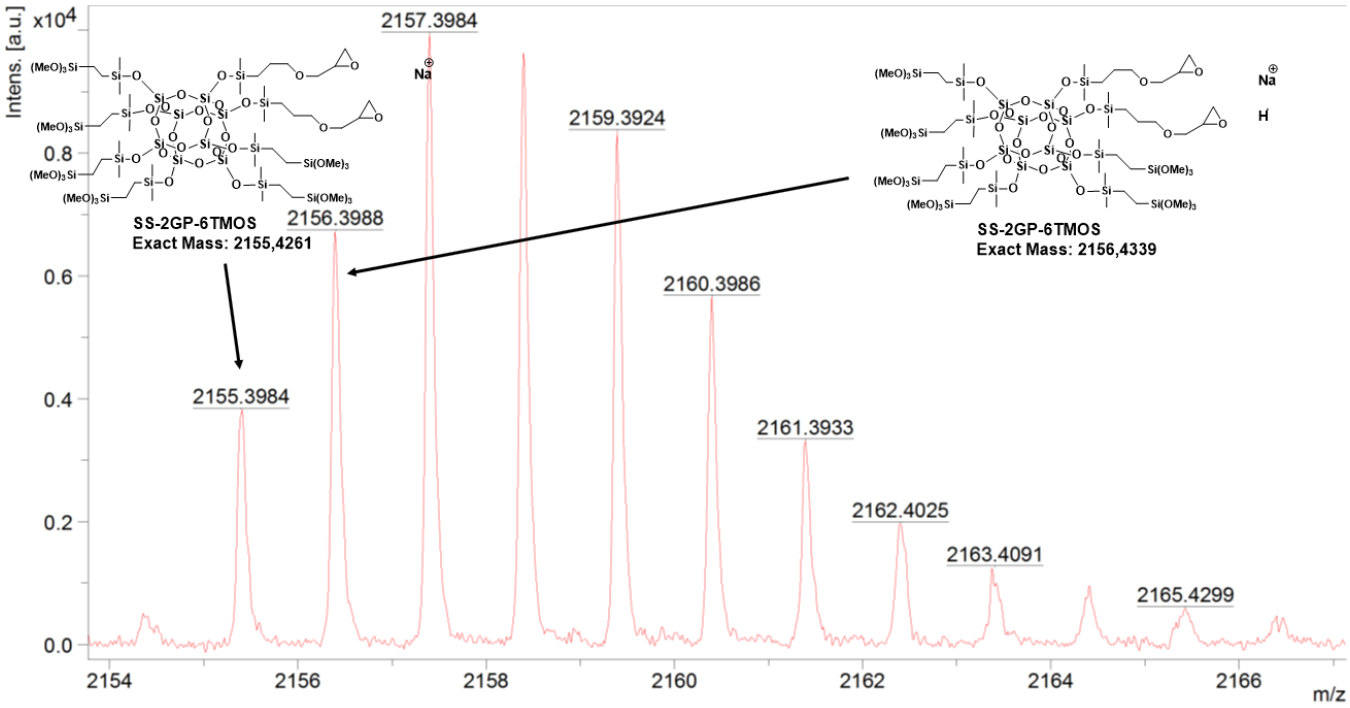
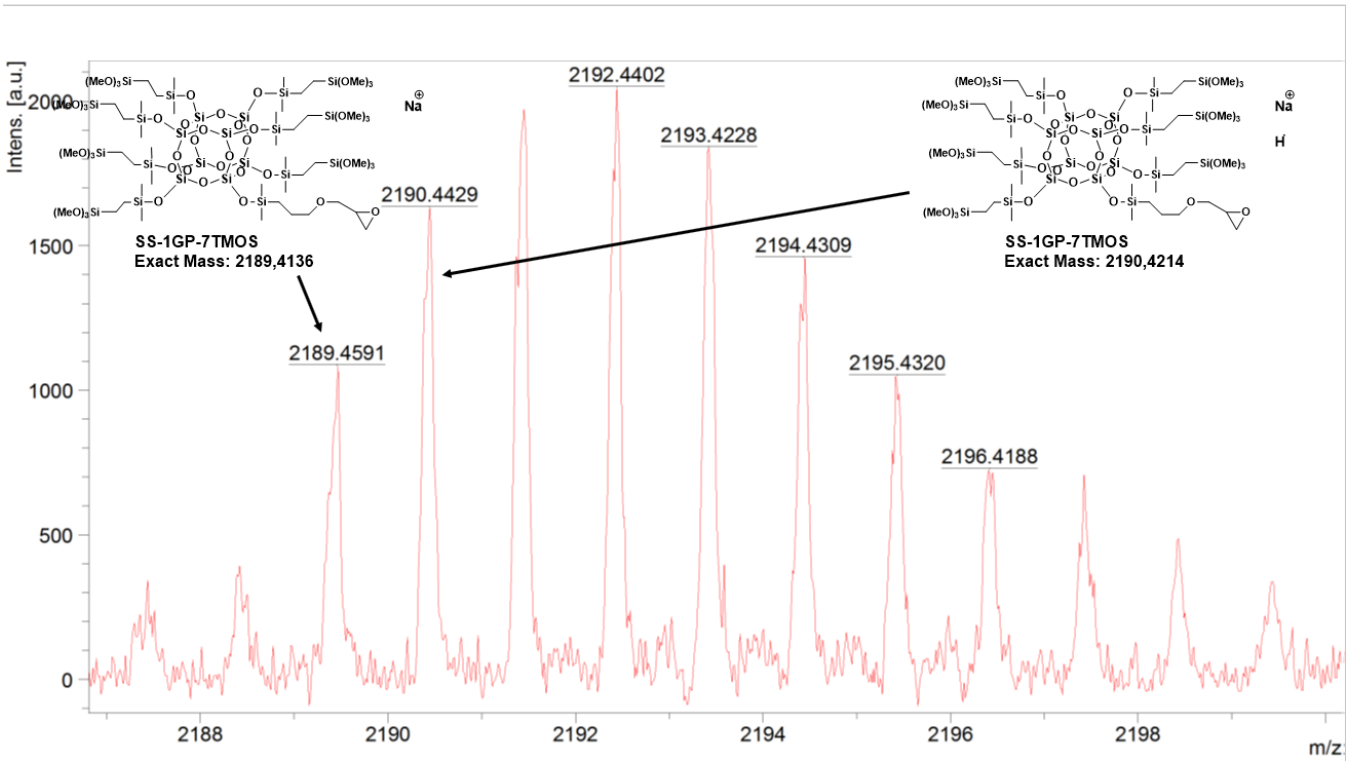
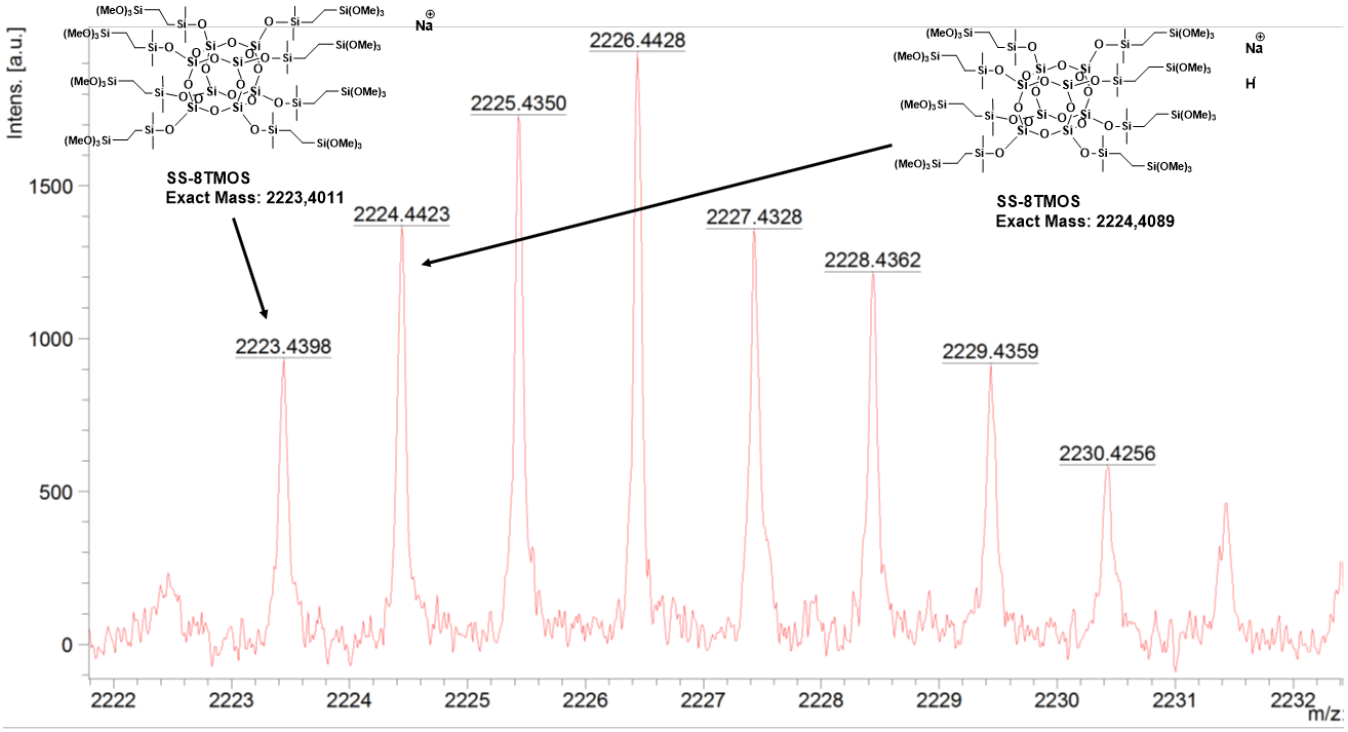
Exact Mass: 2054,4715
Na
H


Intens. [a.u.]
x10^4
2089.4179
2090.4184
2088.4182
2091.4192
2087.4154
2092.4168
2093.4162
2094.4188
2086.3936
SS-4GP-4TMOS
Exact Mass: 2087,4511
SS-4GP-4TMOS
Exact Mass: 2088,4590
m/z


Intens. [a.u.]
x10^4
2123.4074
2124.4071
2122.4047
2125.4071
2121.4072
2126.4074
2127.4073
2128.4073
2129.4041
2130.4036
2120.3873
SS-3GP-5TMOS
Exact Mass: 2121,4386
SS-3GP-5TMOS
Exact Mass: 2122,4465
m/z

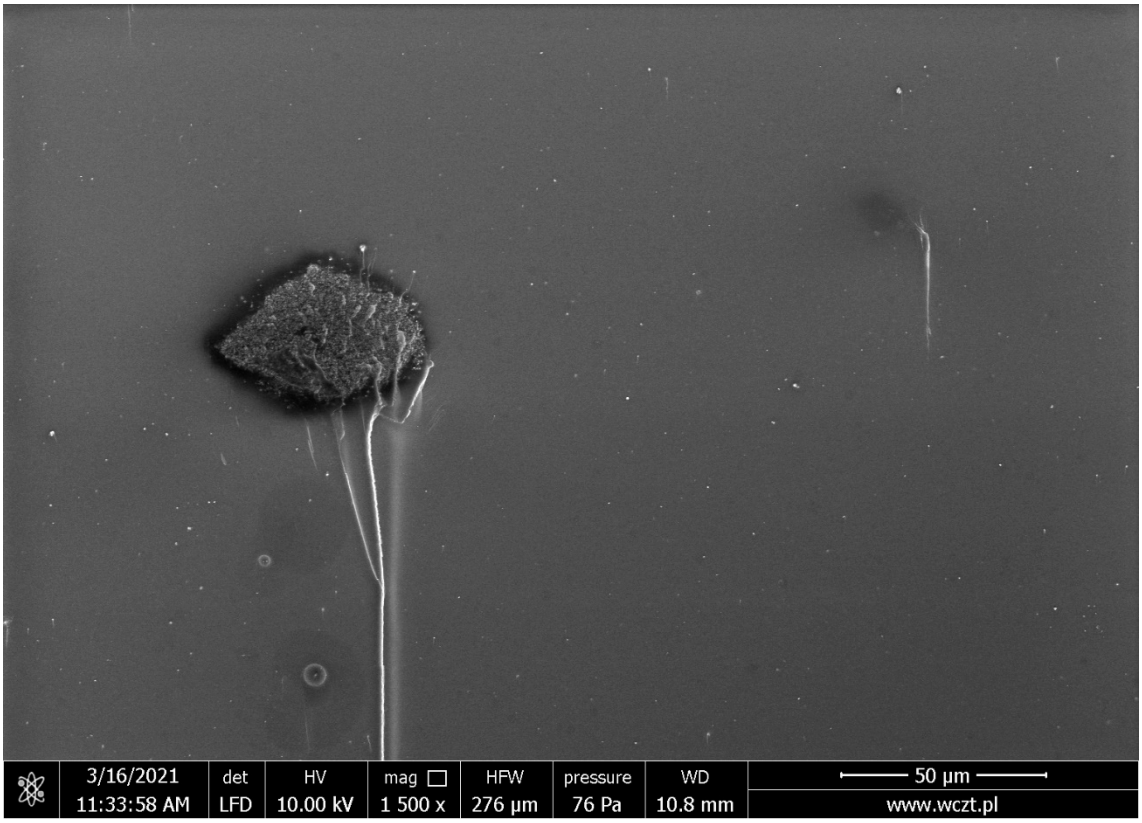

x10^4
Intens. [a.u.]
0.8
0.6
0.4
0.2
0.0
2157.3984
2159.3924
2156.3988
2160.3986
2155.3984
2161.3933
2162.4025
2163.4091
2165.4299
2154
2156
2158
2160
2162
2164
2166
m/z
Na
H
SS-2GP-6TMOS
Exact Mass: 2155,4261
SS-2GP-6TMOS
Exact Mass: 2156,4339

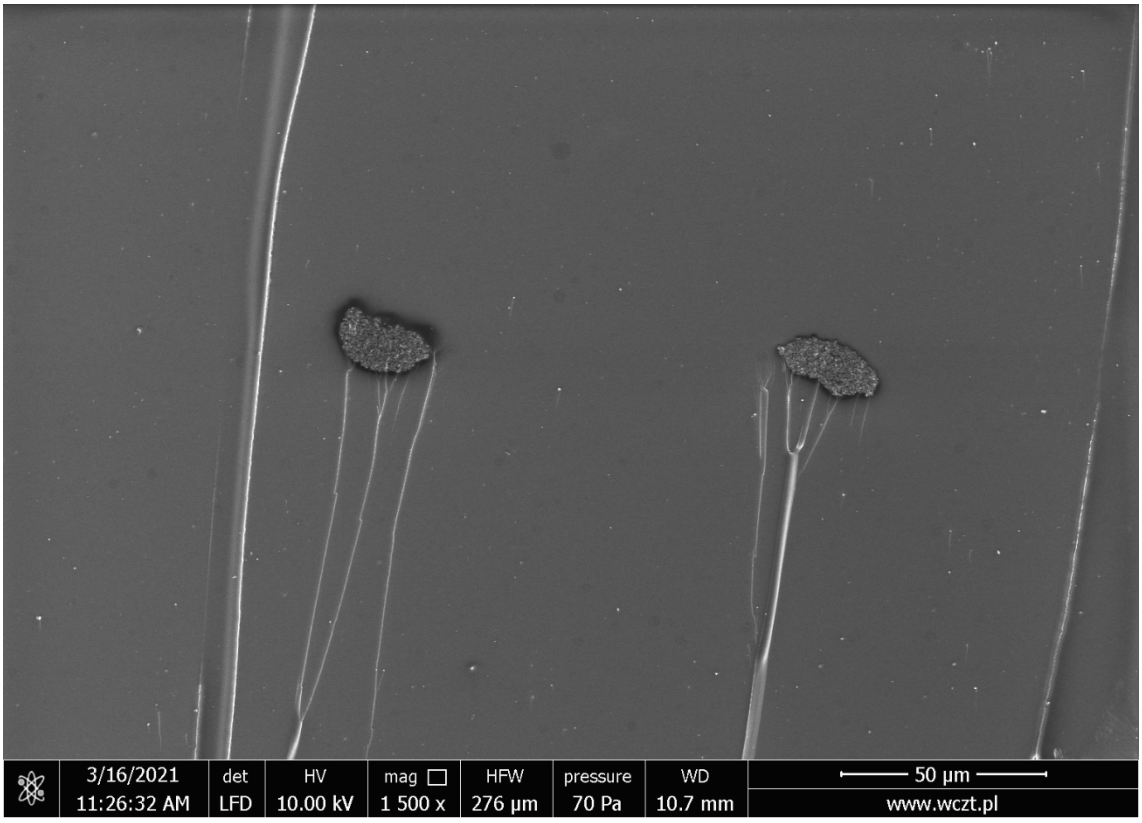

Intens. [a.u.]
2000
1500
1000
500
0
2192.4402
2193.4228
2190.4429
2194.4309
2189.4591
2195.4320
2196.4188
2188
2190
2192
2194
2196
2198
m/z
Na
H
SS-1GP-7TMOS
Exact Mass: 2189,4136
SS-1GP-7TMOS
Exact Mass: 2190,4214

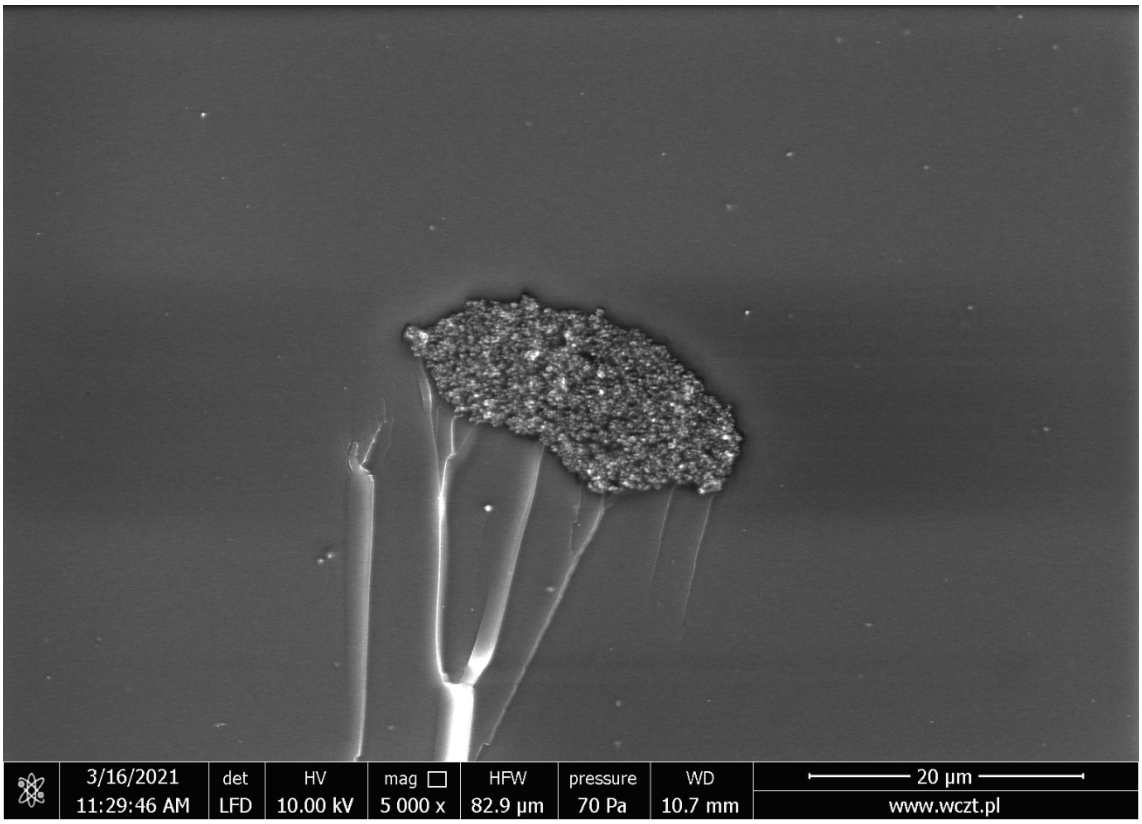

Intens. [a.u.]
1500
1000
500
0
2222
2223
2224
2225
2226
2227
2228
2229
2230
2231
2232
m/z
2223.4398
2224.4423
2225.4350
2226.4428
2227.4328
2228.4362
2229.4359
2230.4256
SS-8TMOS
Exact Mass: 2223,4011
SS-8TMOS
Exact Mass: 2224,4089
Na
H

## 4. SEM images of the $TiO_2$/EP composites

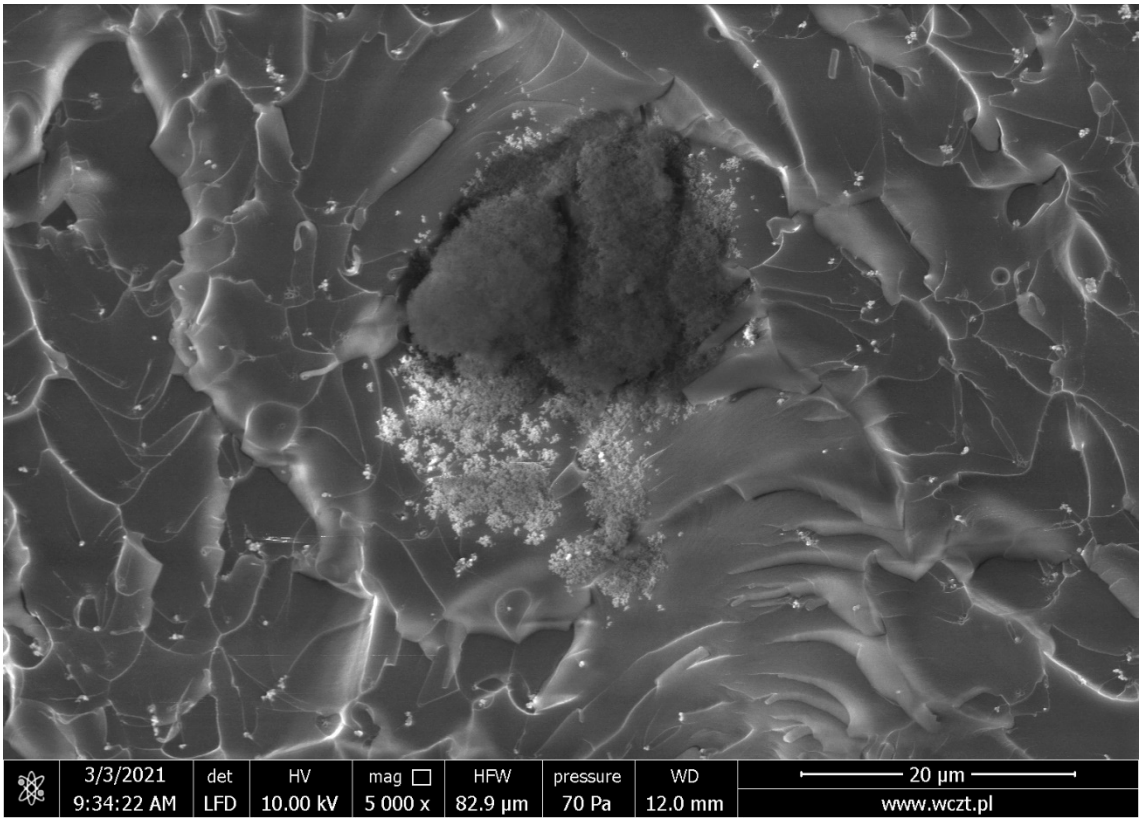
### 1% $TiO_2$, unmodified, mechanical stirrer

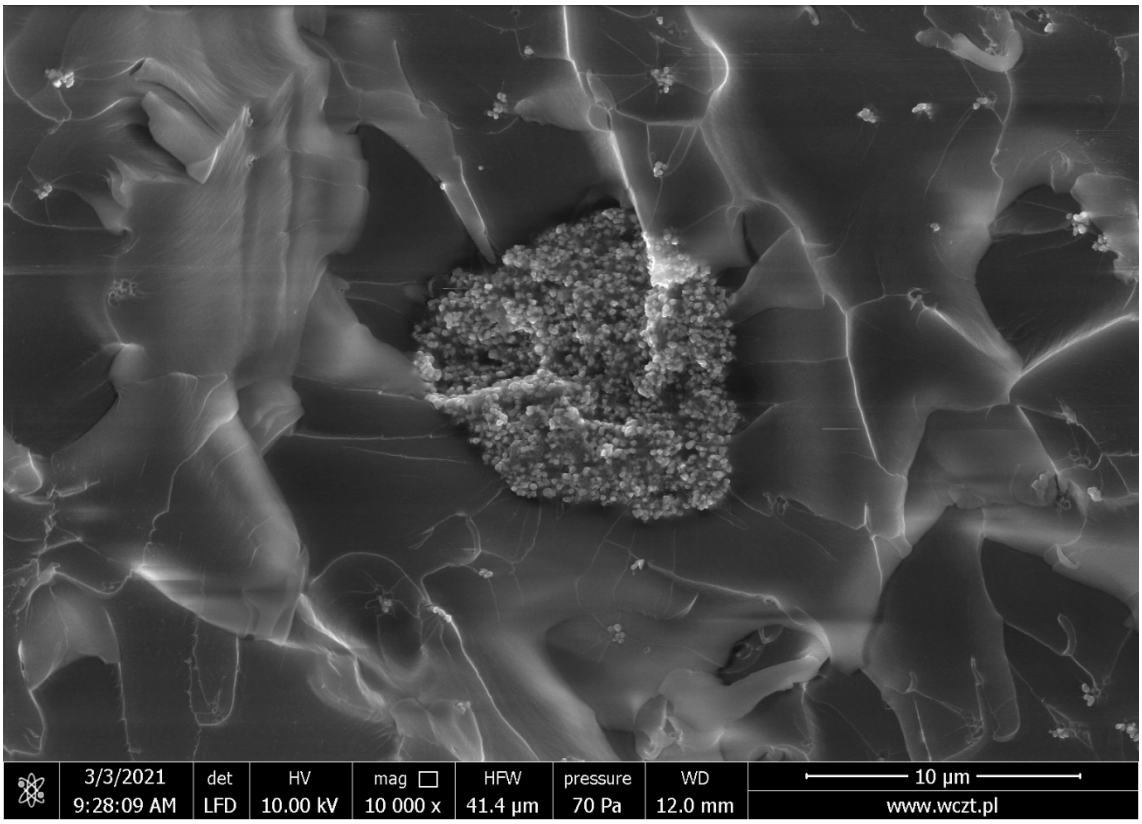


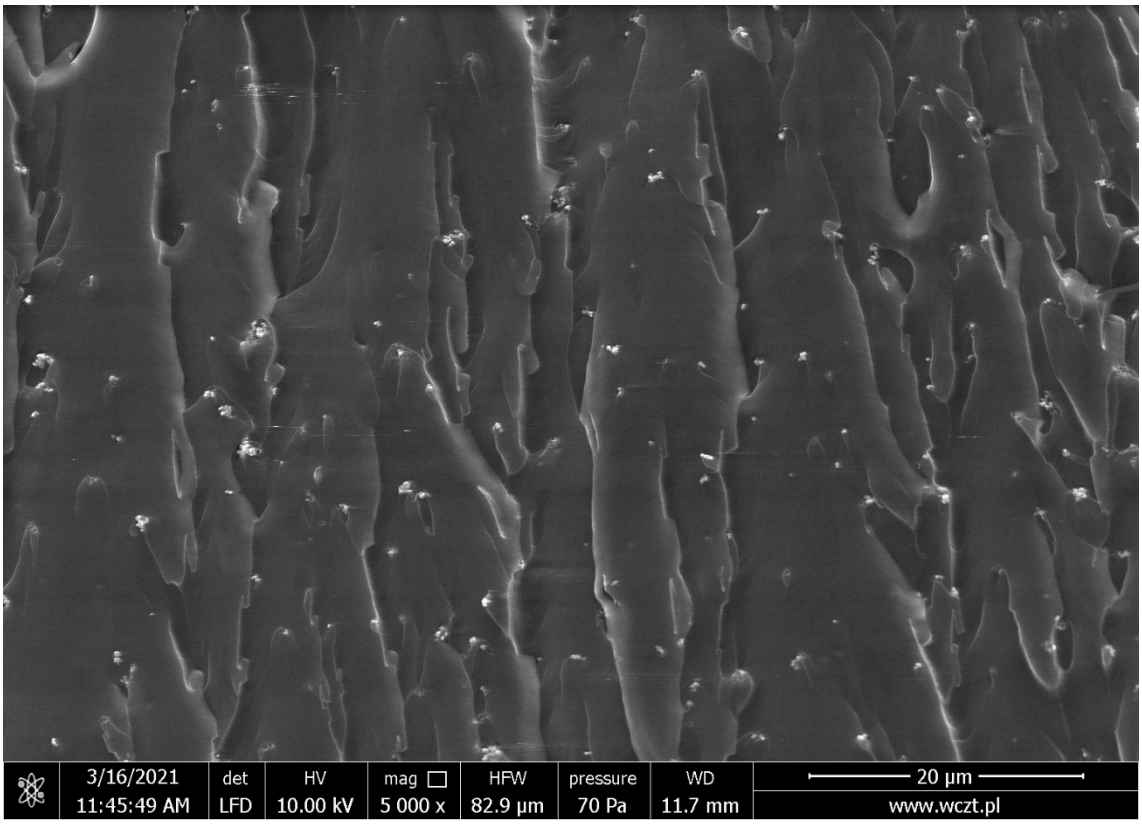




3/16/2021
11:29:46 AM
det
LFD
HV
10.00 kV
mag
5 000 x
HFW
82.9 µm
pressure
70 Pa
WD
10.7 mm
20 µm
www.wczt.pl

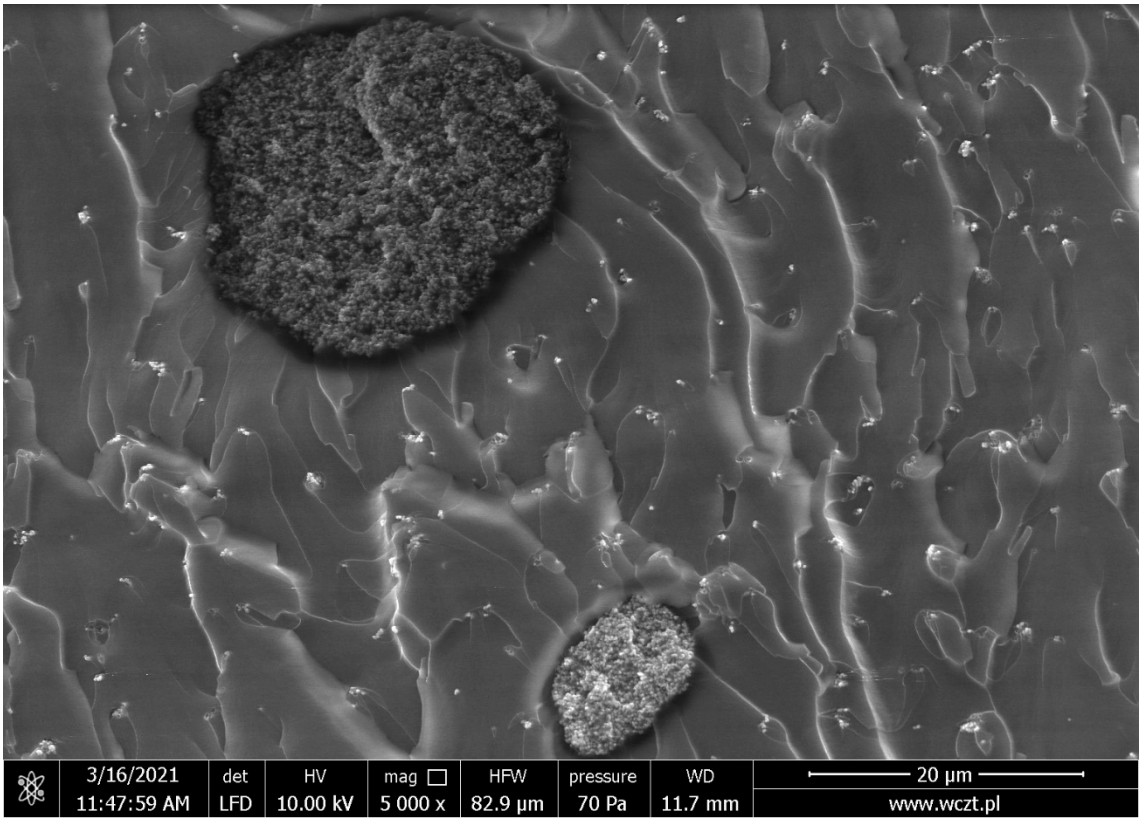
**1% $TiO_2$, unmodified, mixing pump**

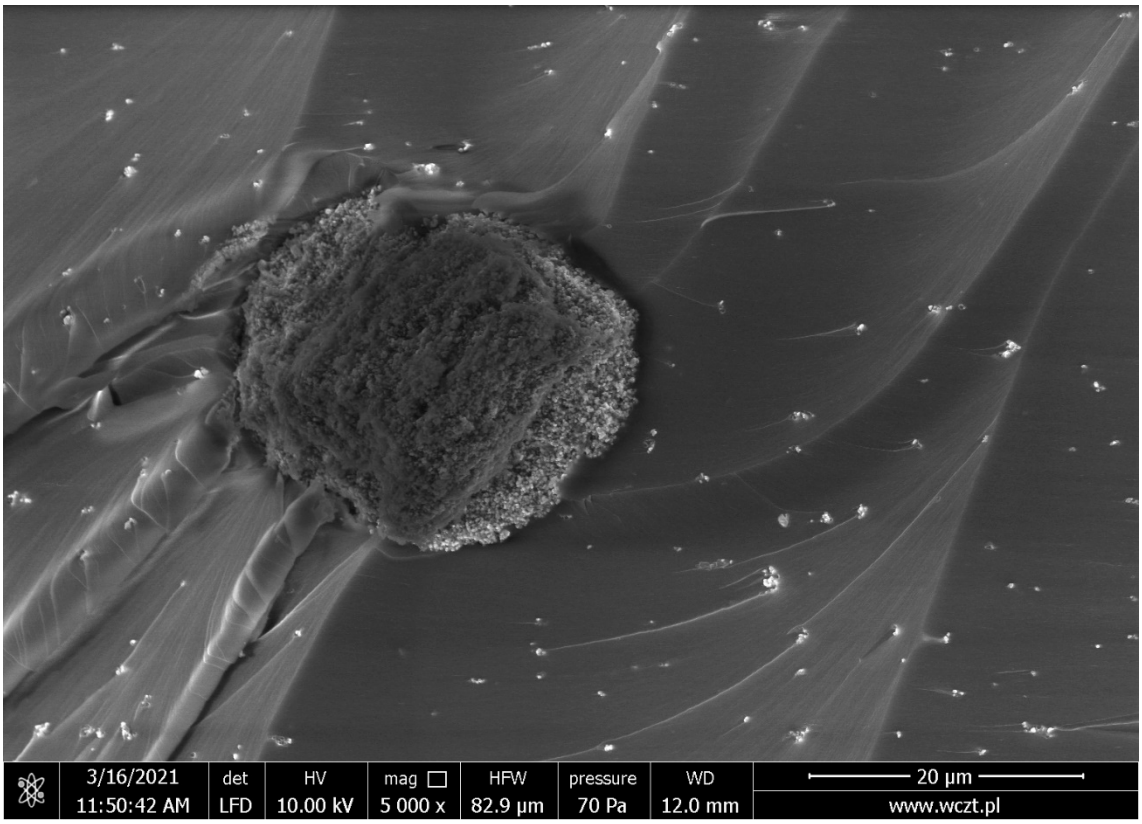


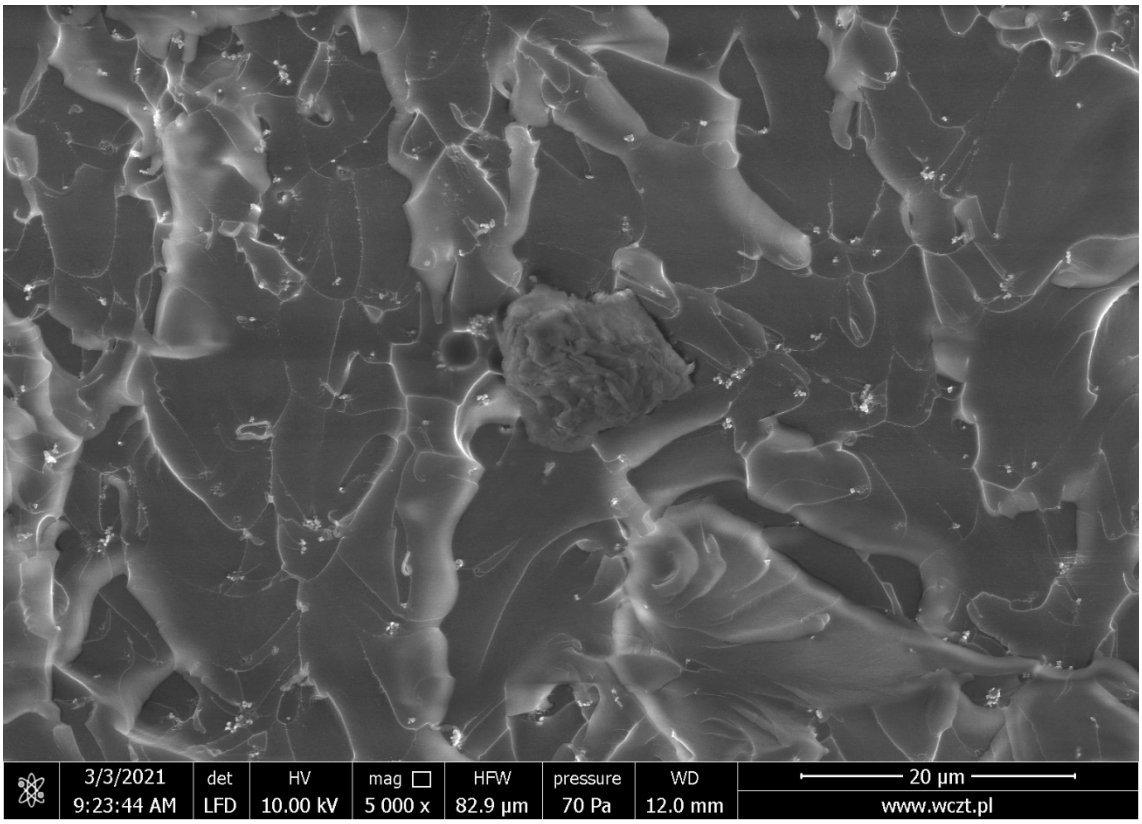




3/16/2021
11:45:49 AM
det
LFD
HV
10.00 kV
mag
5 000 x
HFW
82.9 µm
pressure
70 Pa
WD
11.7 mm
20 µm
www.wczt.pl

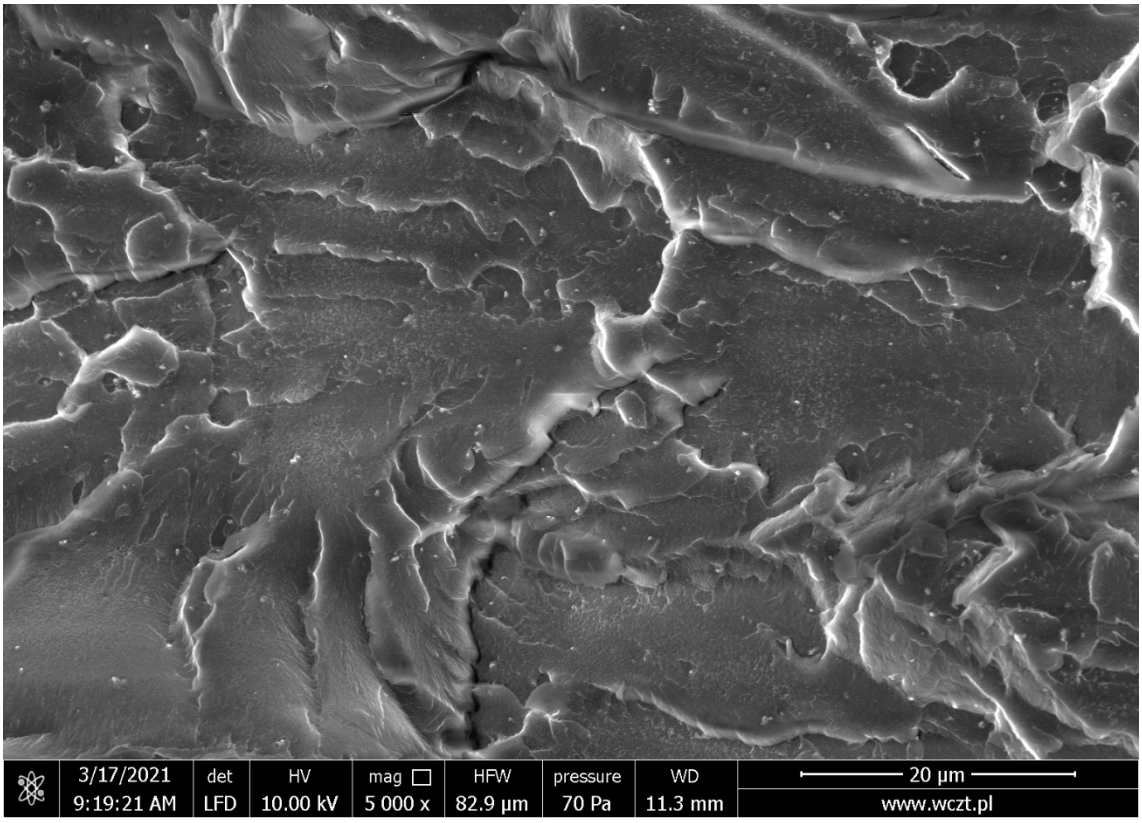
**2% $TiO_2$, unmodified, mixing pump**

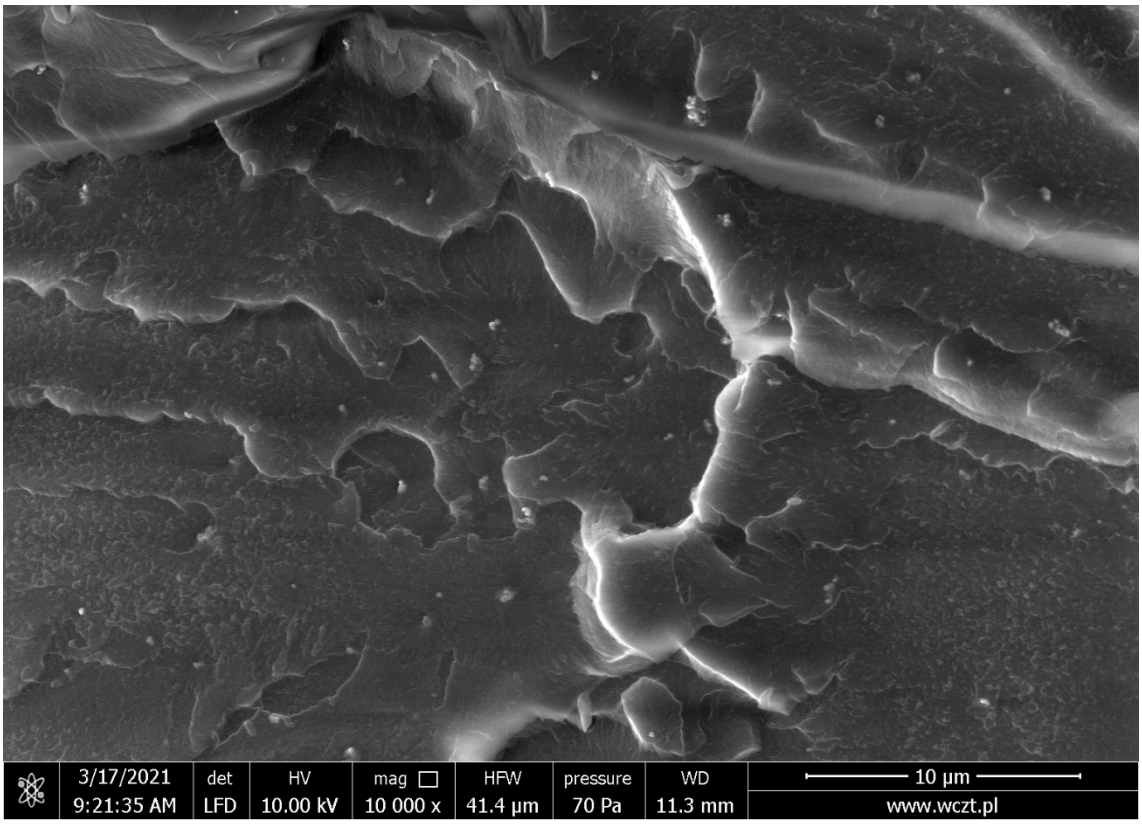


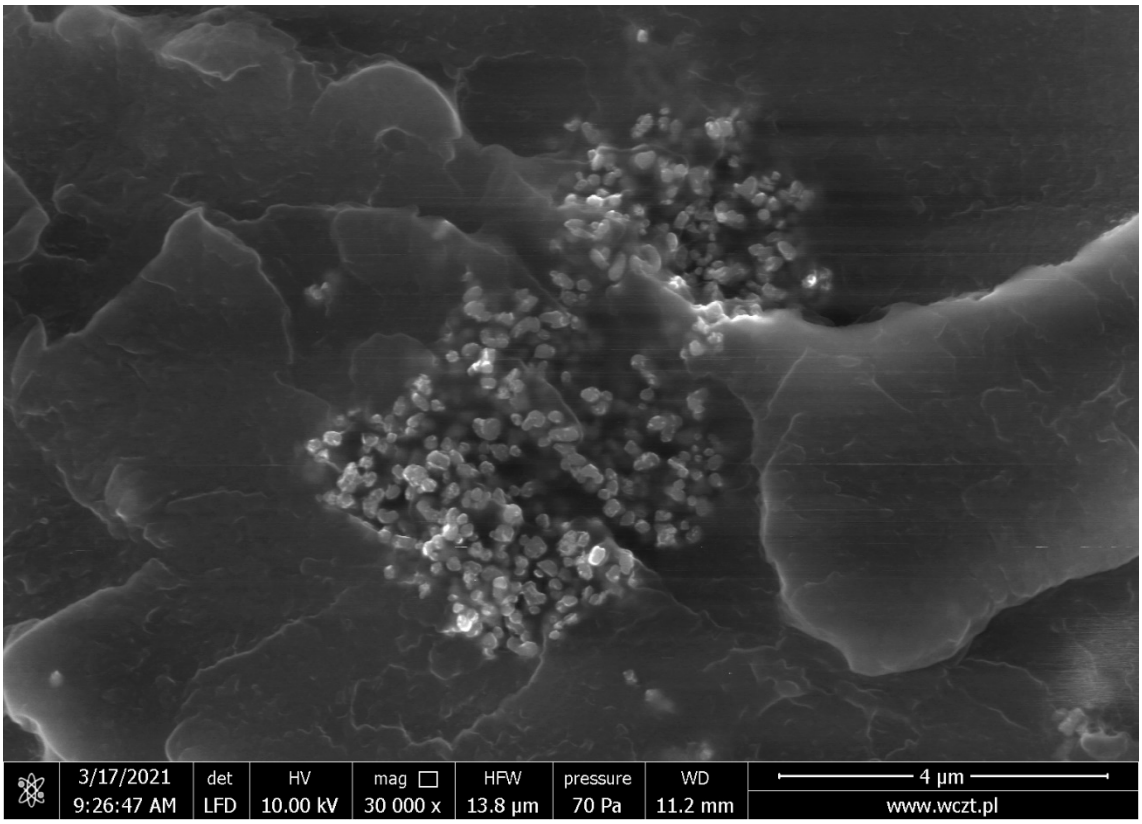




3/3/2021
9:23:44 AM
det
LFD
HV
10.00 kV
mag
5 000 x
HFW
82.9 µm
pressure
70 Pa
WD
12.0 mm
20 µm
www.wczt.pl

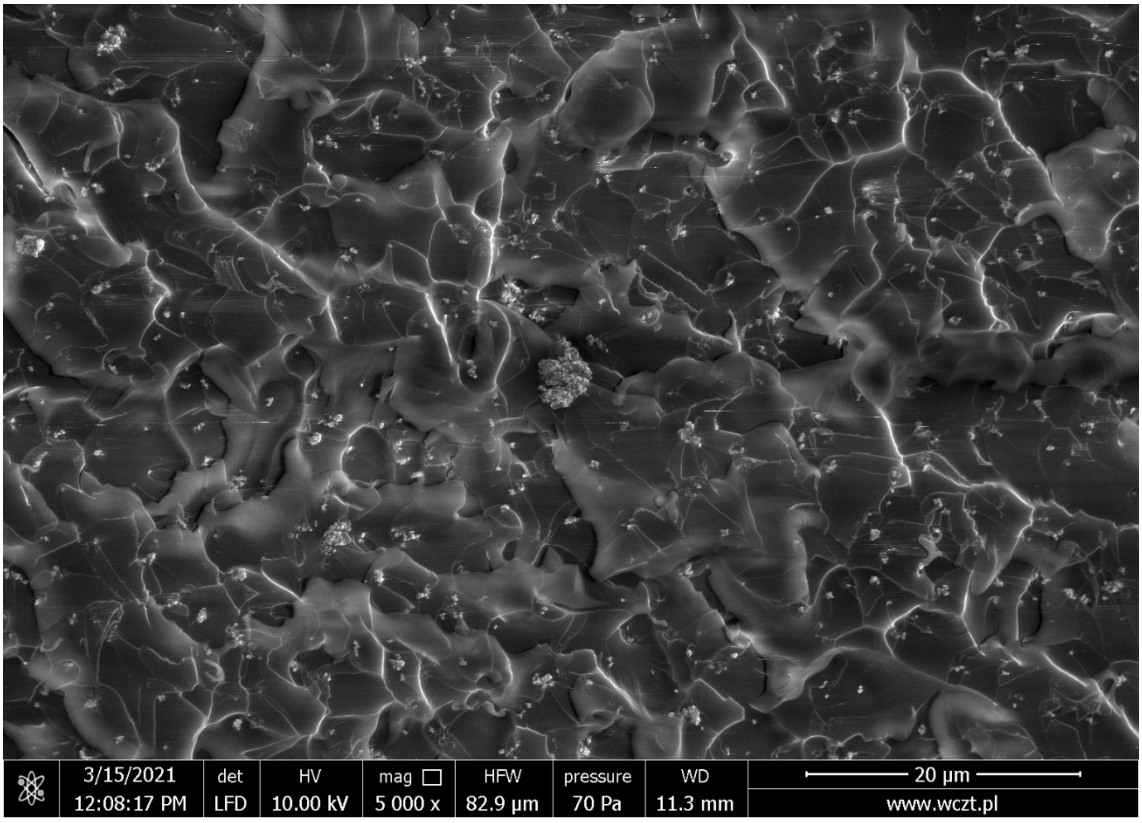
**1%$TiO_2$, 0.5% iBuTMOS, mixing pump**

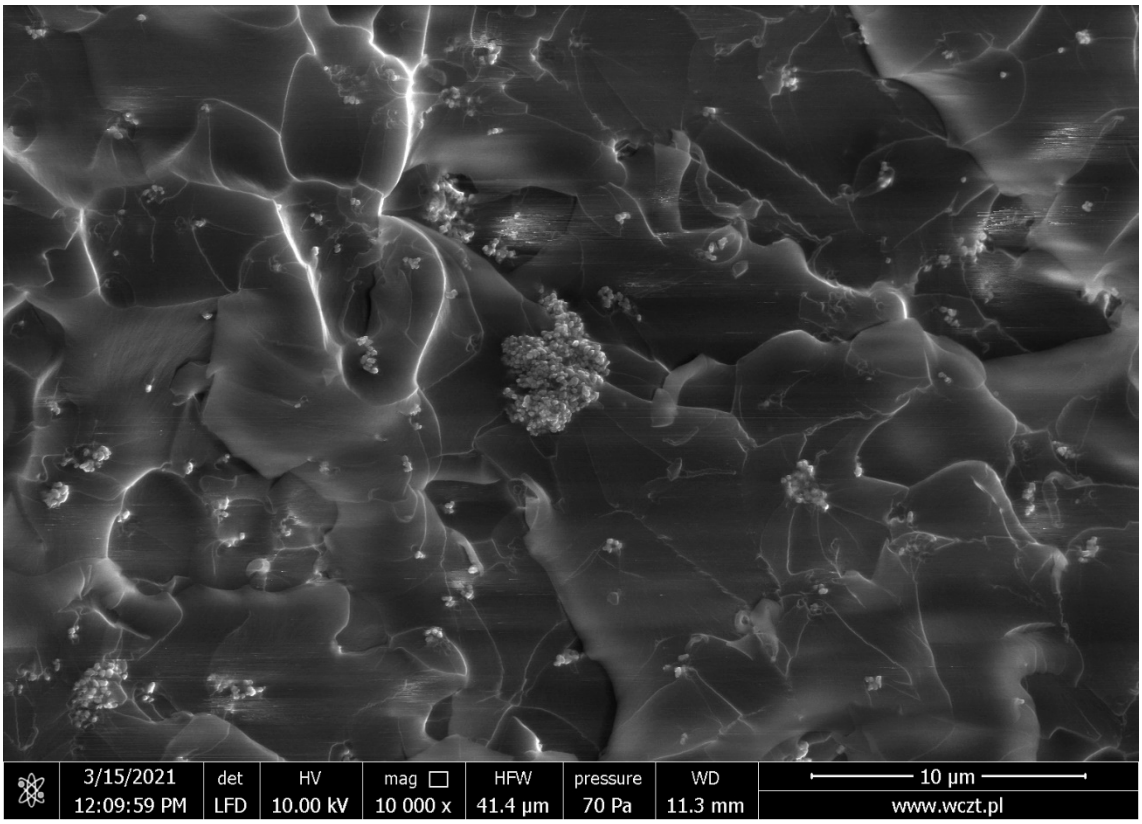


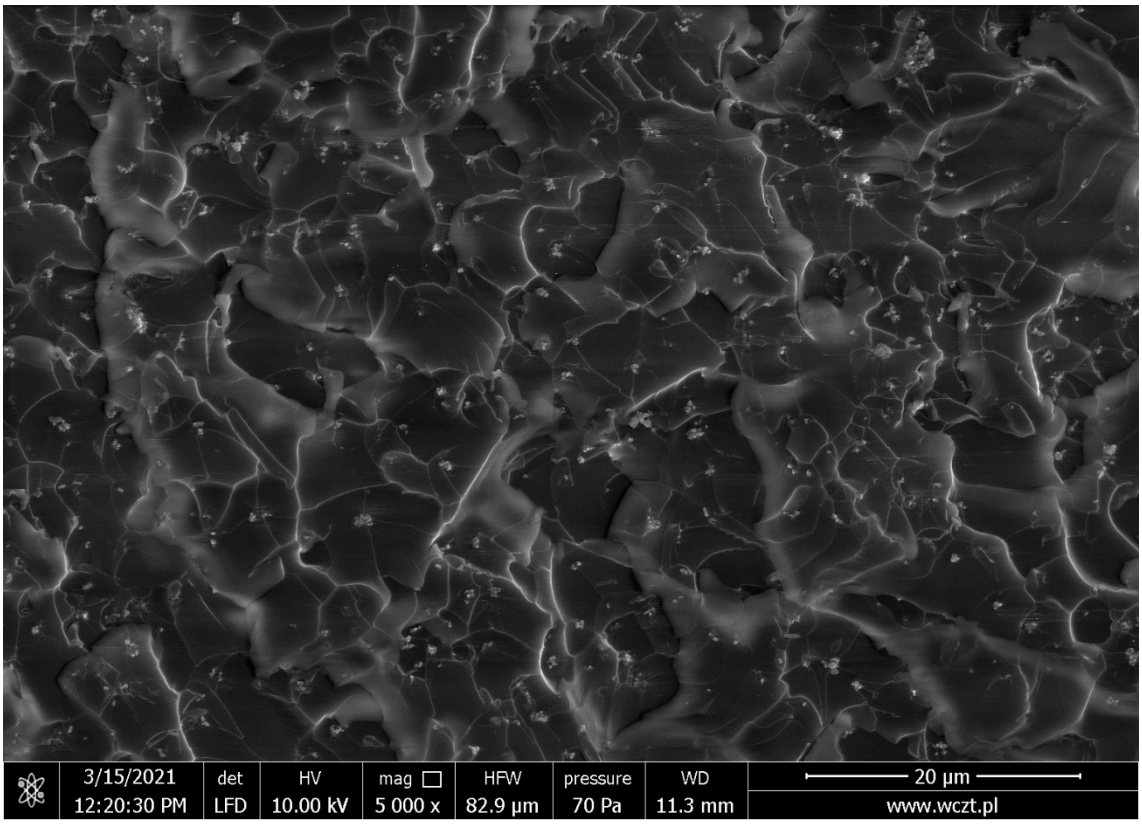




3/17/2021
9:26:47 AM
det
LFD
HV
10.00 kV
mag
30 000 x
HFW
13.8 µm
pressure
70 Pa
WD
11.2 mm
4 µm
www.wczt.pl

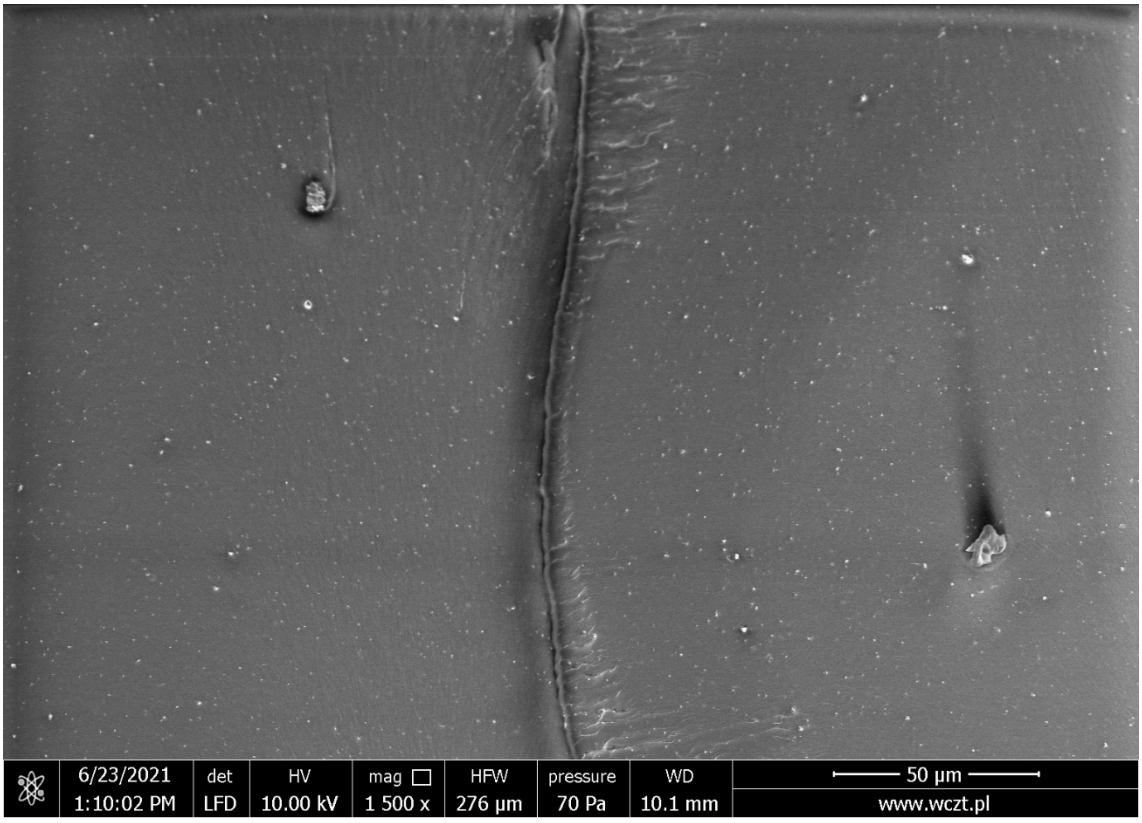
**2%$TiO_2$, 0.5% iBuTMOS, mixing pump**

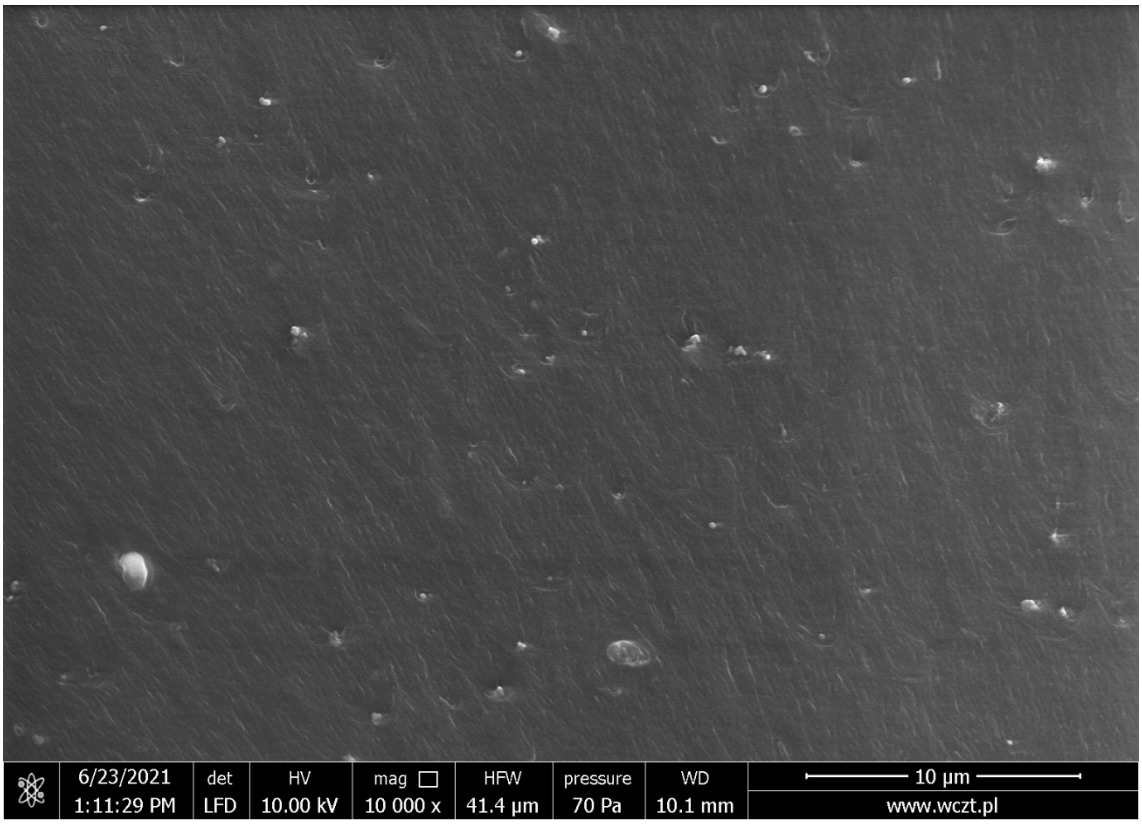


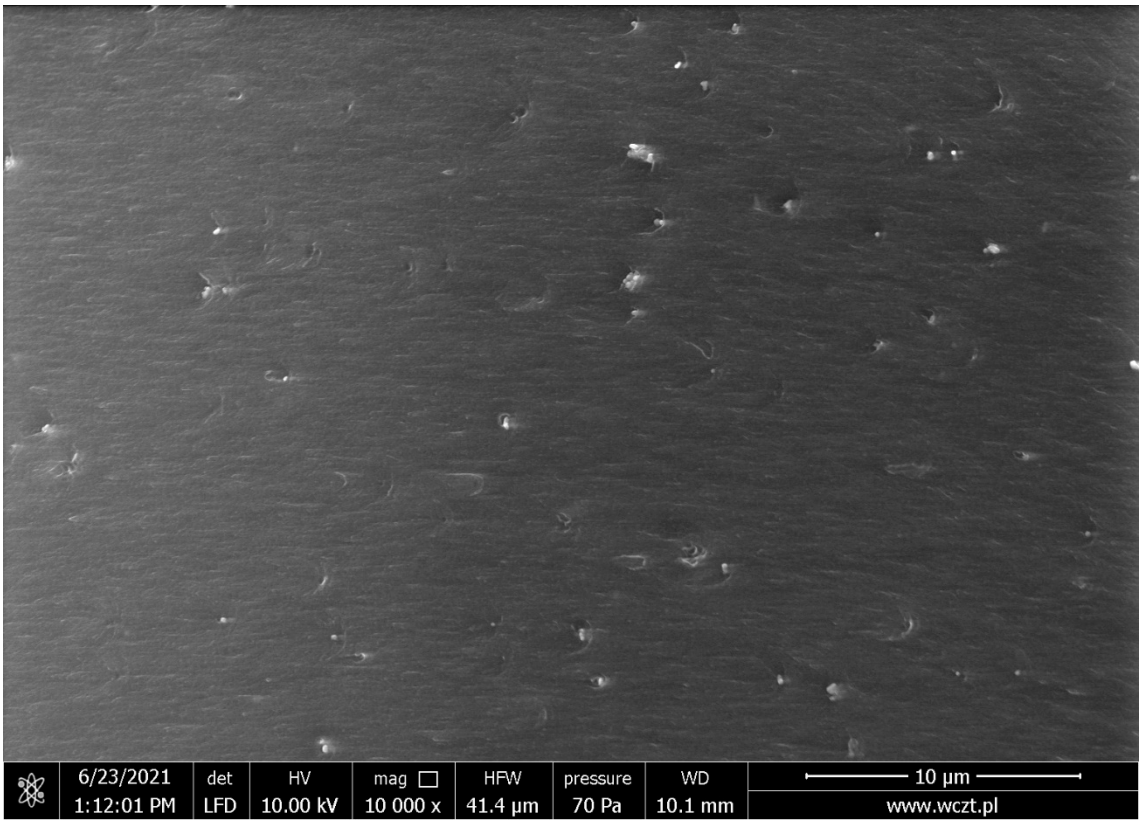




3/15/2021
12:20:30 PM
det
LFD
HV
10.00 kV
mag
5 000 x
HFW
82.9 µm
pressure
70 Pa
WD
11.3 mm
20 µm
www.wczt.pl

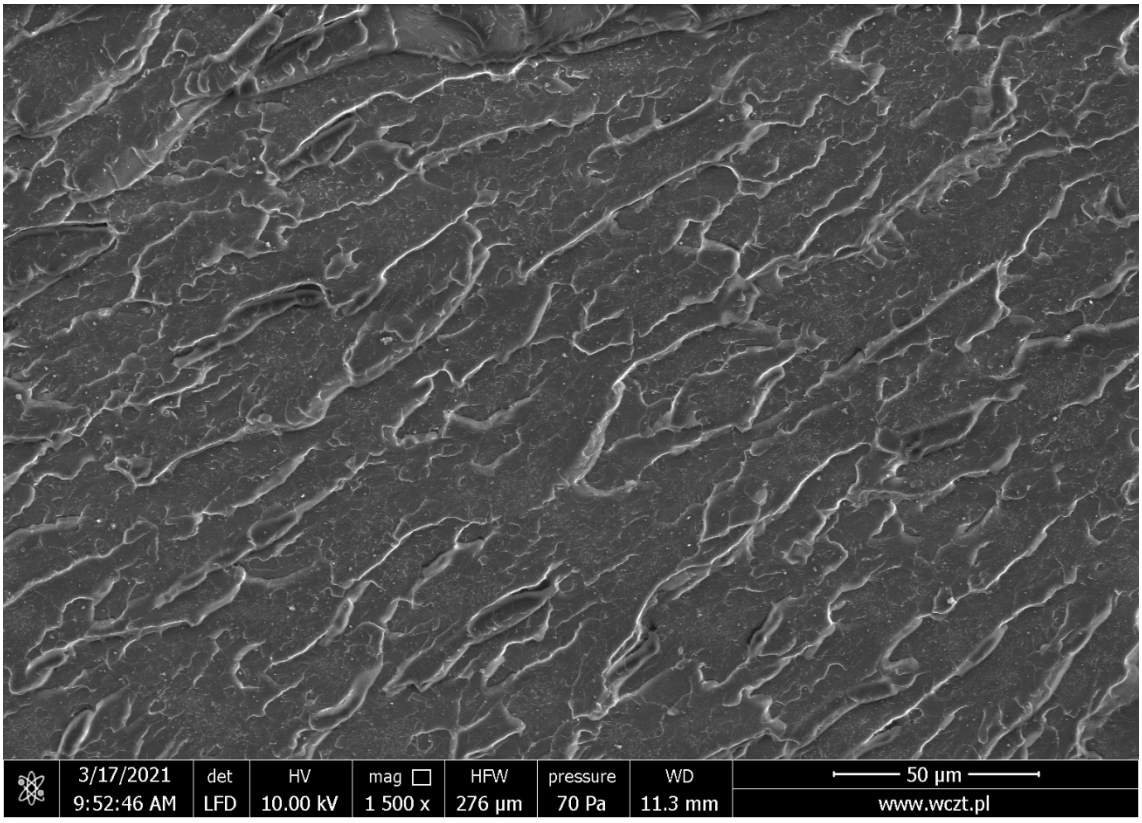
**1%$TiO_2$, 1.5% iBuTMOS, mechanical stirrer**

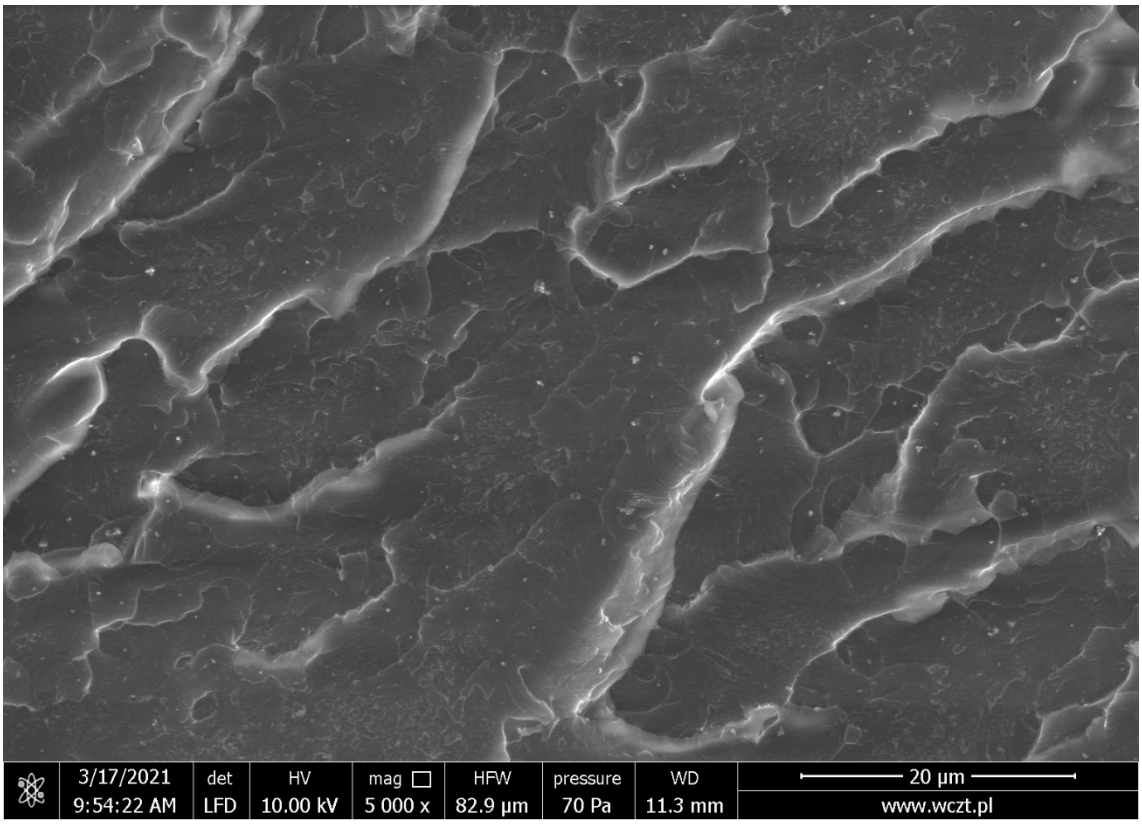


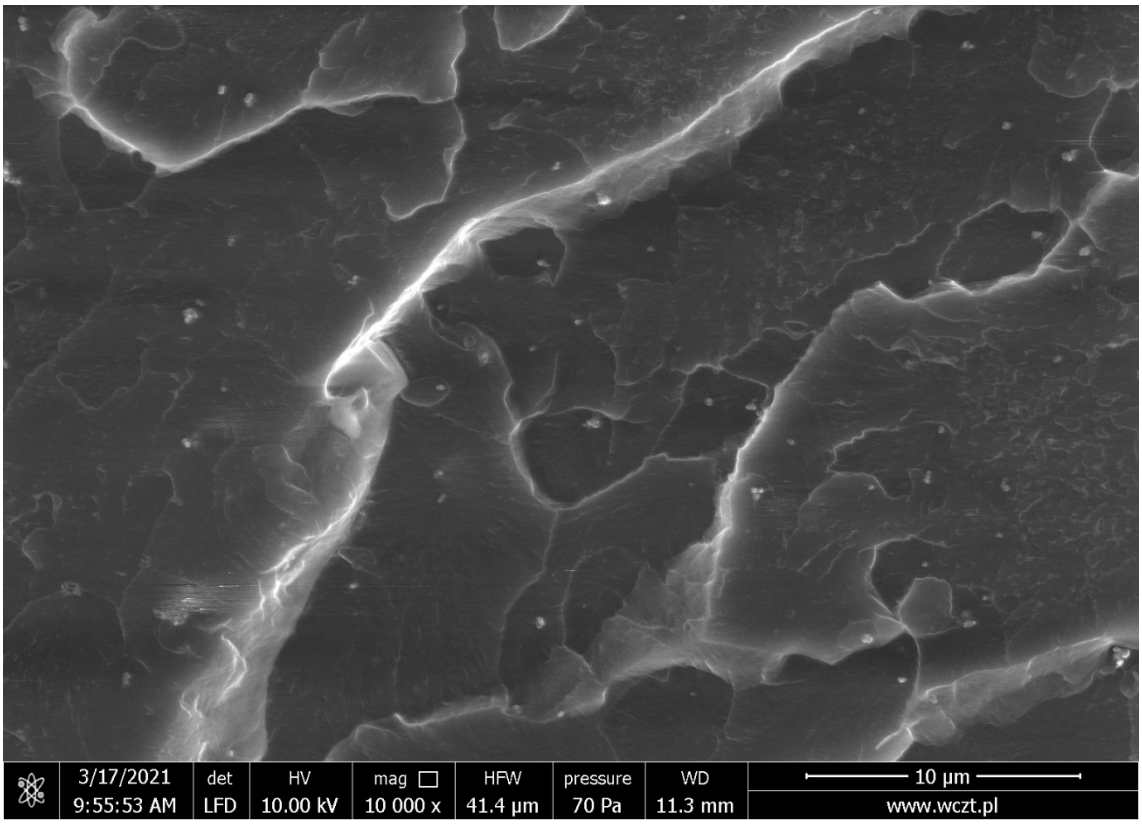




6/23/2021
1:12:01 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.1 mm
10 µm
www.wczt.pl

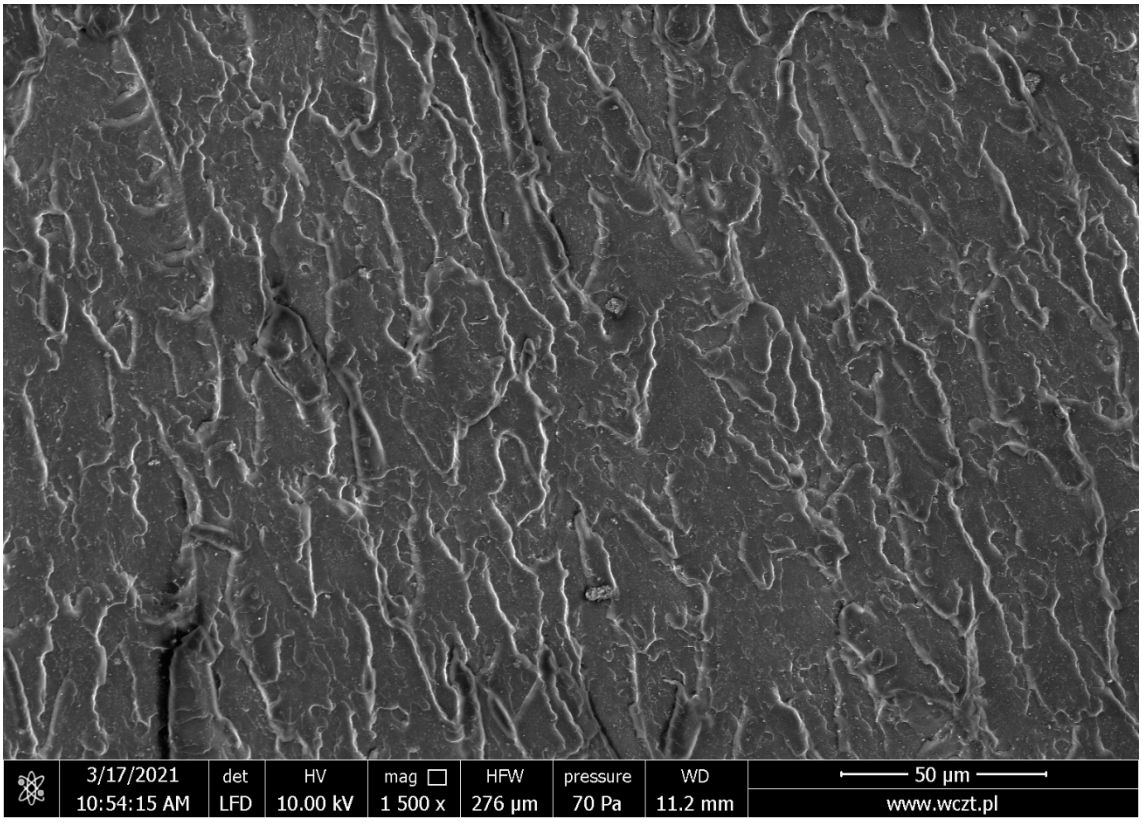
**1%$TiO_2$, 1.5% iBuTMOS, mixing pump**

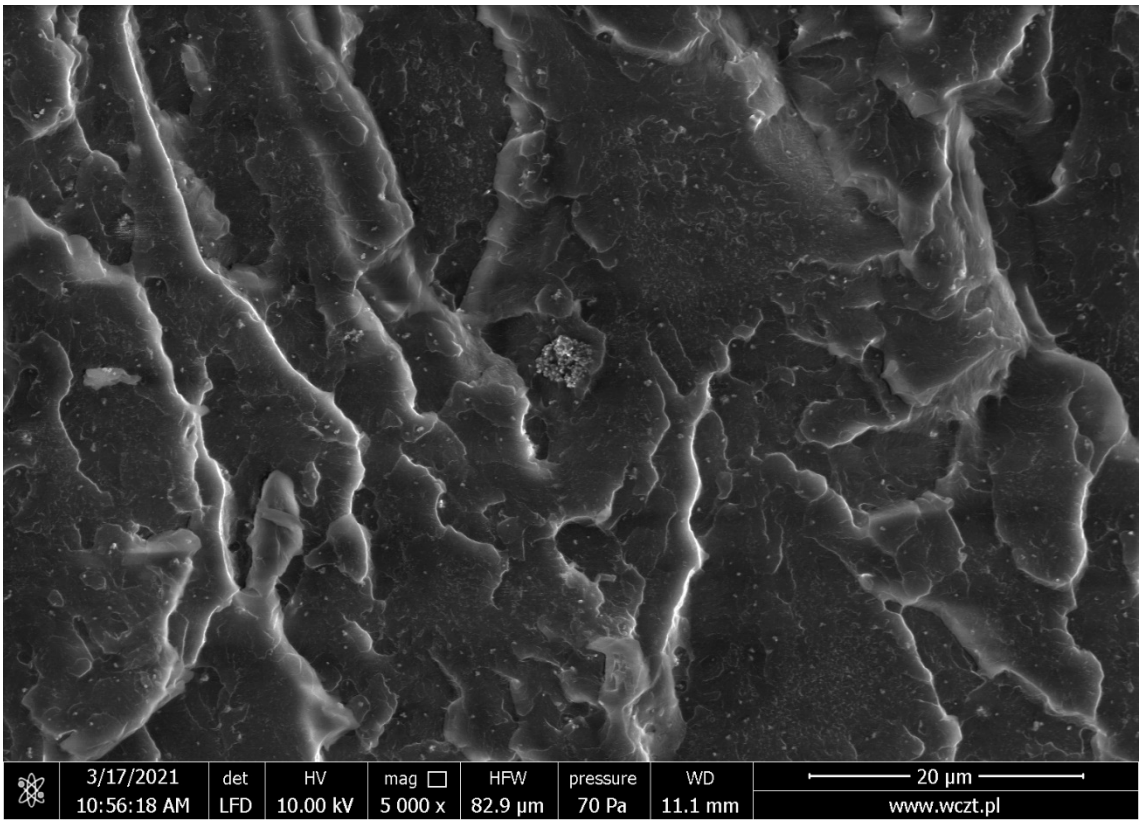


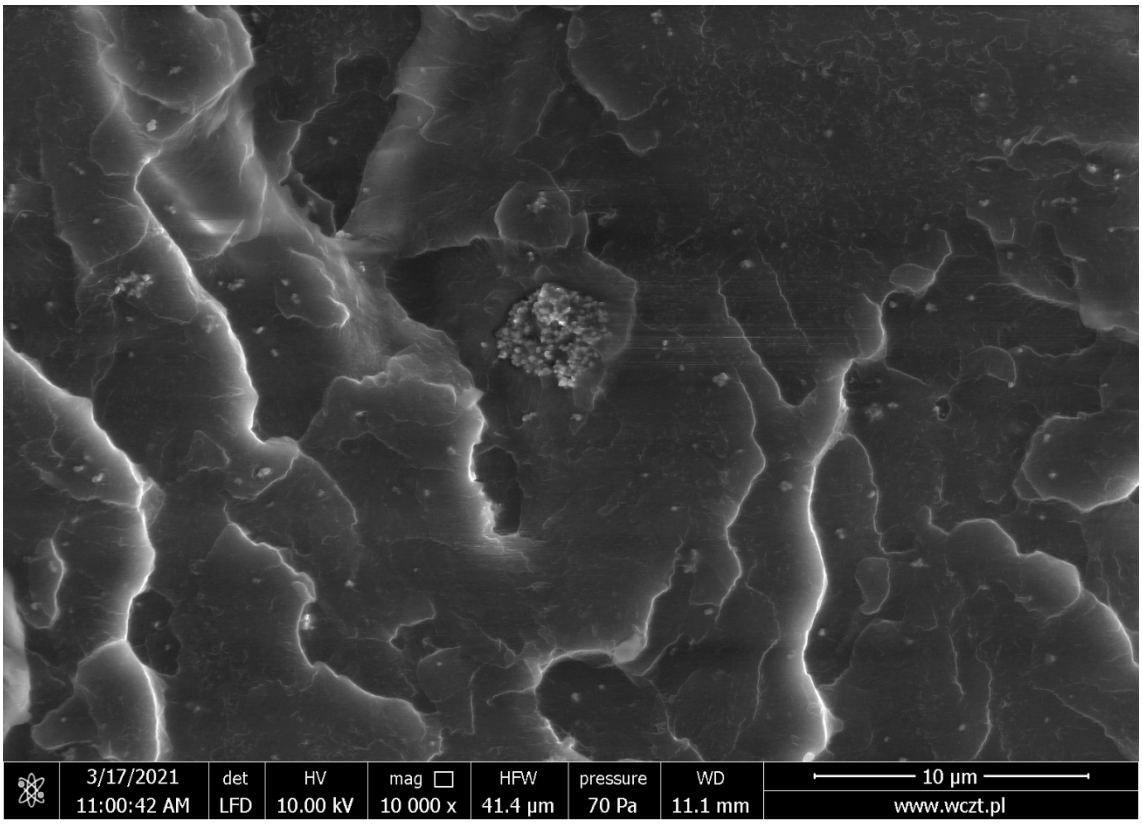




3/17/2021
9:55:53 AM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
11.3 mm
10 µm
www.wczt.pl

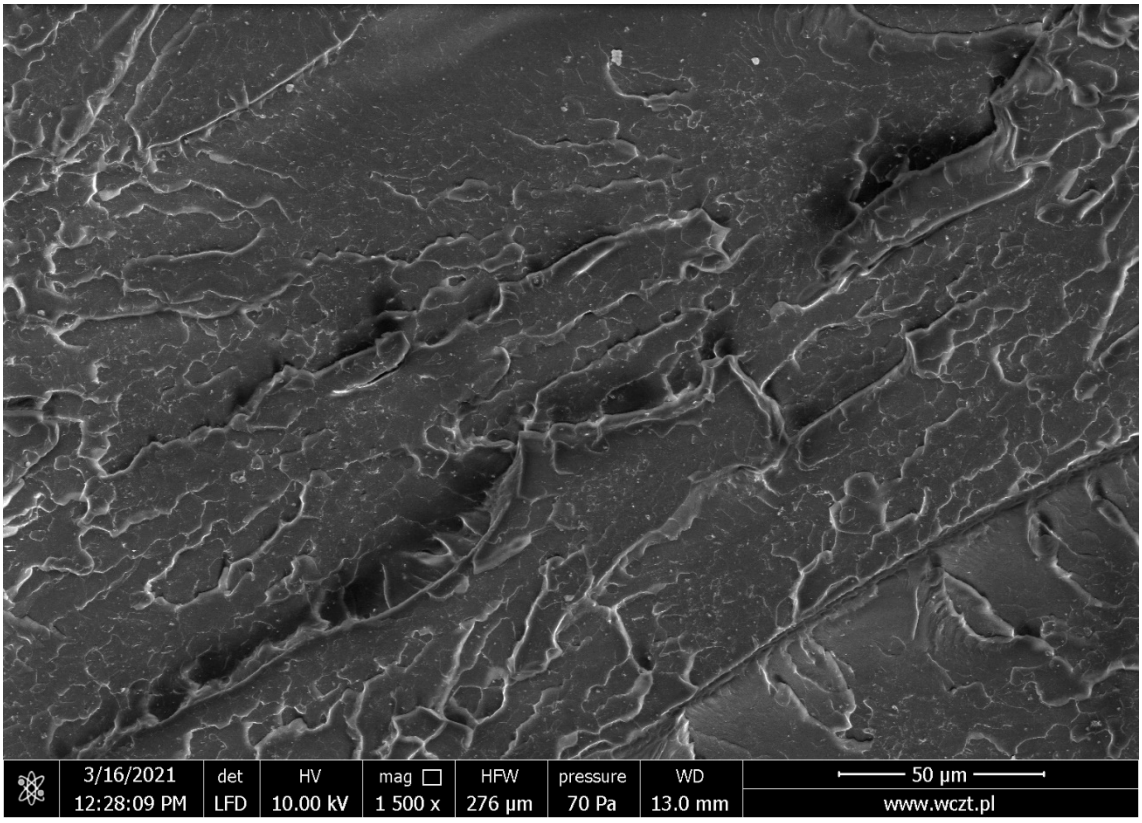
**2%$TiO_2$, 1.5% iBuTMOS, mixing pump**

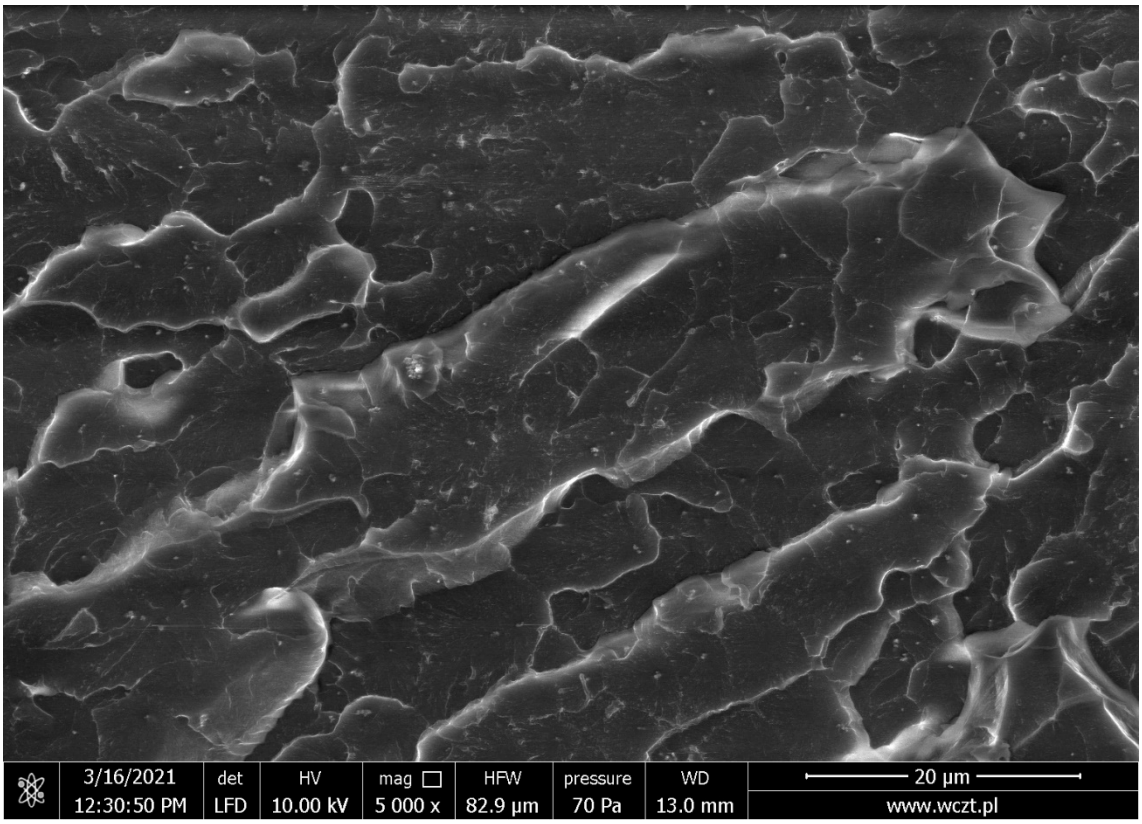


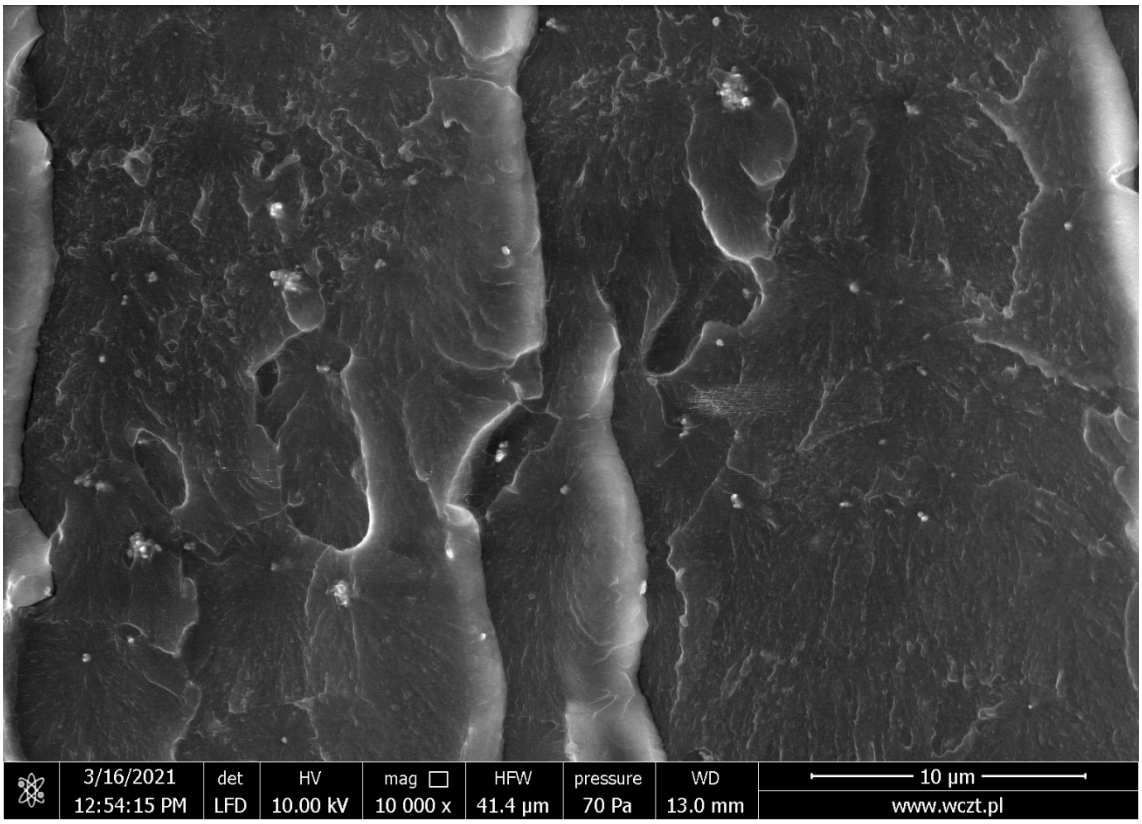




3/17/2021
11:00:42 AM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
11.1 mm
10 µm
www.wczt.pl

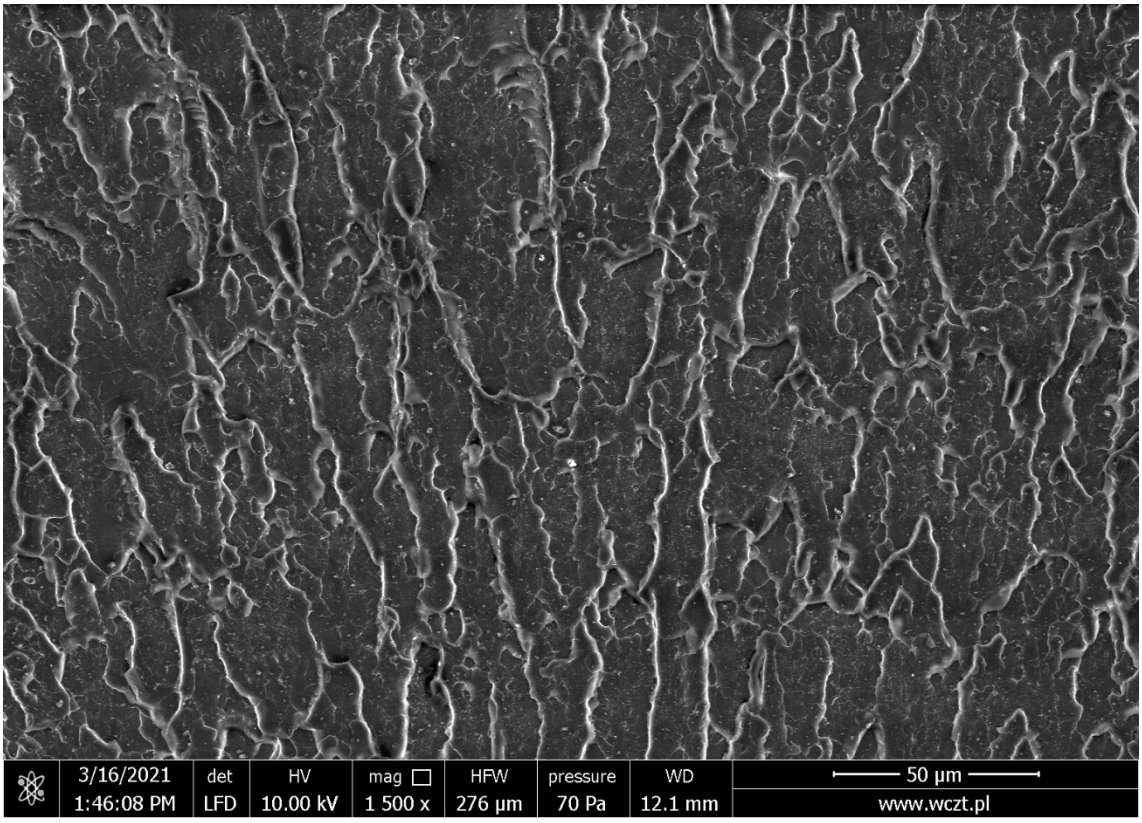
**1%$TiO_2$, 0.5% GPTES, mixing pump**

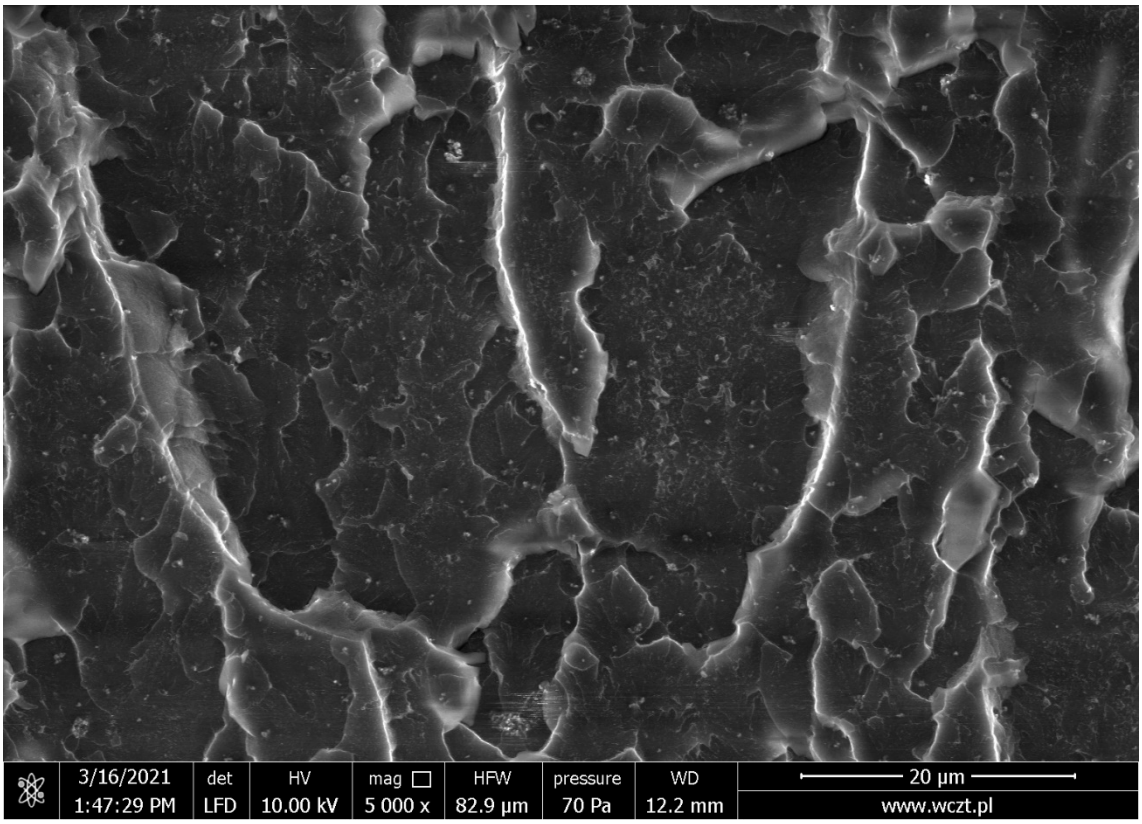


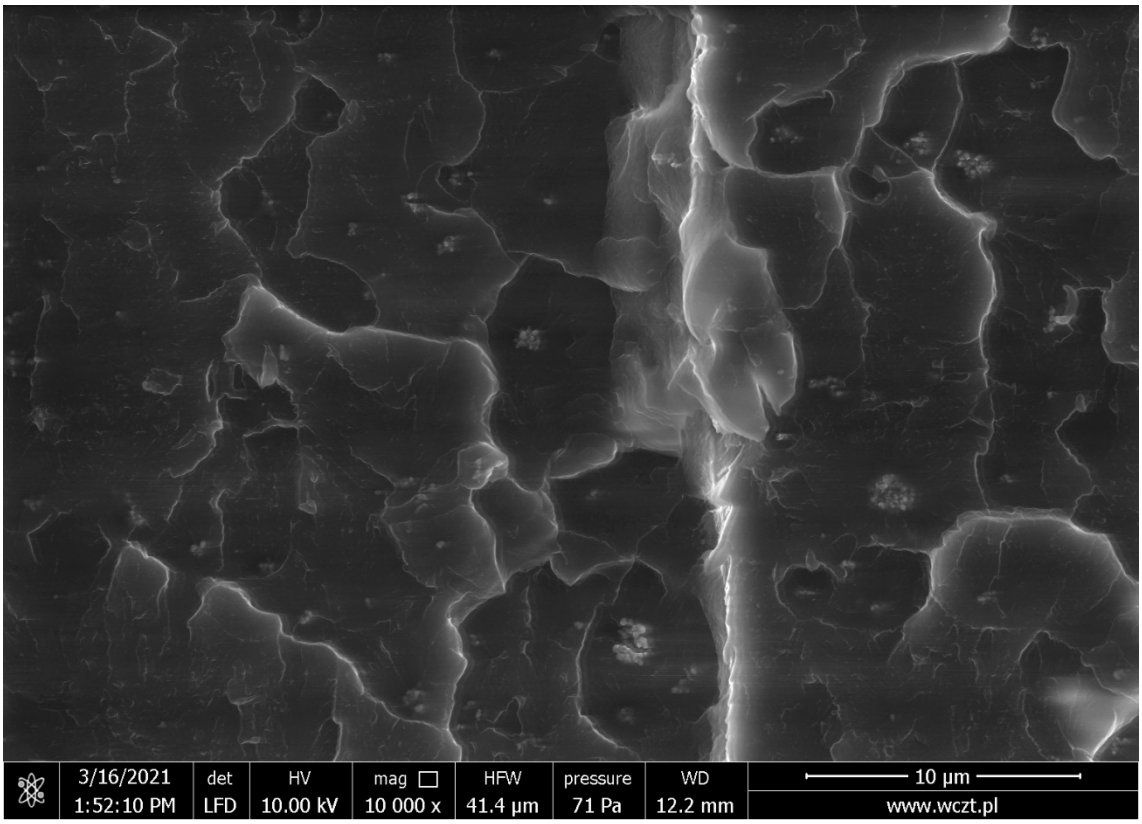




3/16/2021
12:54:15 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
13.0 mm
10 µm
www.wczt.pl

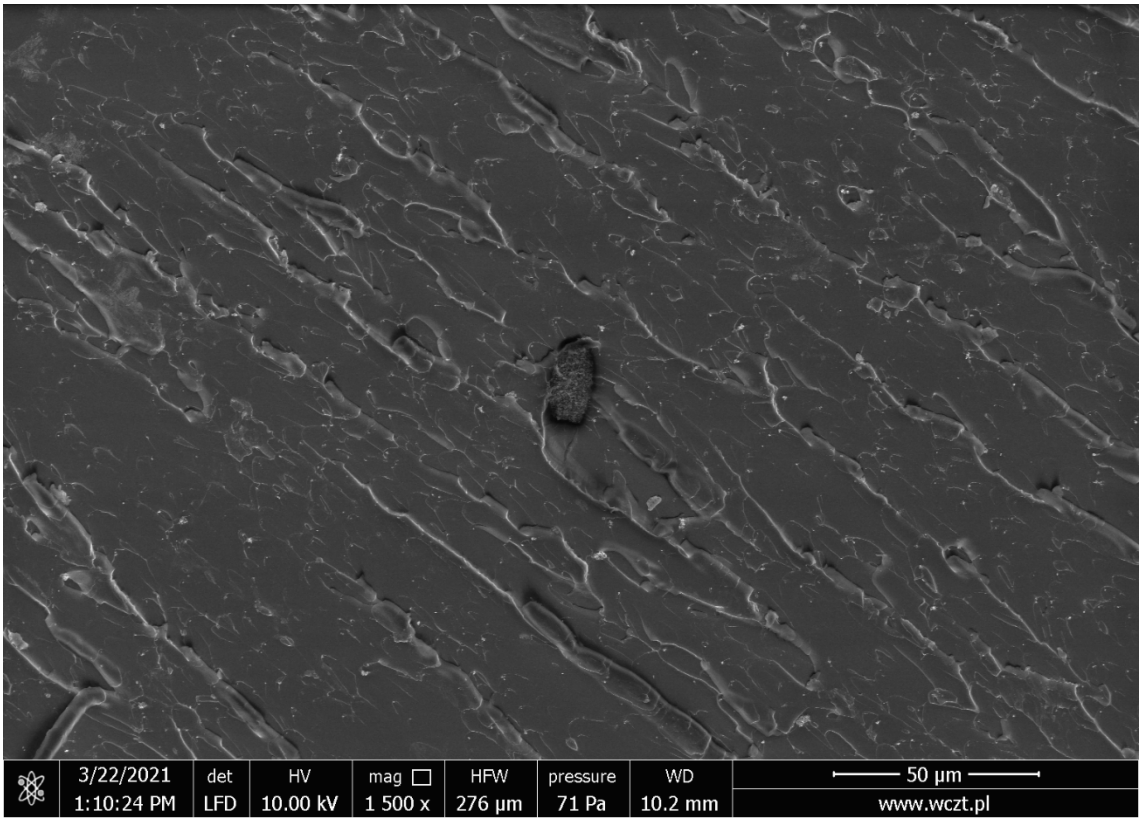
**2%$TiO_2$, 0.5% GPTES, mixing pump**

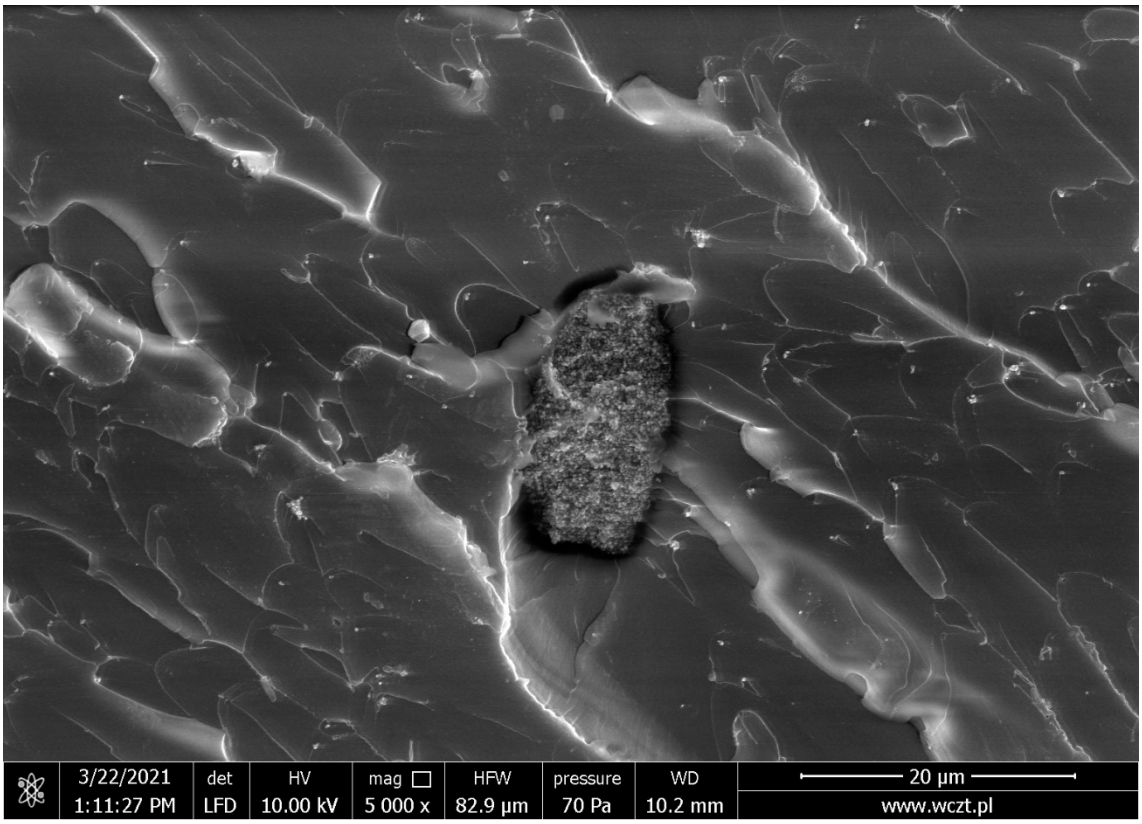


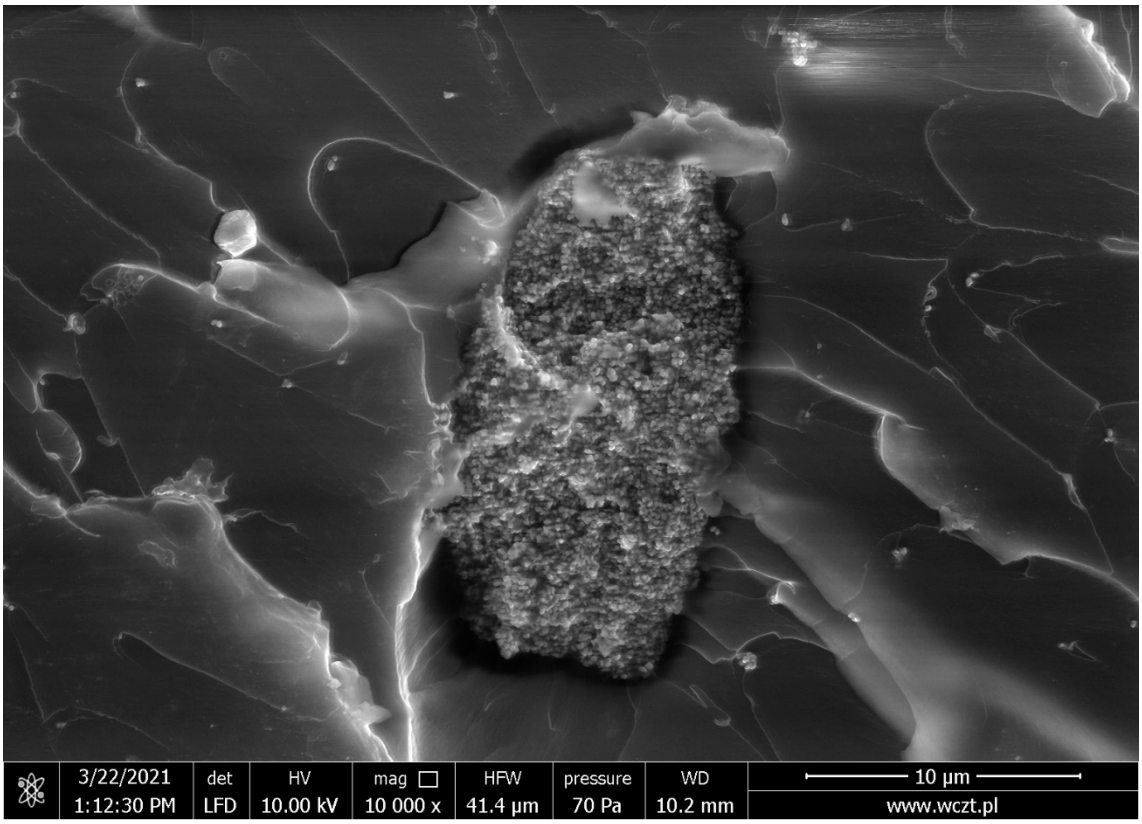




3/16/2021
1:52:10 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
71 Pa
WD
12.2 mm
10 µm
www.wczt.pl

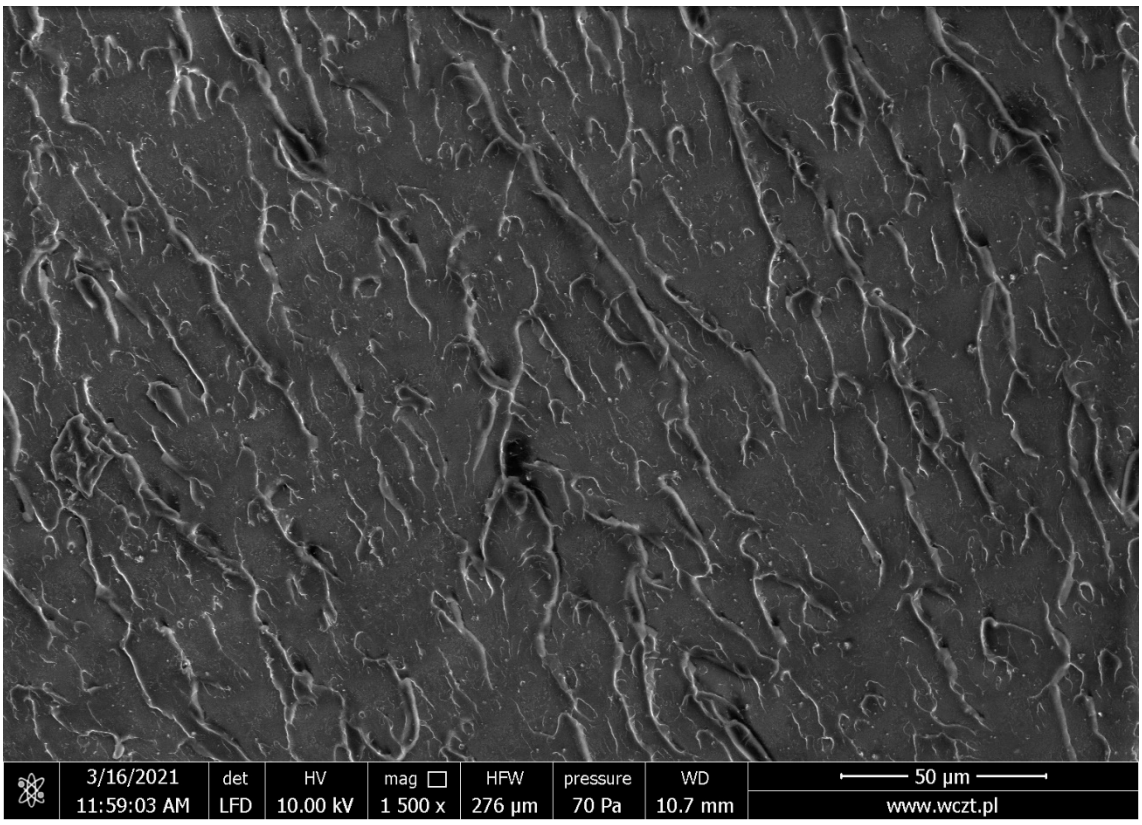
**1%$TiO_2$, 1.5% GPTES, mechanical stirrer**

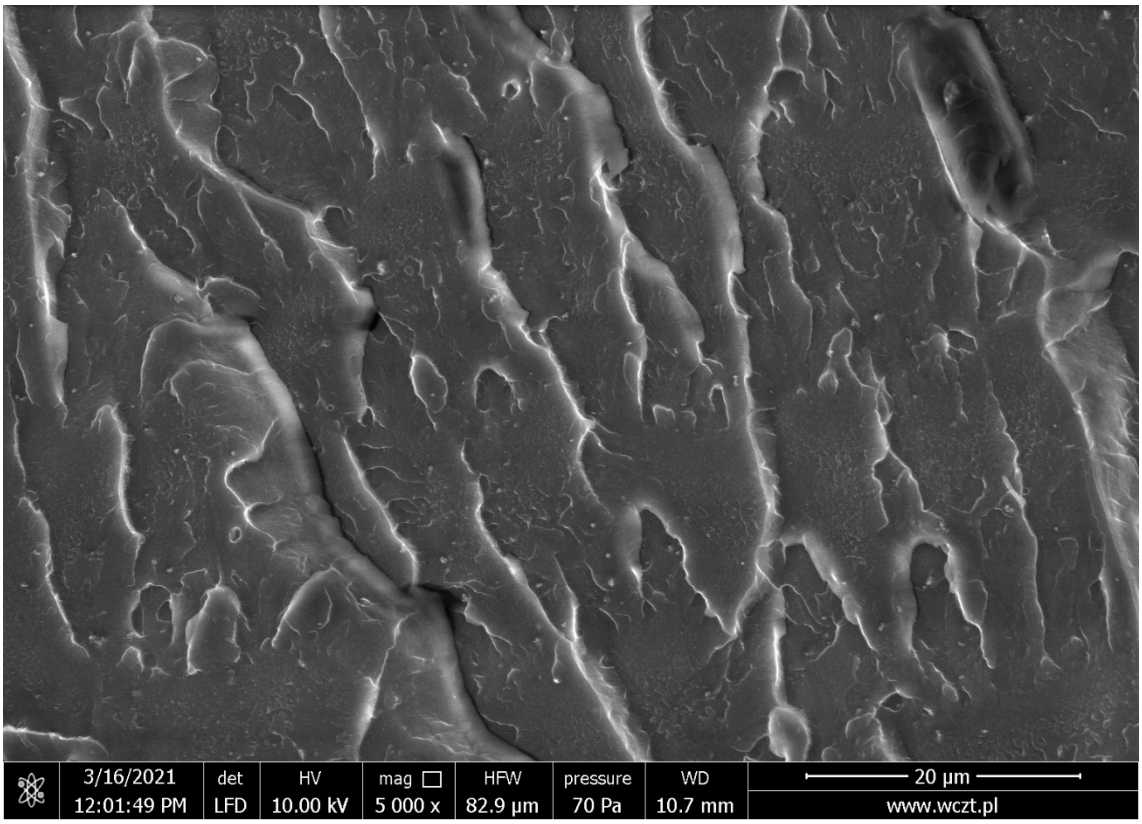


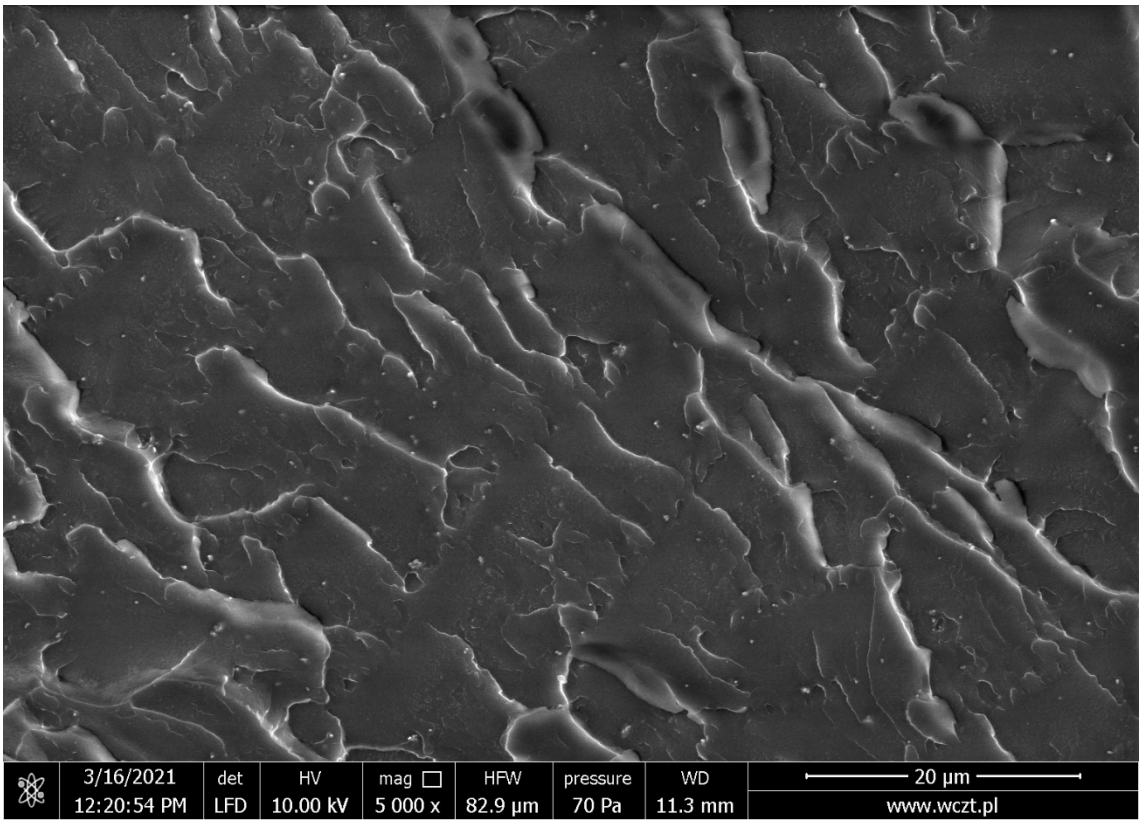




3/22/2021
1:12:30 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.2 mm
10 µm
www.wczt.pl

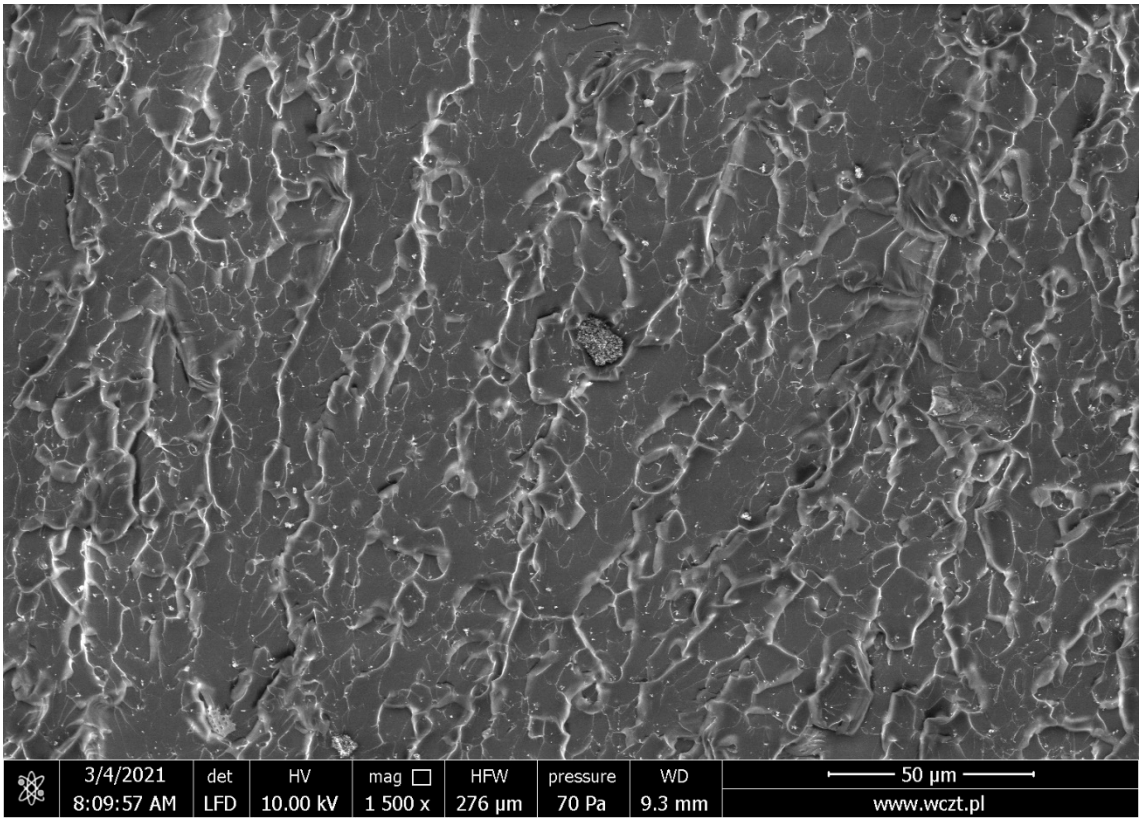
**1%$TiO_2$, 1.5% GPTES, mixing pump**

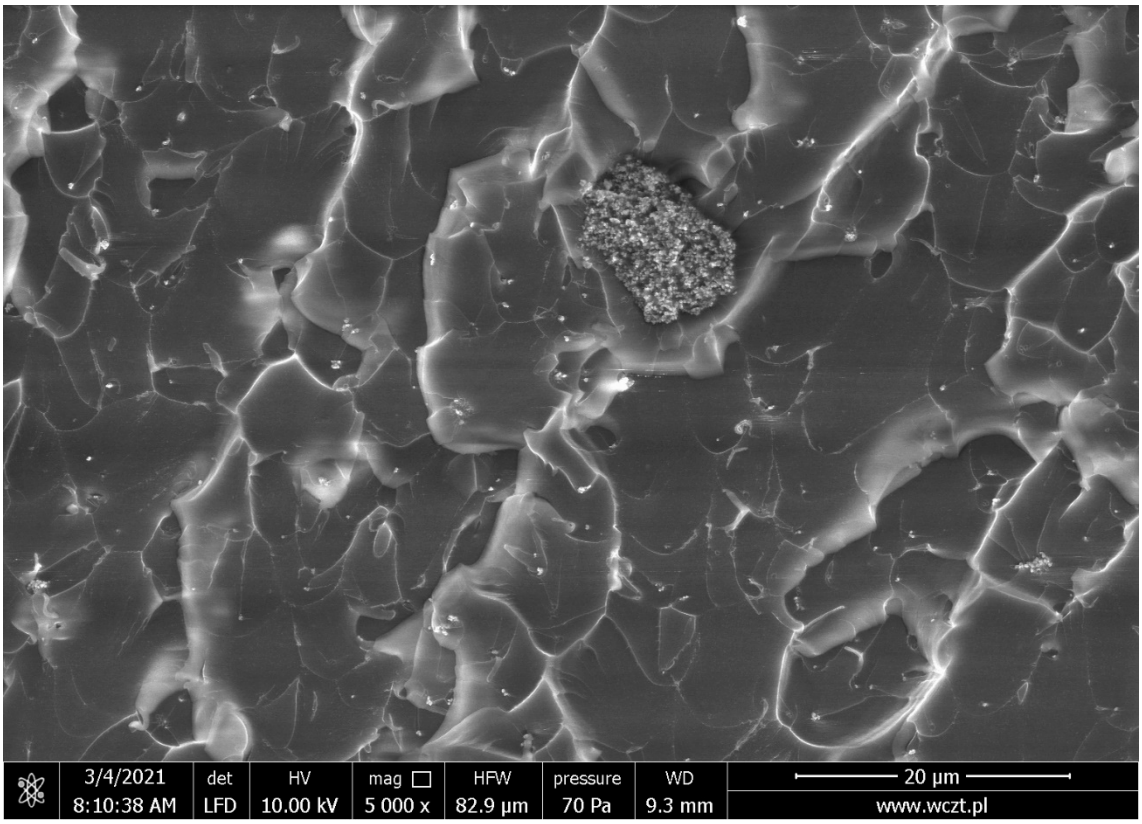


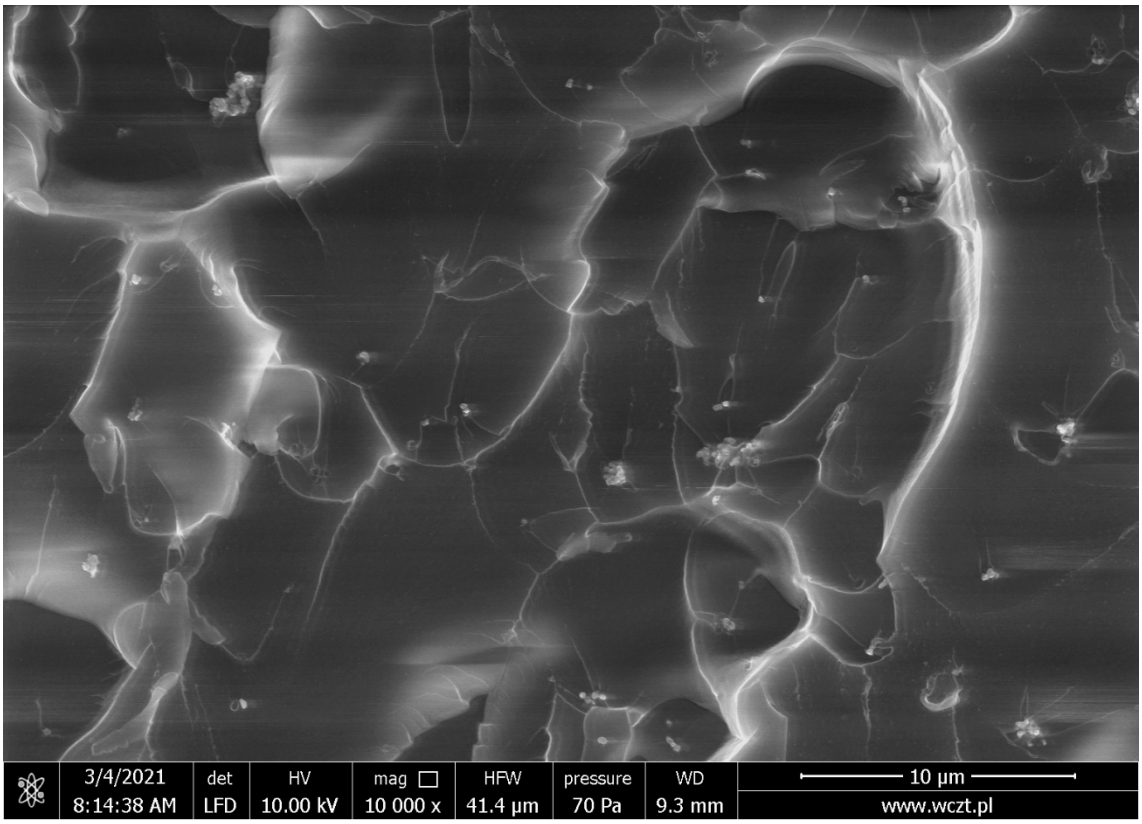




3/16/2021
12:20:54 PM
det
LFD
HV
10.00 kV
mag
5 000 x
HFW
82.9 µm
pressure
70 Pa
WD
11.3 mm
20 µm
www.wczt.pl

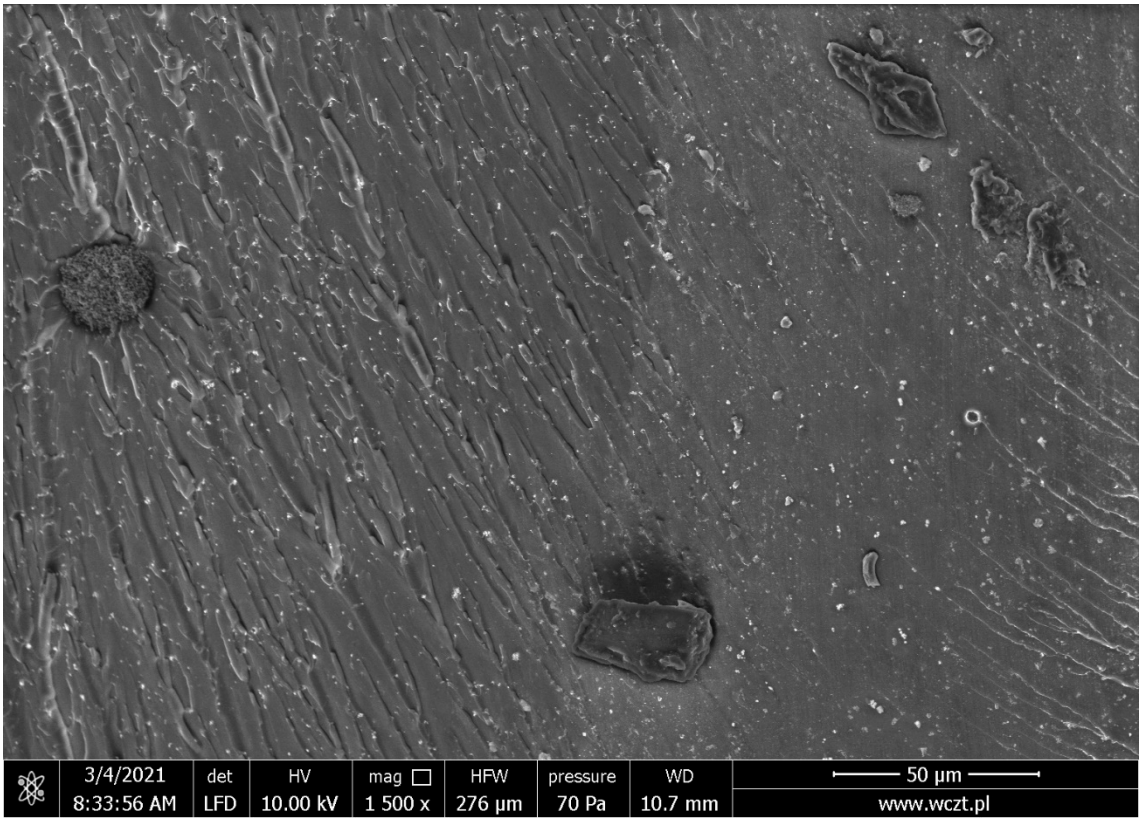
**2%$TiO_2$, 1.5% GPTES, mixing pump**

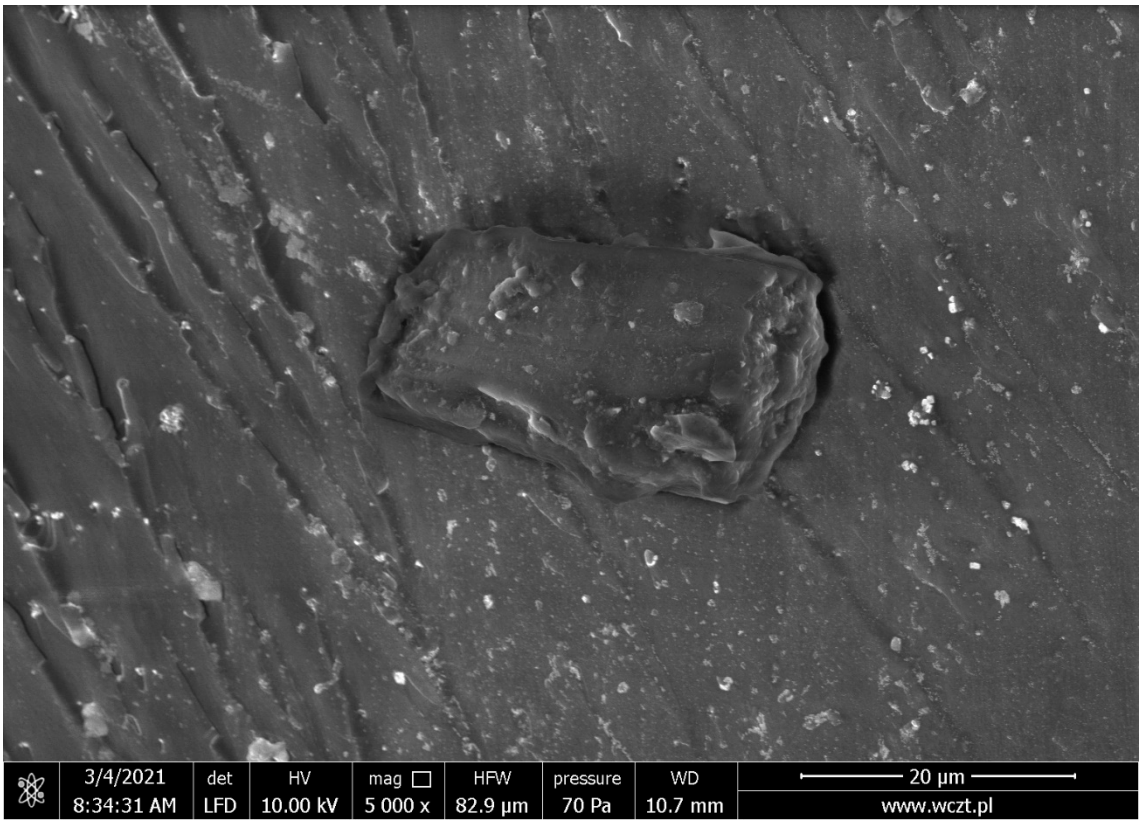


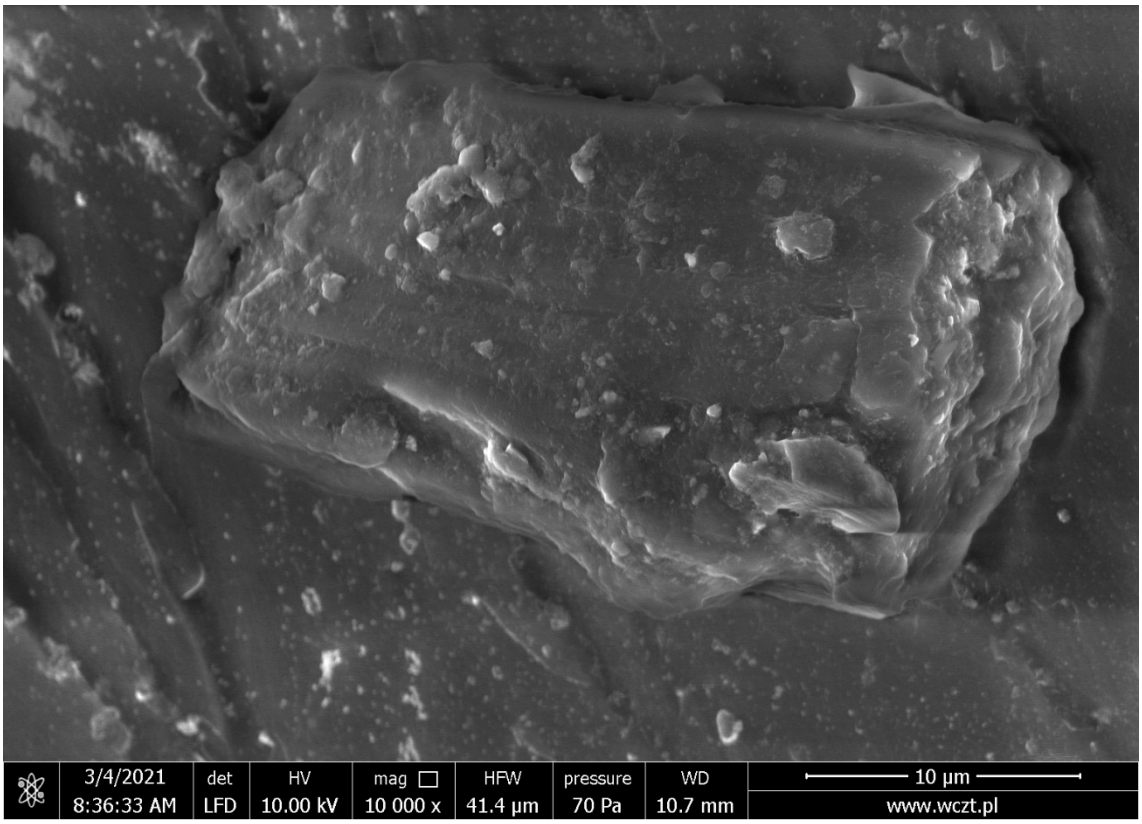




3/4/2021
8:14:38 AM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
9.3 mm
10 µm
www.wczt.pl

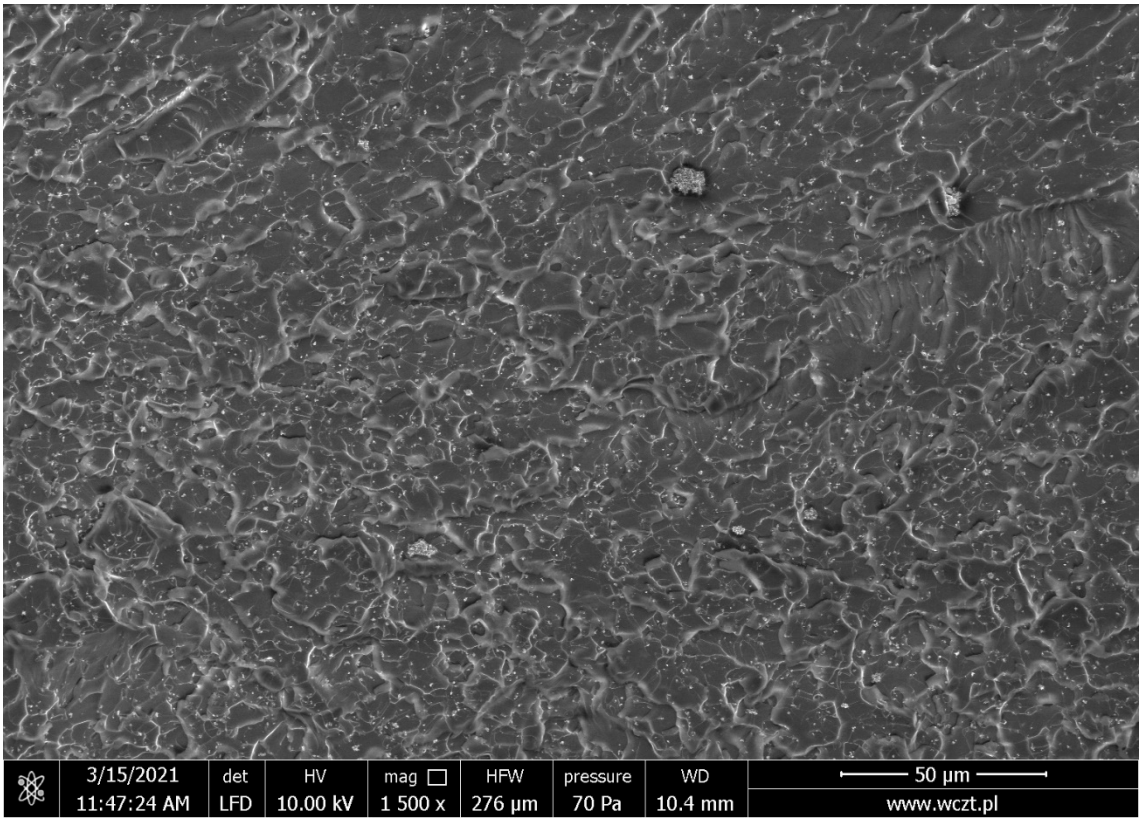
**1%$TiO_2$, 0.5% $iBu_7$SSQ-OEt, mixing pump**

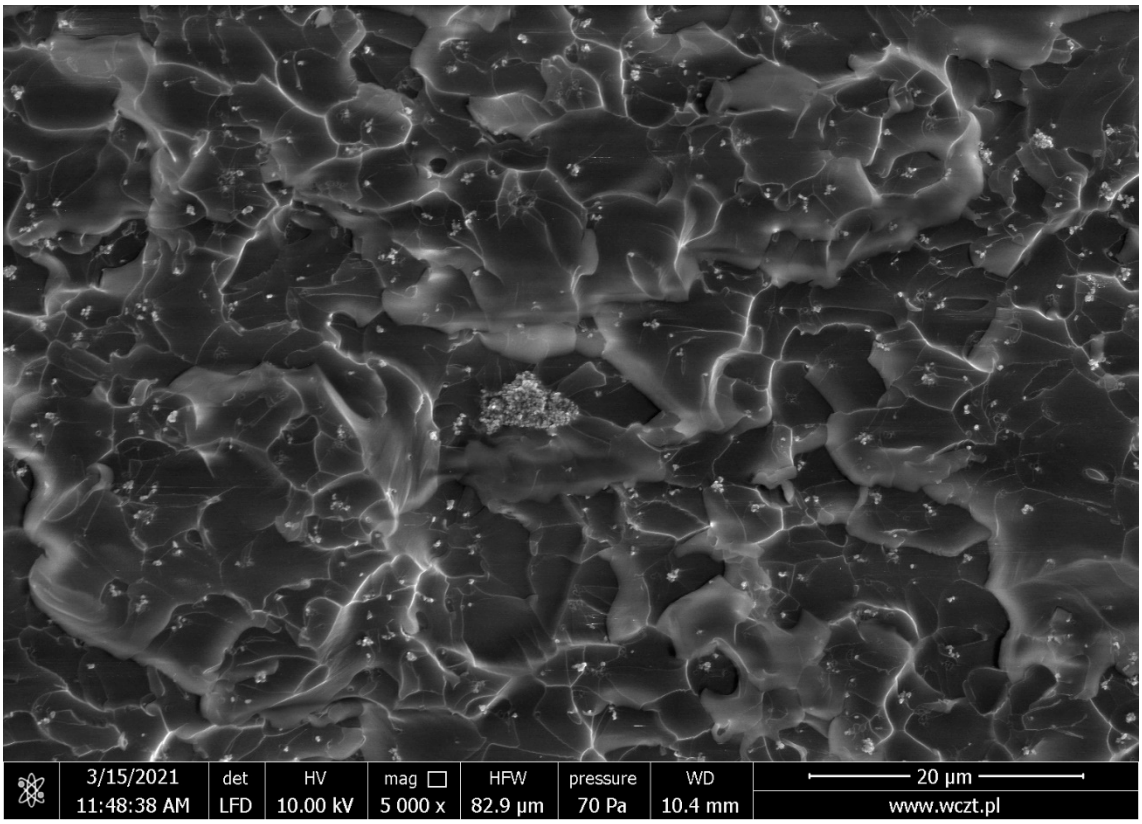


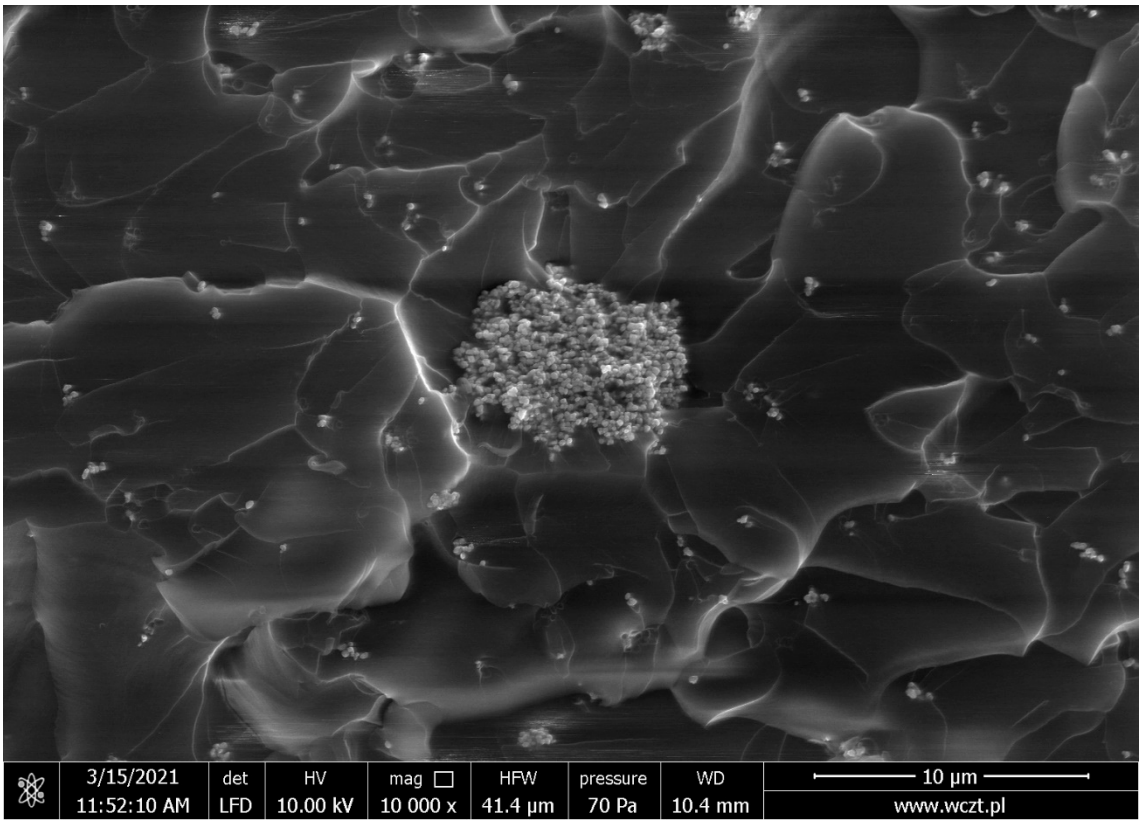




3/4/2021
8:36:33 AM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.7 mm
10 µm
www.wczt.pl

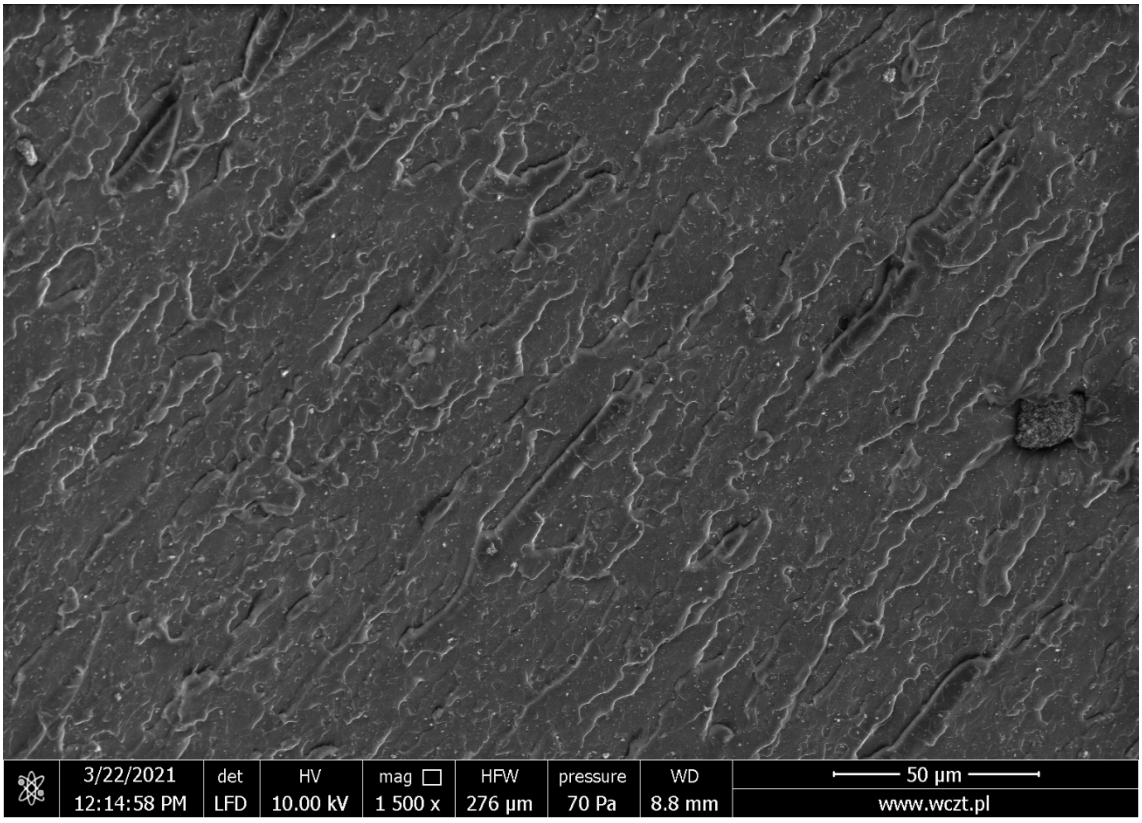
**2%$TiO_2$, 0.5% $iBu_7SSQ$-OEt, mixing pump**

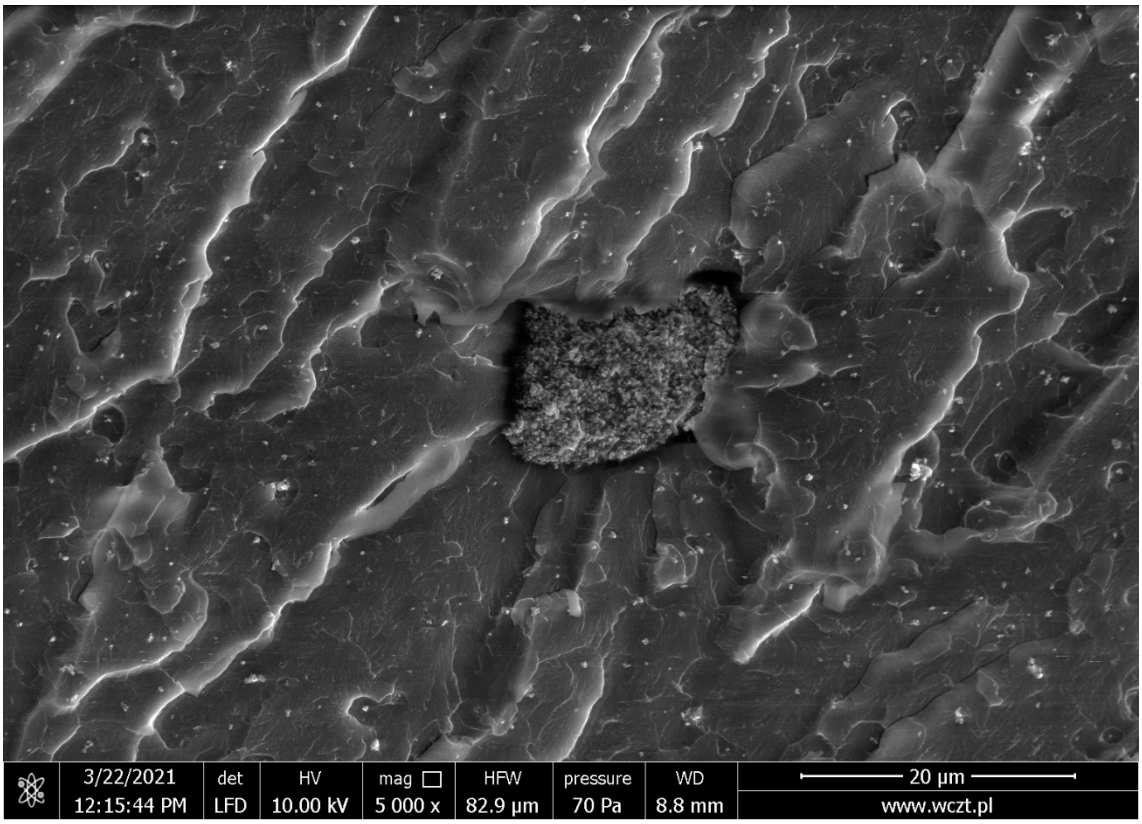


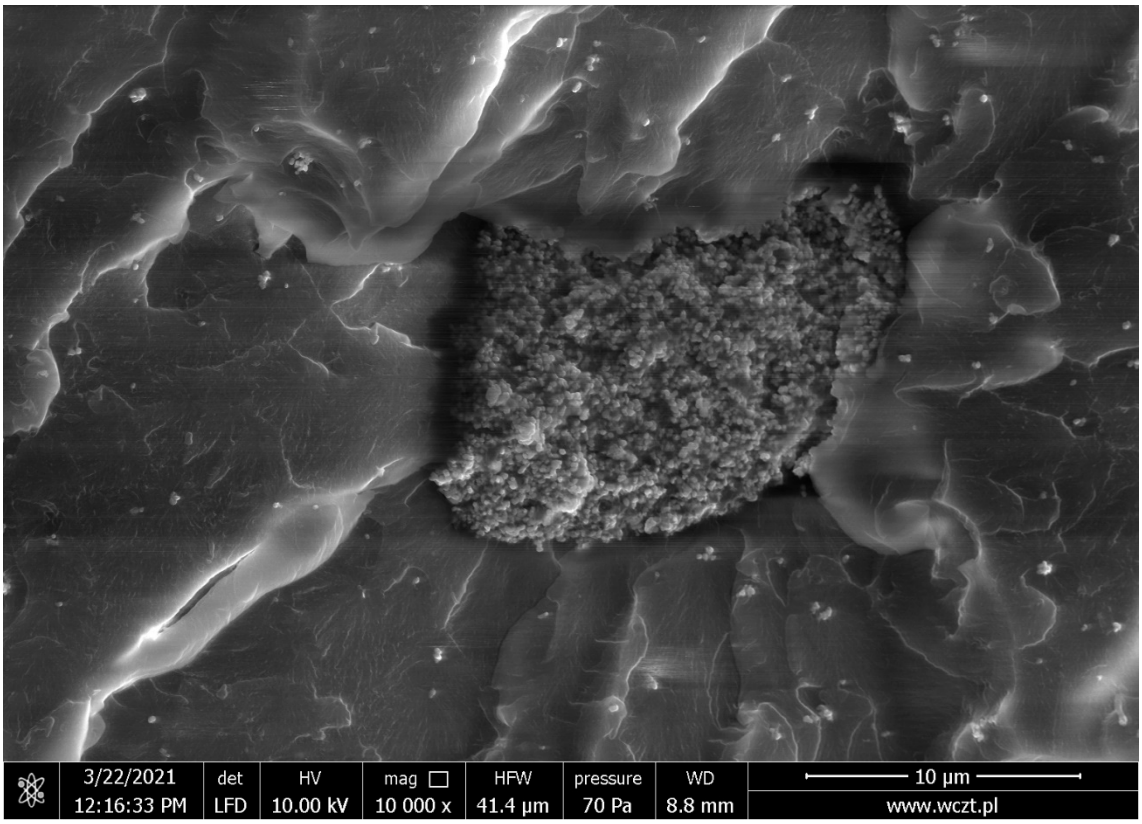




3/15/2021
11:52:10 AM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.4 mm
10 µm
www.wczt.pl

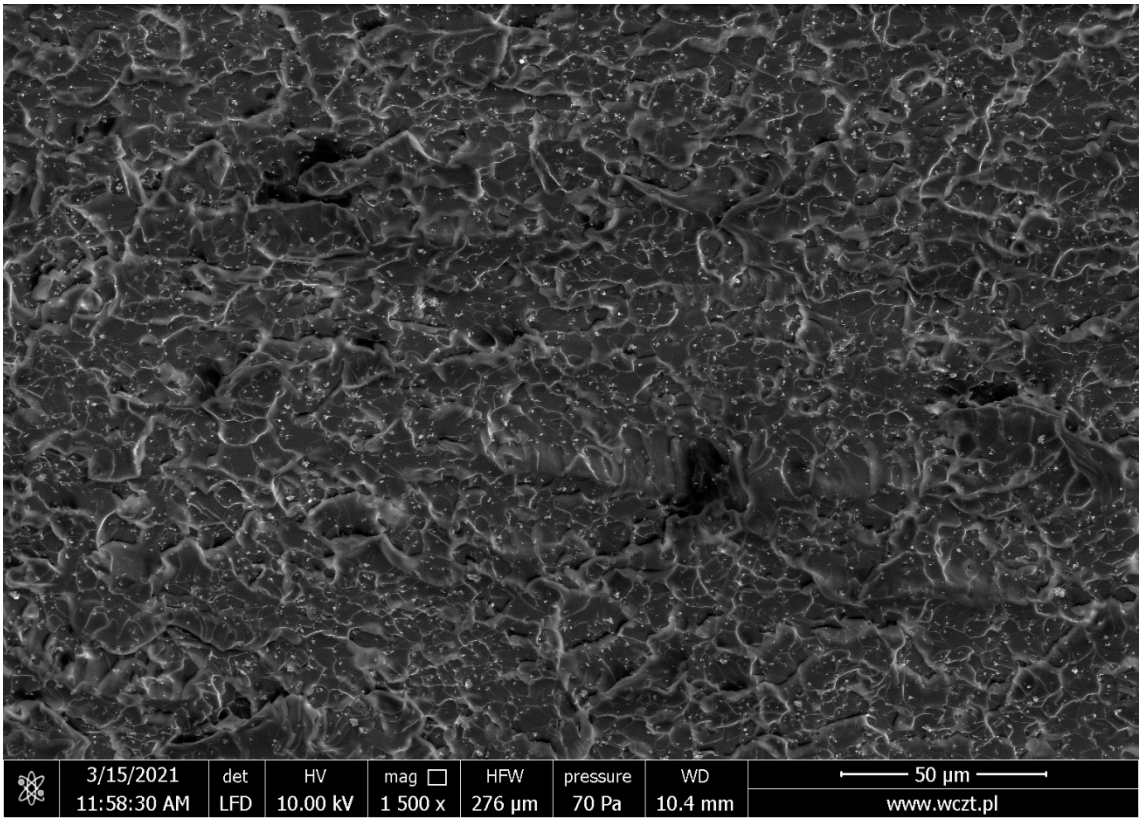
**1%$TiO_2$, 1.5% $iBu_7SSQ$-OEt, mechanical stirrer**

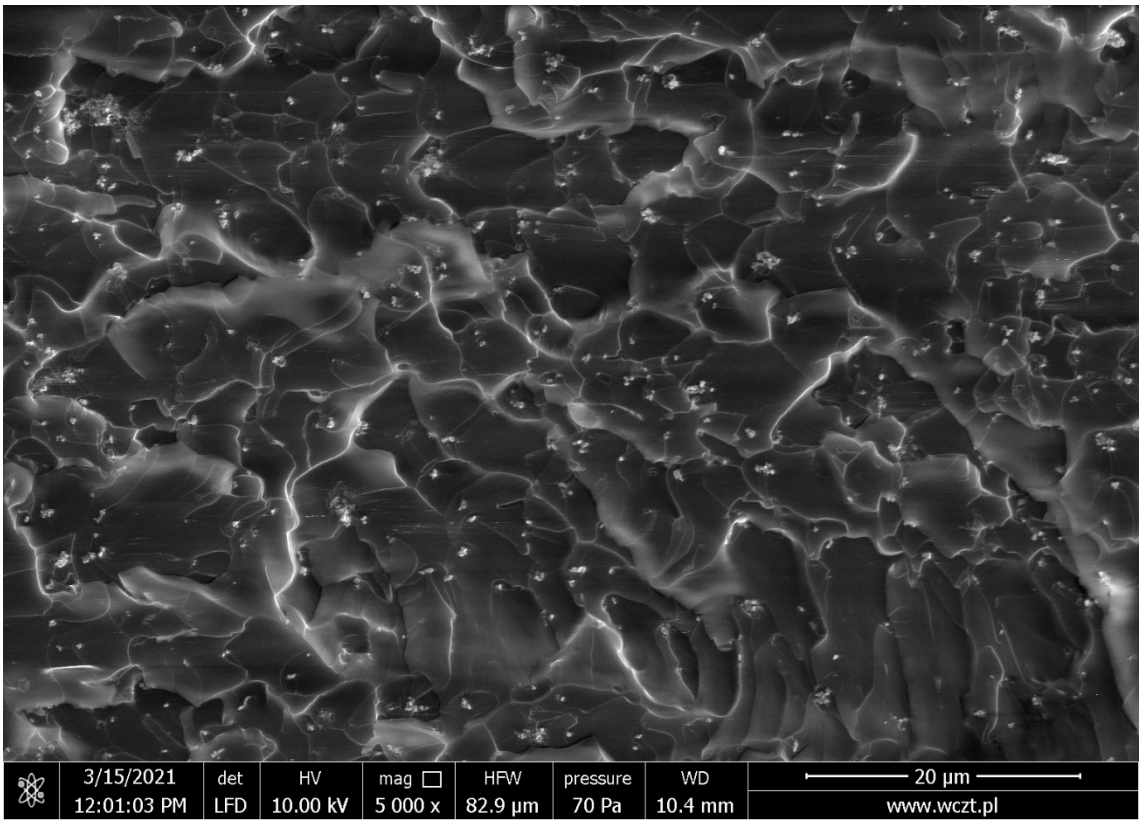


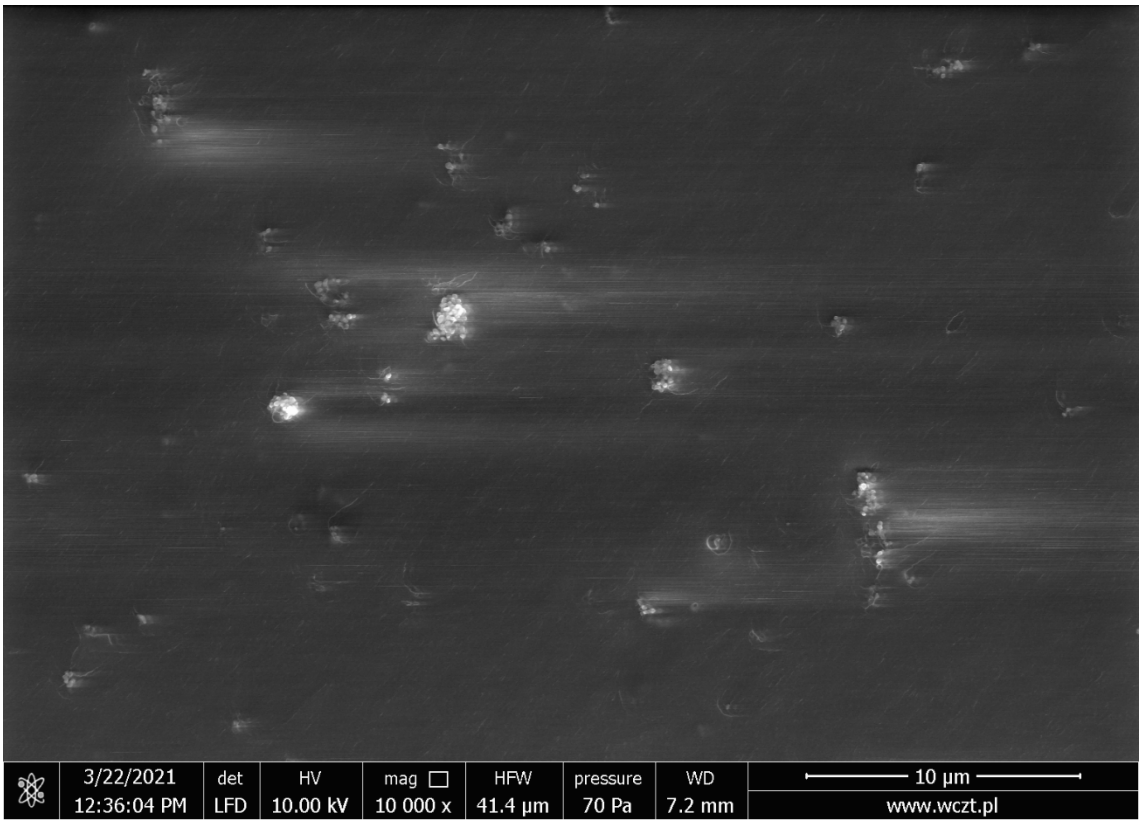




3/22/2021
12:16:33 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
8.8 mm
10 µm
www.wczt.pl

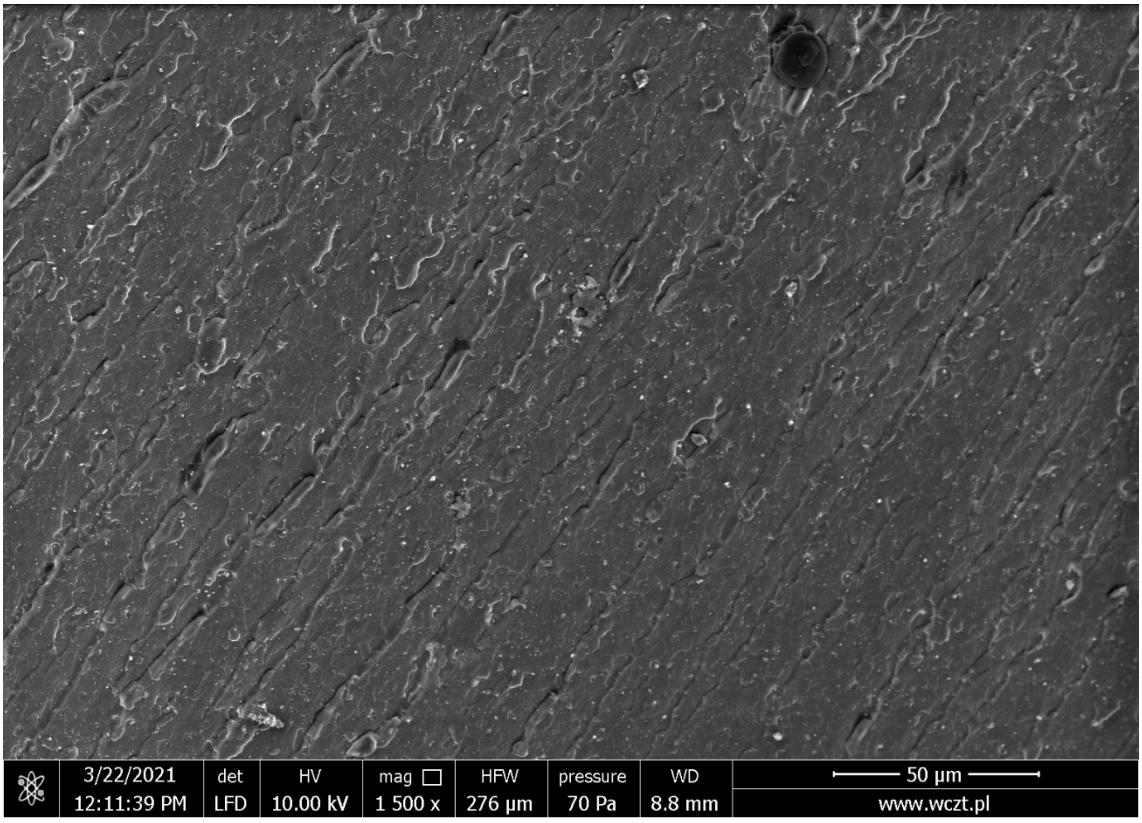
**1%$TiO_2$, 1.5% $iBu_7SSQ$-OEt, mixing pump**

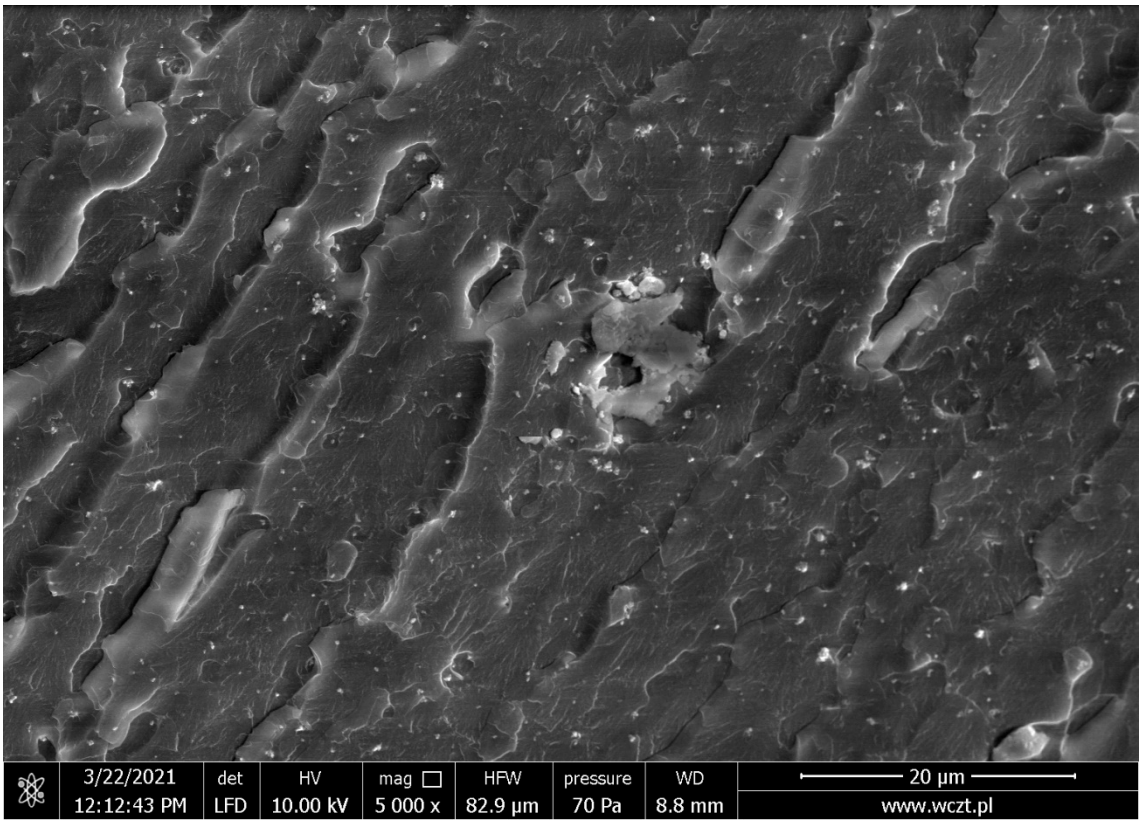


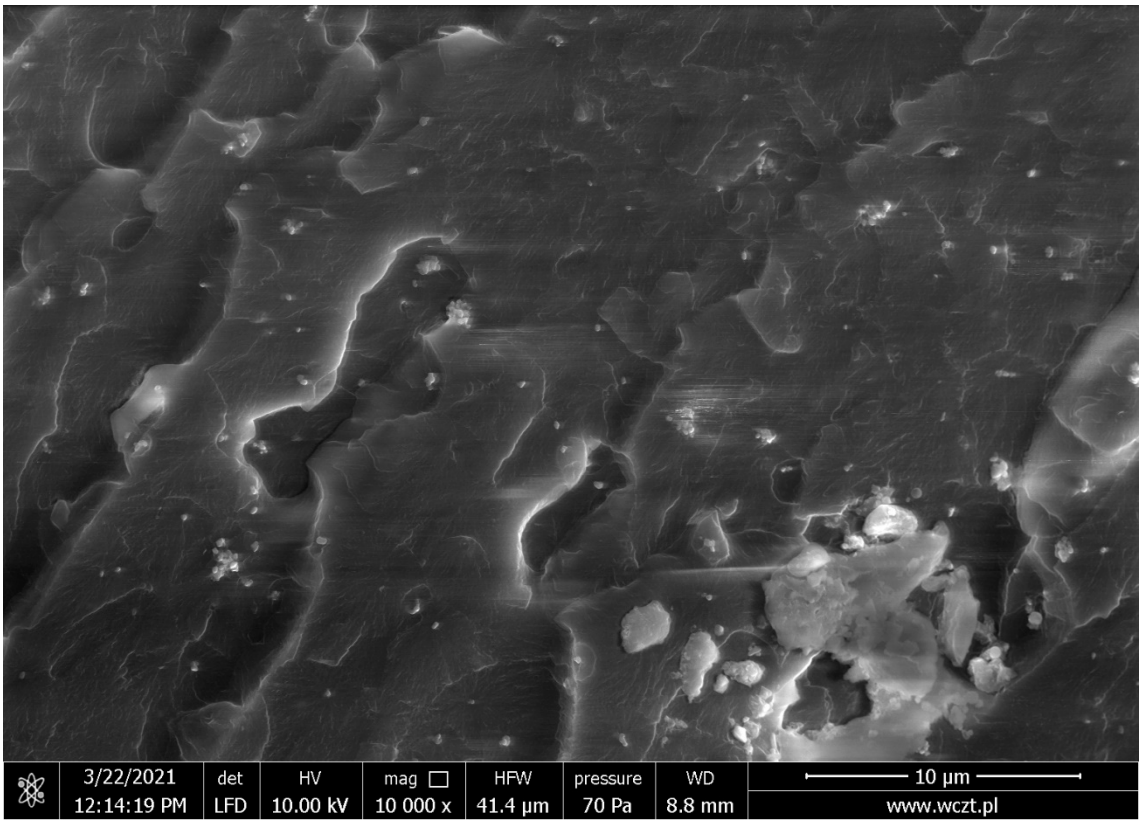




3/22/2021
12:36:04 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
7.2 mm
10 µm
www.wczt.pl

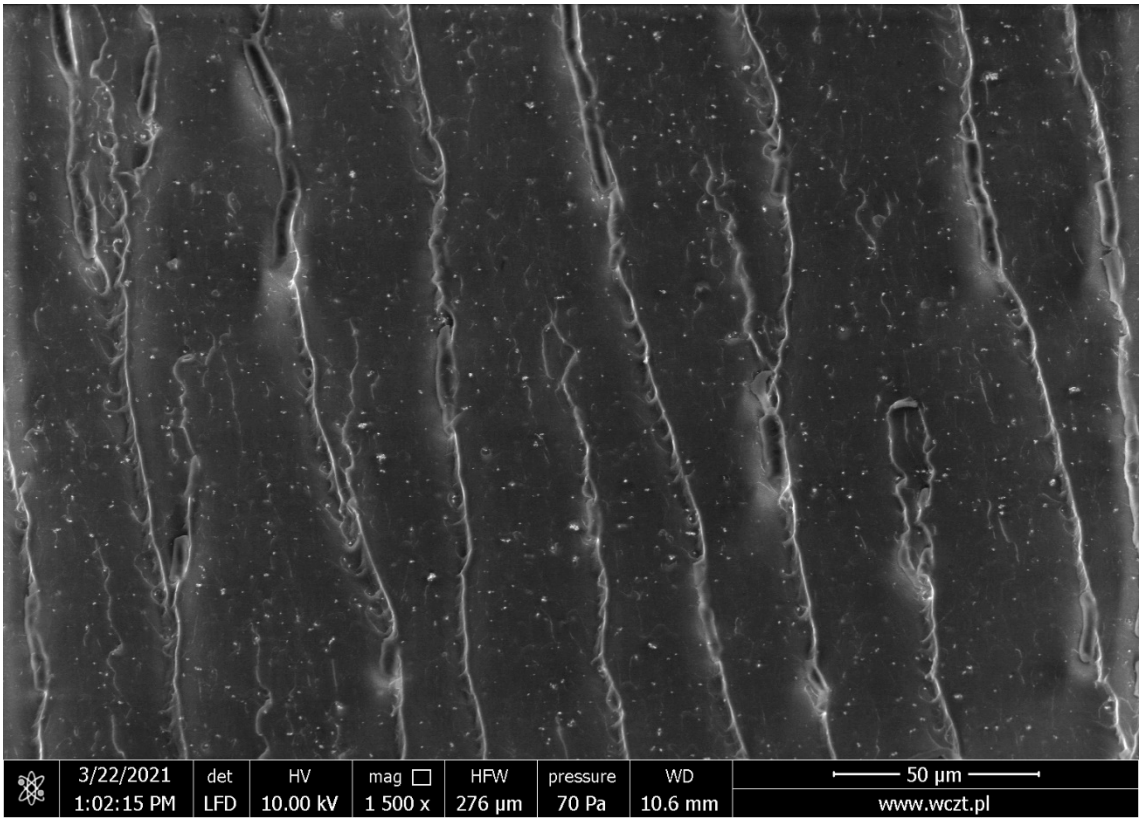
**2%$TiO_2$, 1.5% $iBu_7SSQ$-OEt, mixing pump**

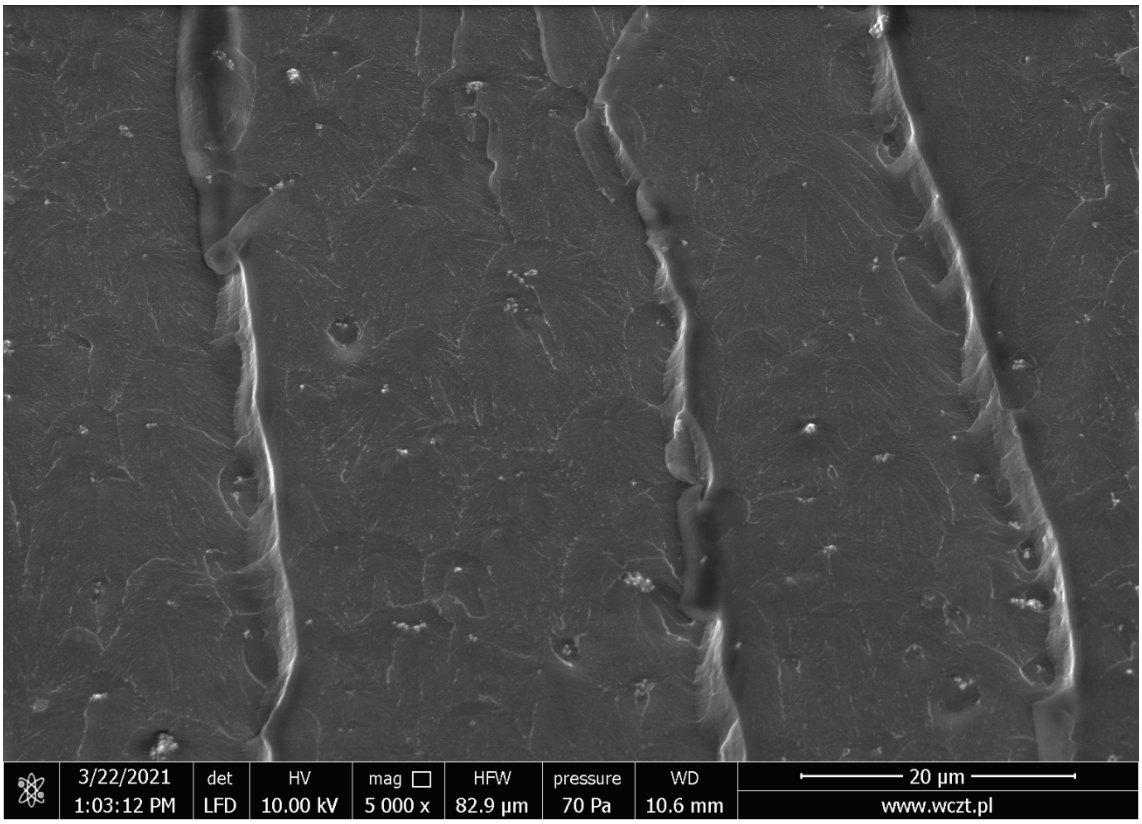


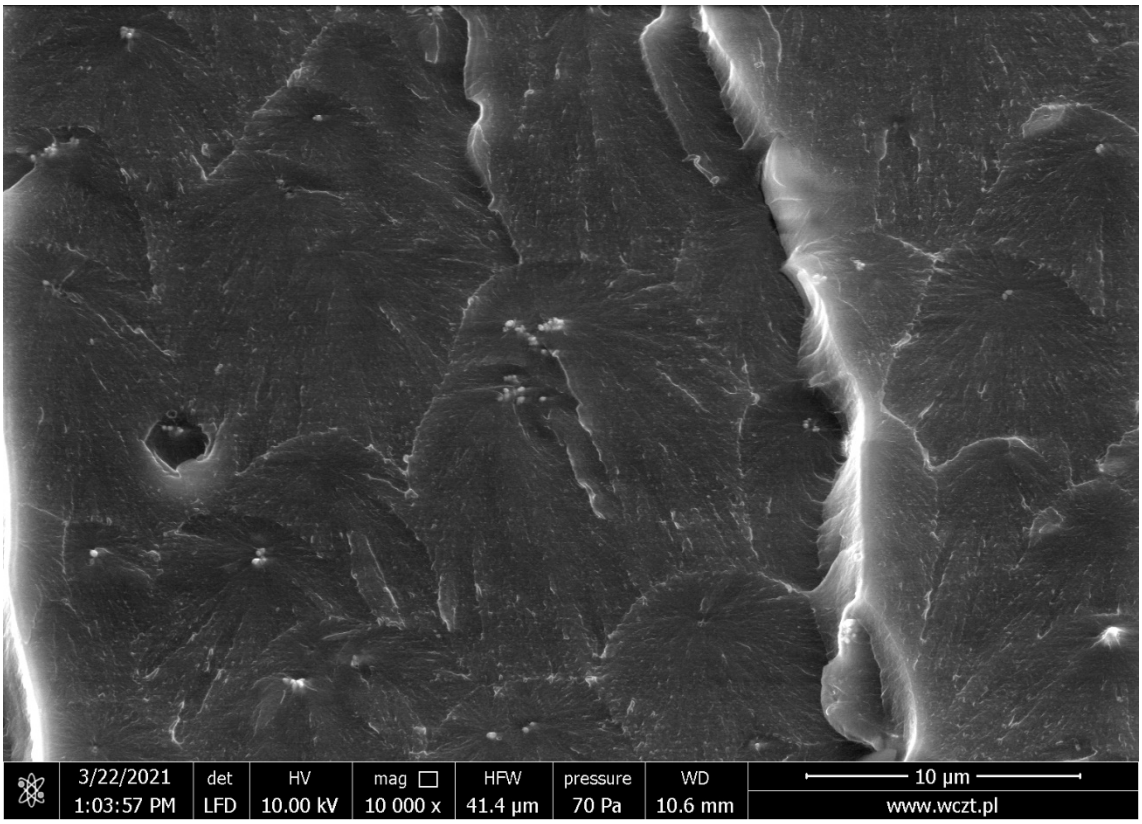




3/22/2021
12:14:19 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
8.8 mm
10 µm
www.wczt.pl

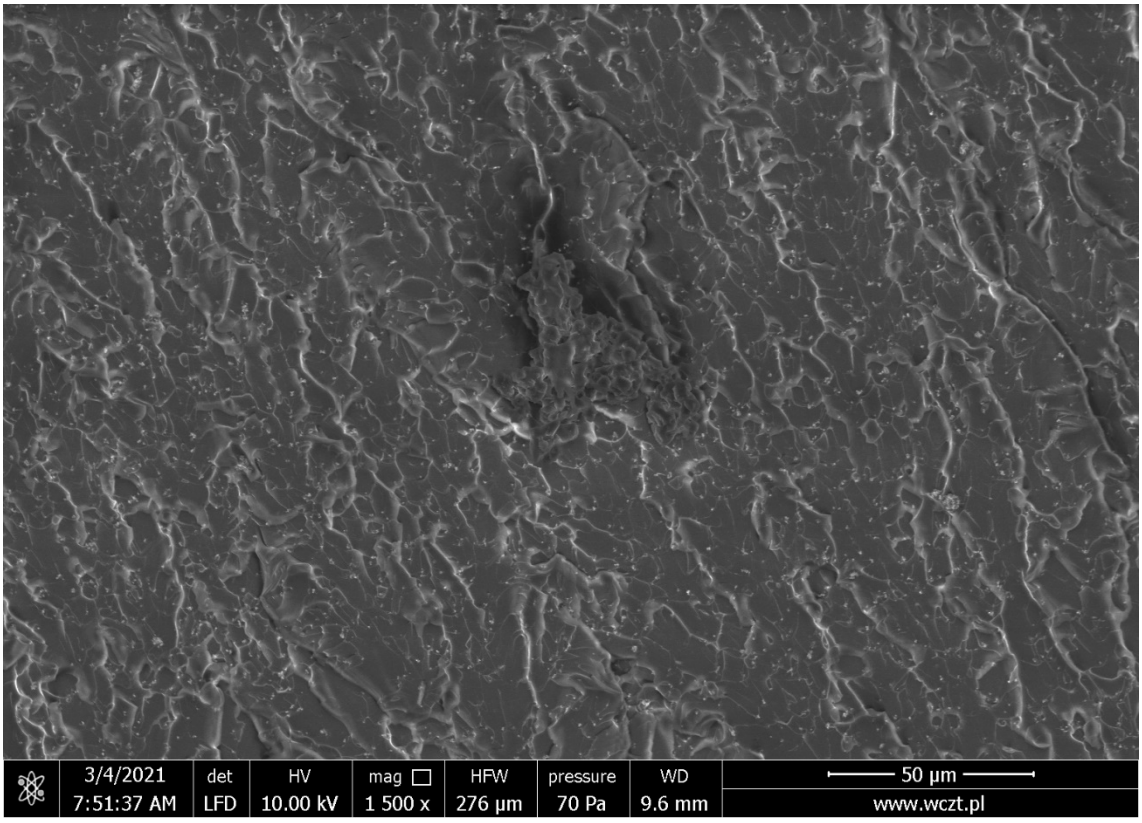
**1%$TiO_2$, 0.5% SS-6GP-2TMOS, mixing pump**

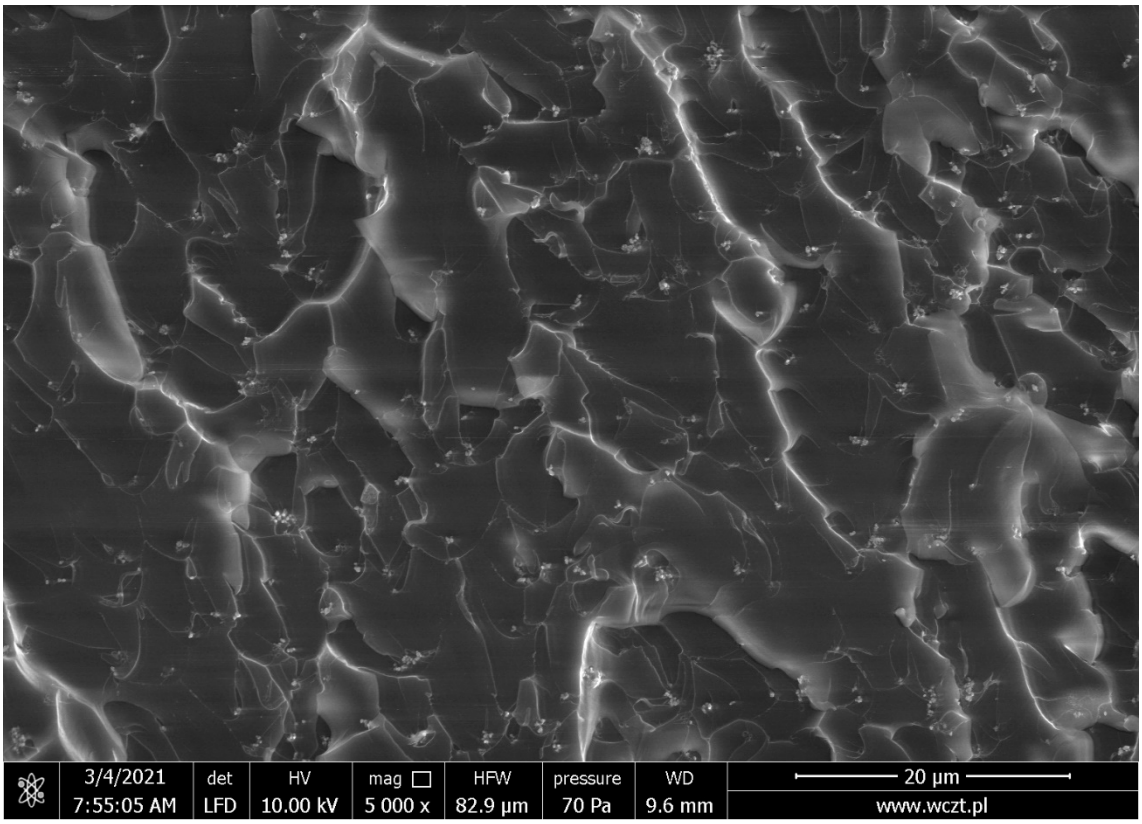


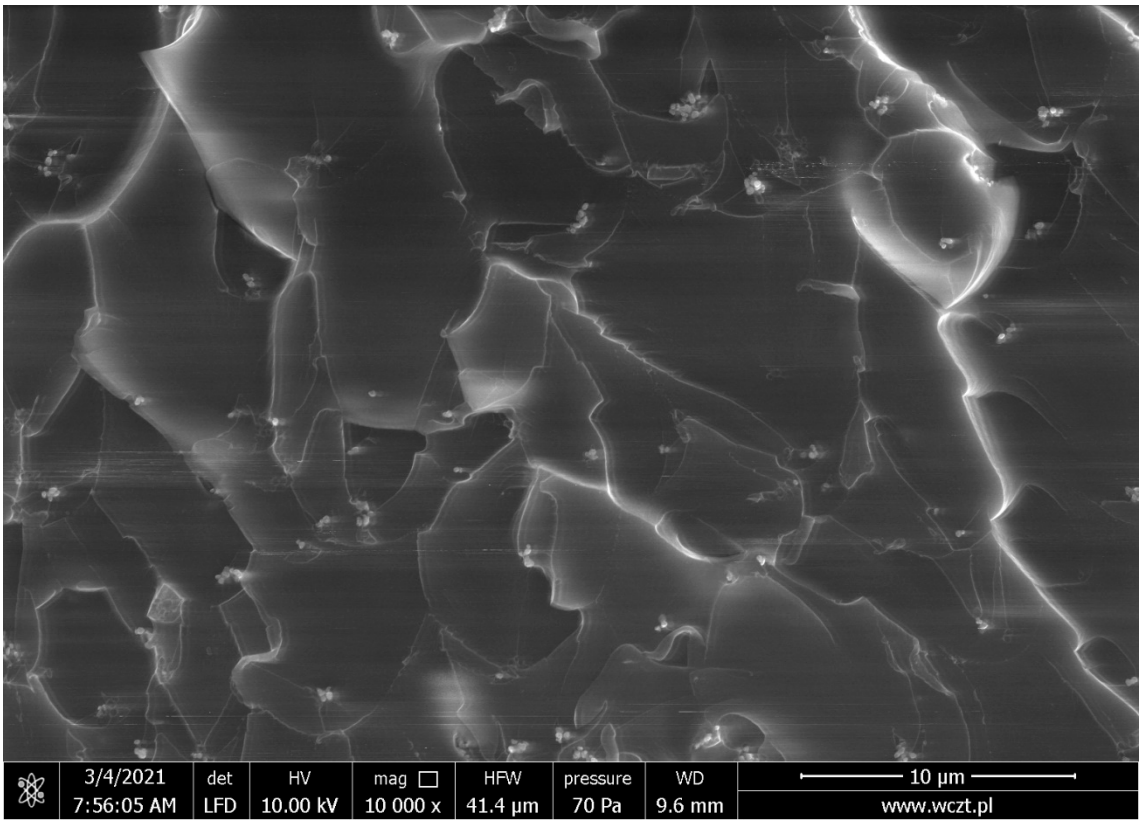




3/22/2021
1:03:57 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.6 mm
10 µm
www.wczt.pl

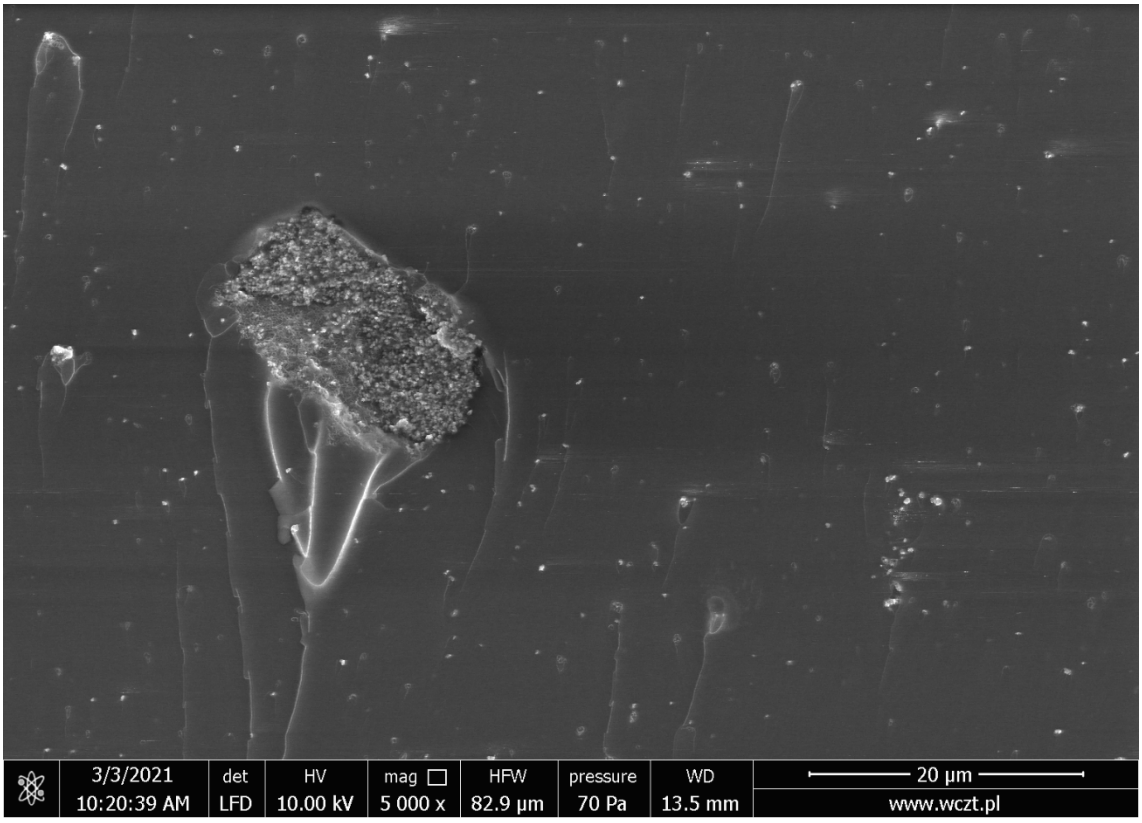
**2%$TiO_2$, 0.5% SS-6GP-2TMOS, mixing pump**

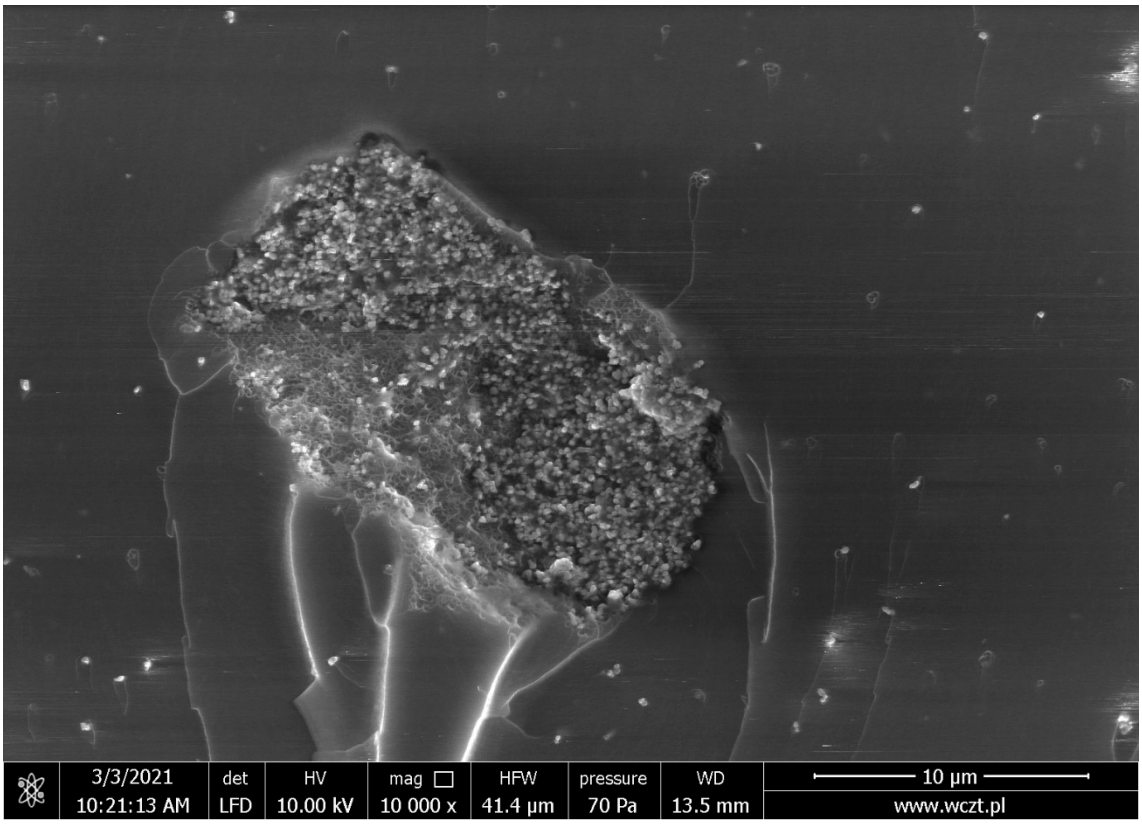


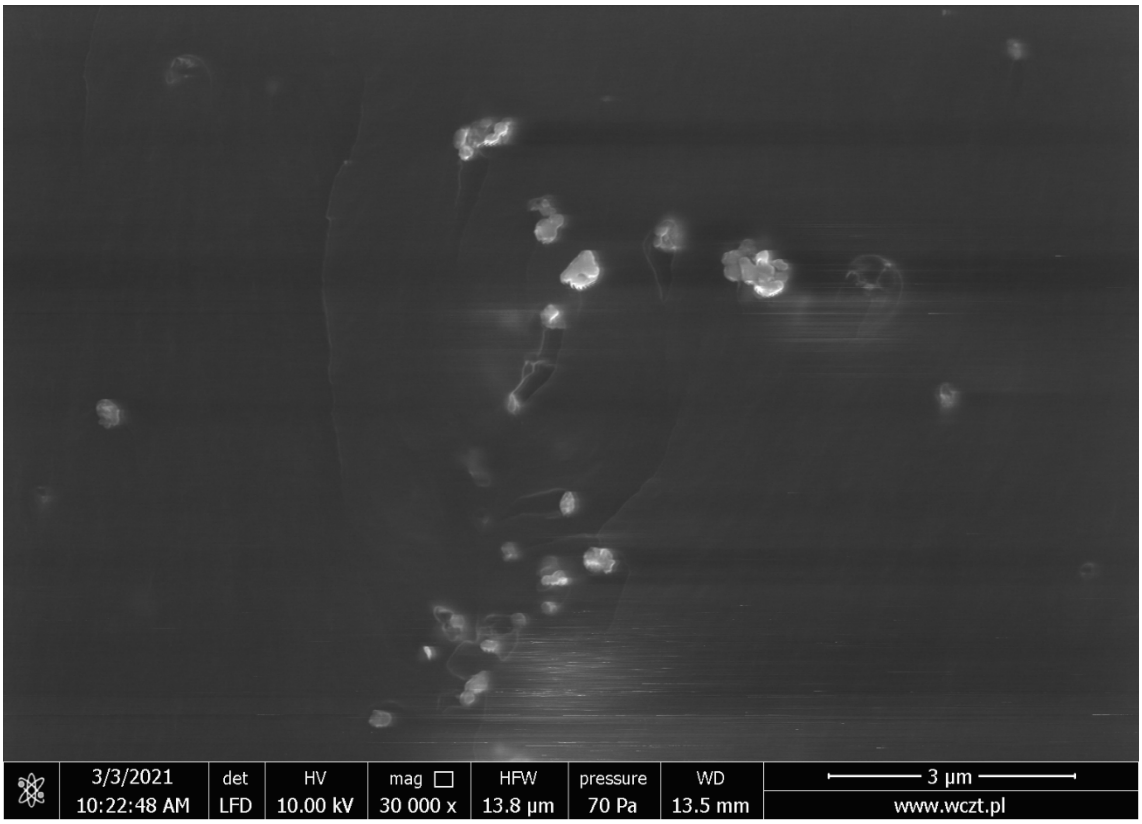




3/4/2021
7:56:05 AM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
9.6 mm
10 µm
www.wczt.pl

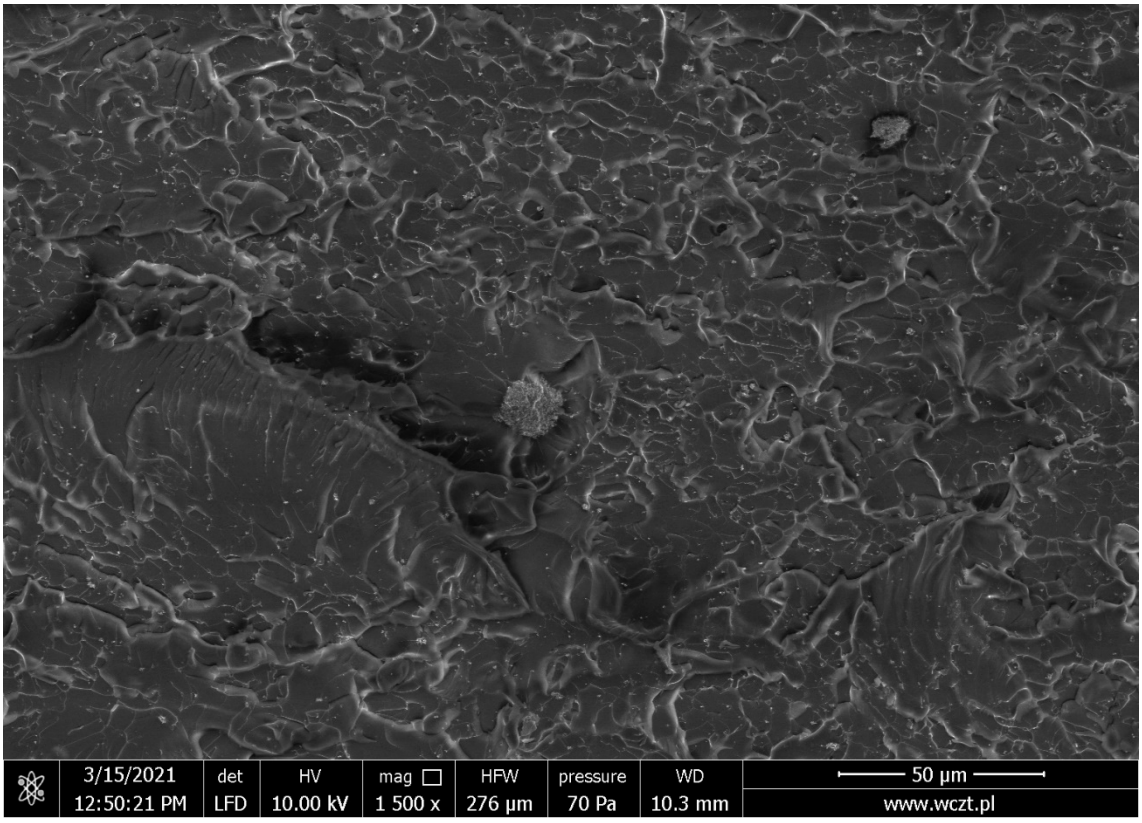
**1%$TiO_2$, 1.5% SS-6GP-2TMOS, mechanical stirrer**

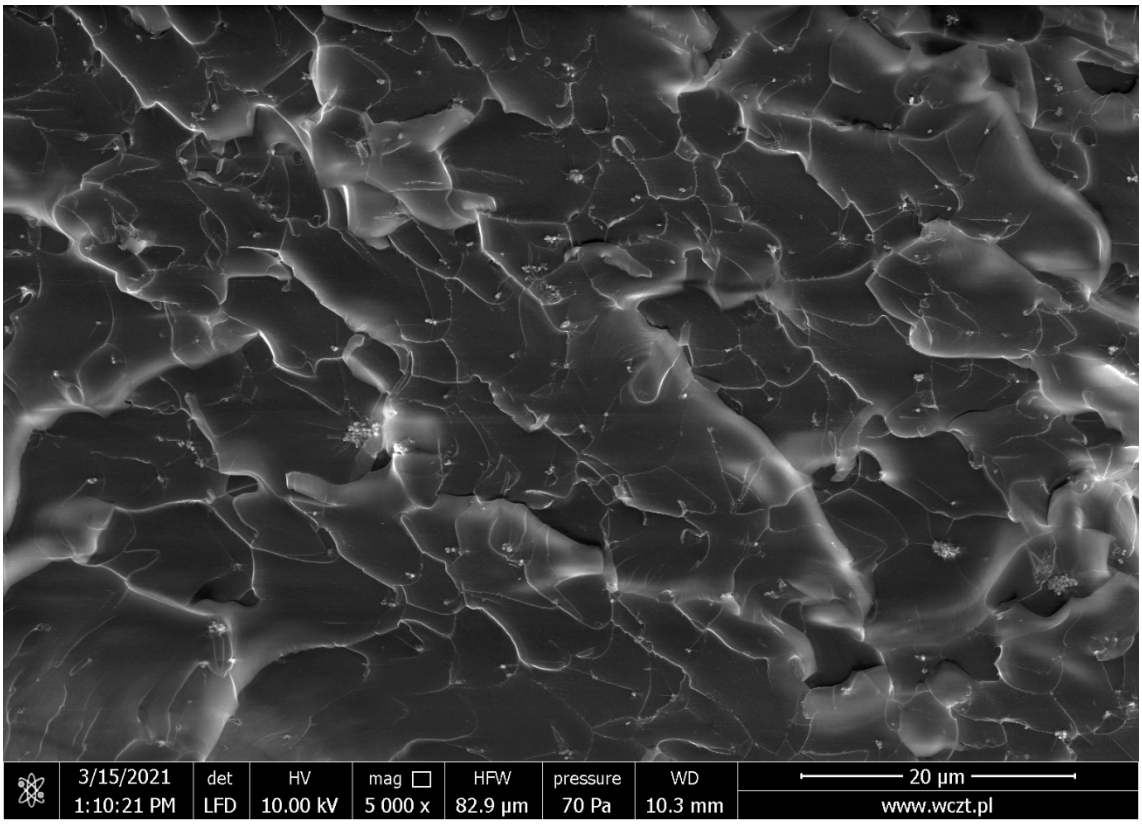


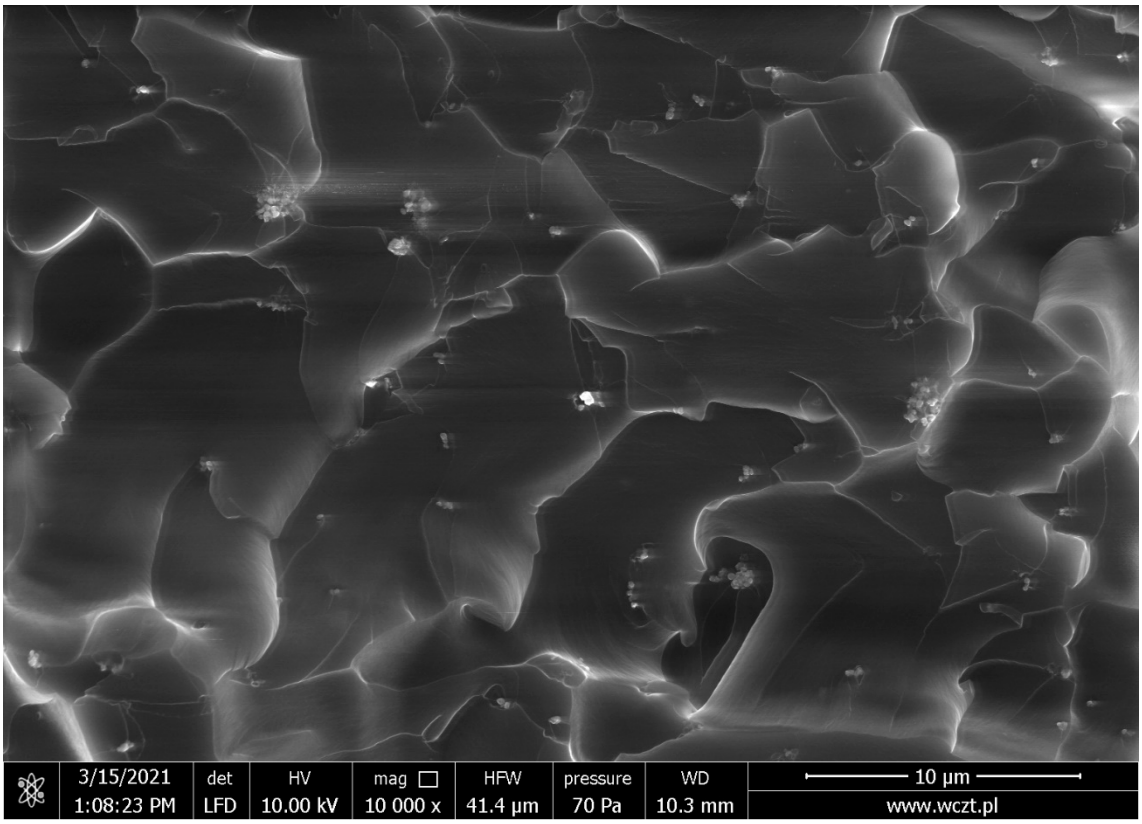




3/3/2021
10:22:48 AM
det
LFD
HV
10.00 kV
mag
30 000 x
HFW
13.8 µm
pressure
70 Pa
WD
13.5 mm
3 µm
www.wczt.pl

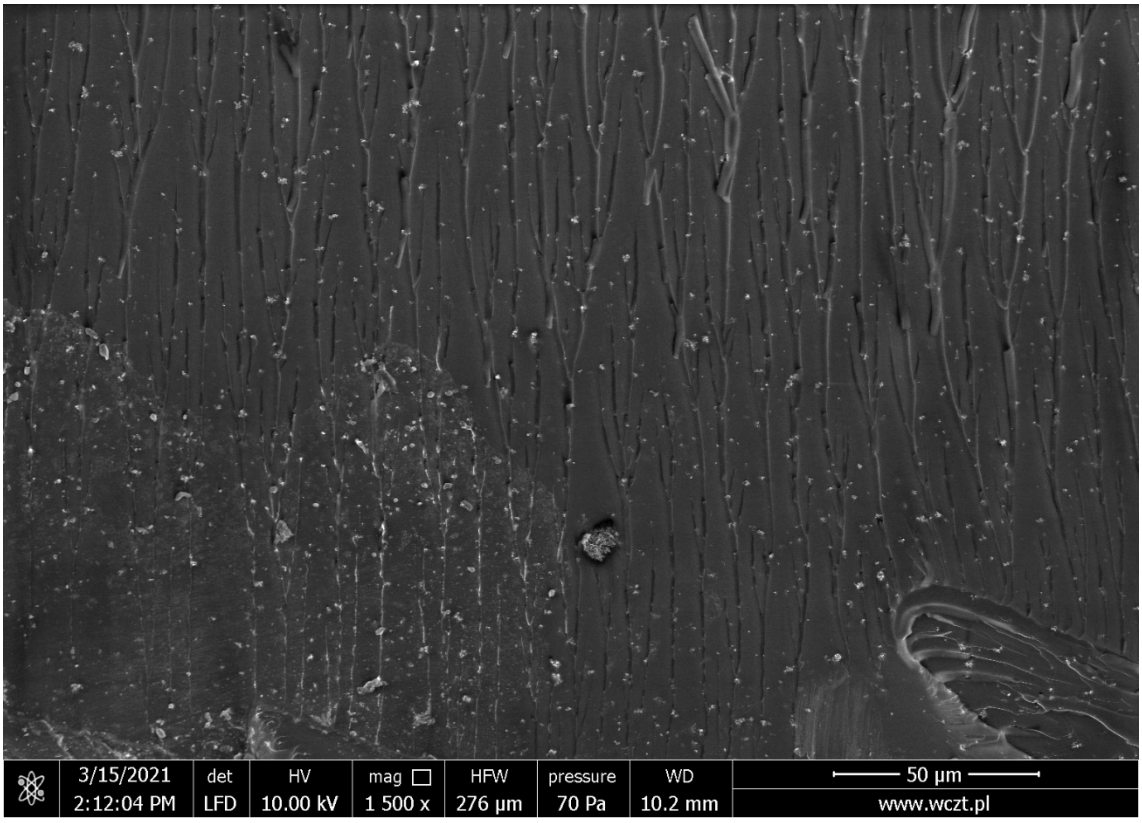
**1%$TiO_2$, 1.5% SS-6GP-2TMOS, mixing pump**

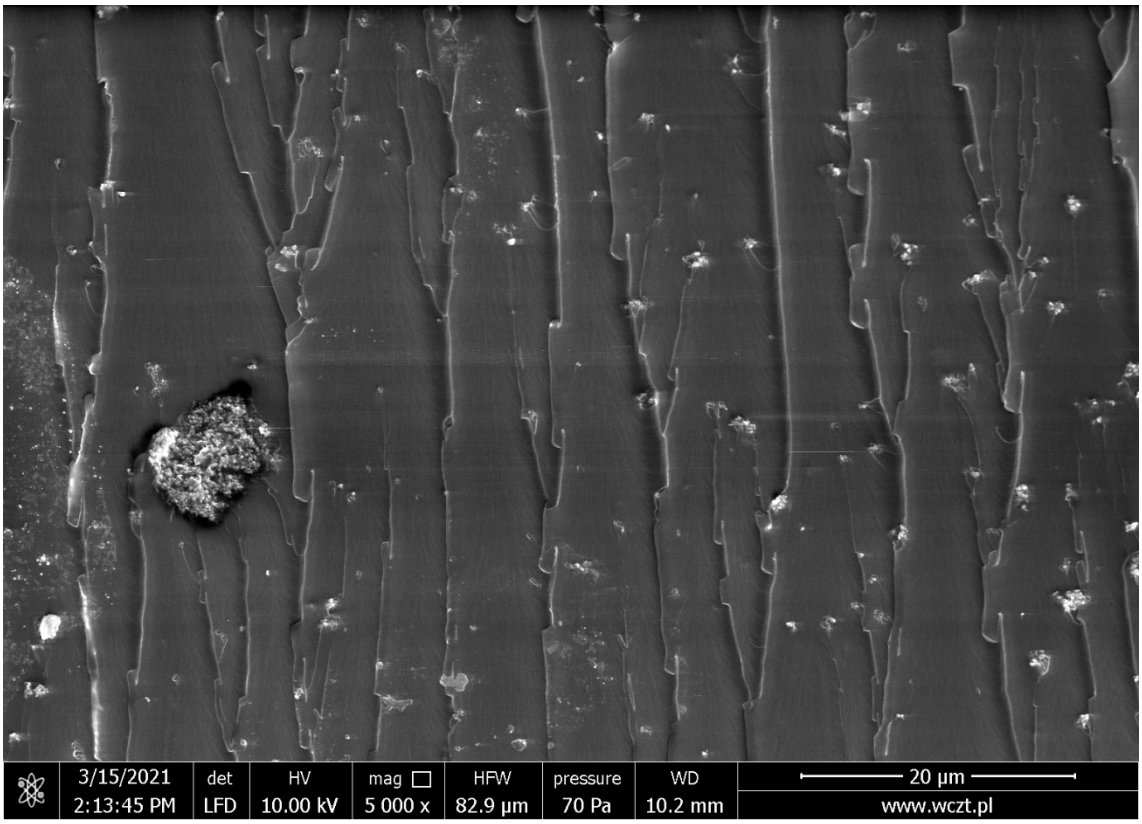


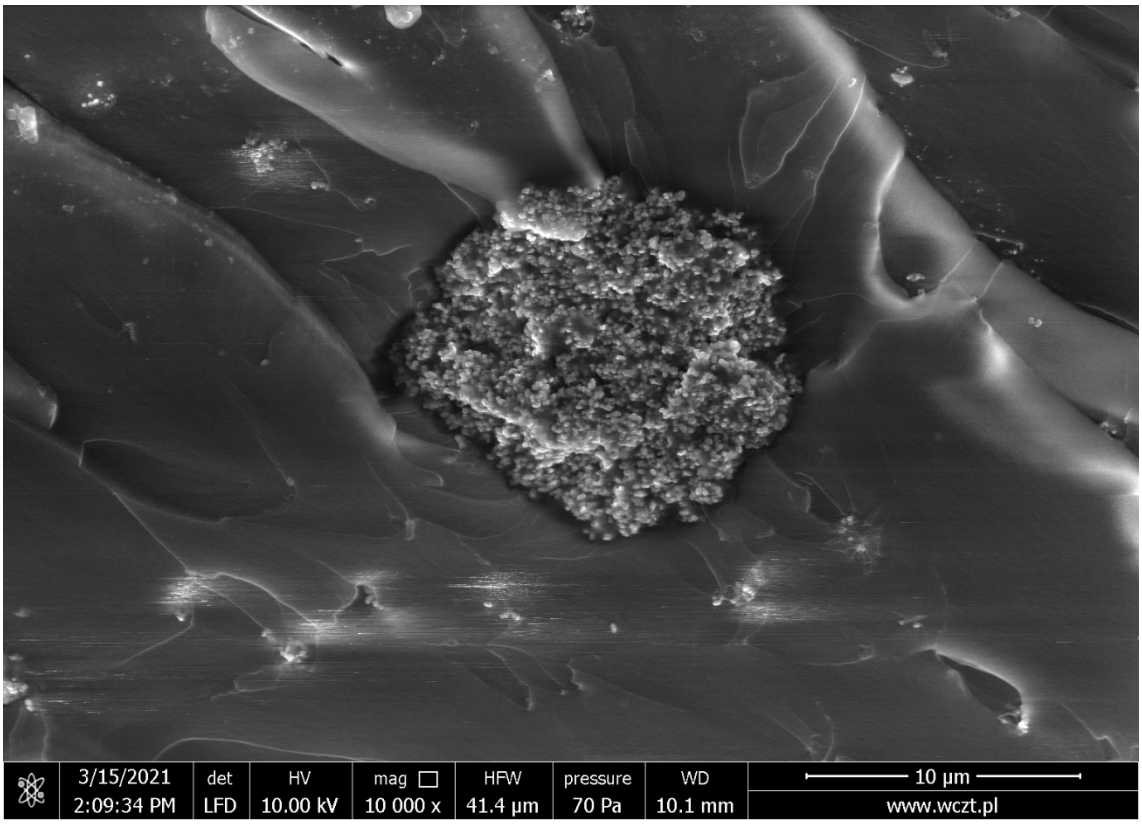




3/15/2021
1:08:23 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.3 mm
10 µm
www.wczt.pl

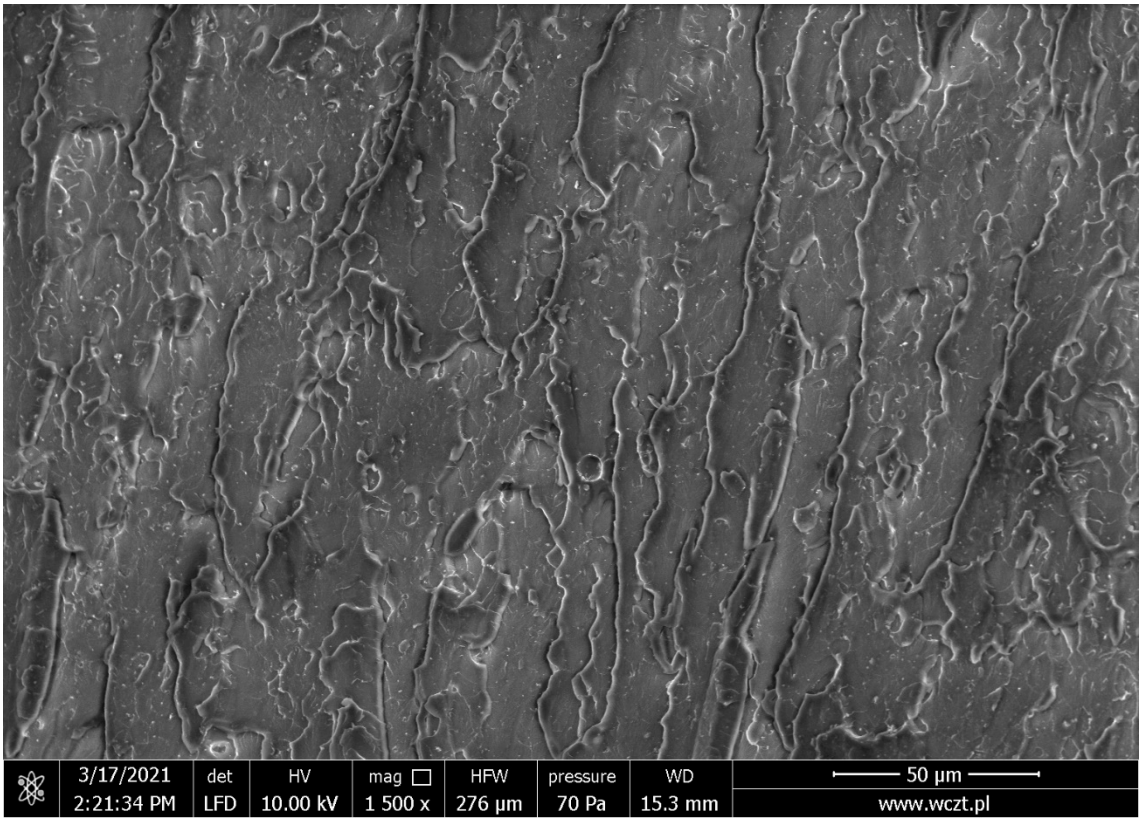
**2%$TiO_2$, 1.5% SS-6GP-2TMOS, mixing pump**

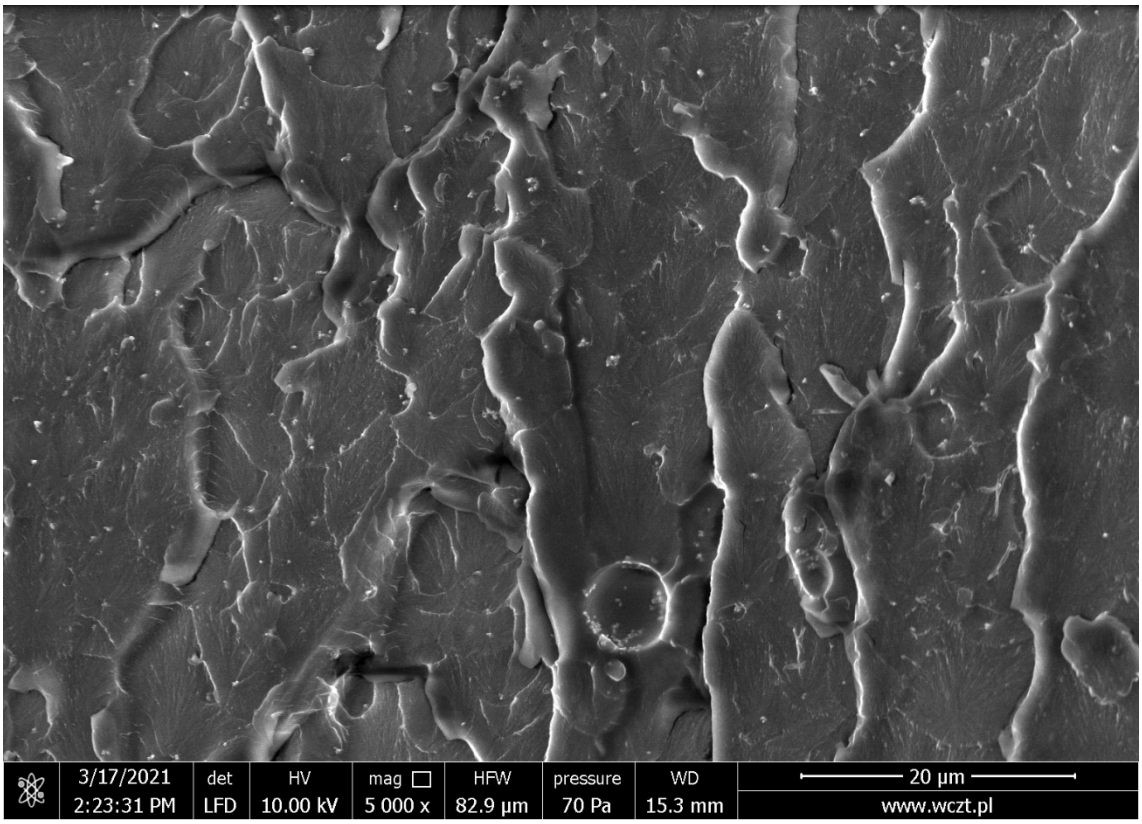


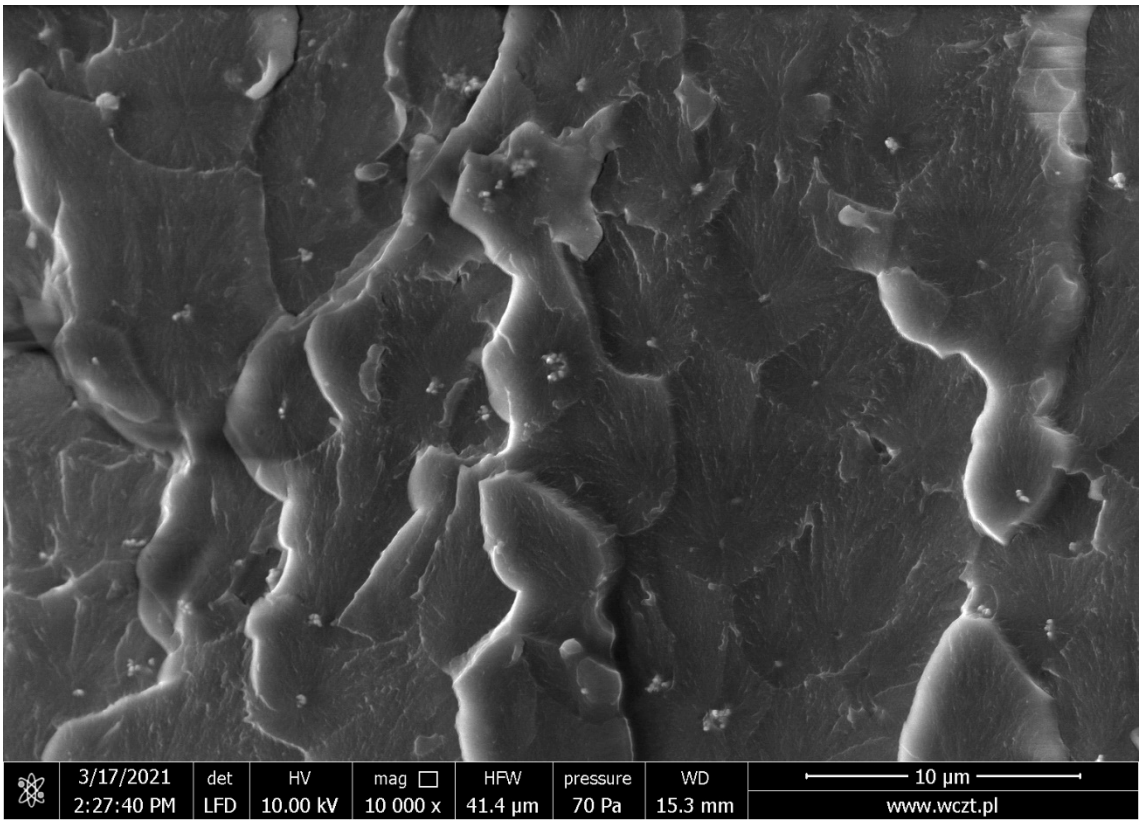




3/15/2021
2:09:34 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.1 mm
10 µm
www.wczt.pl

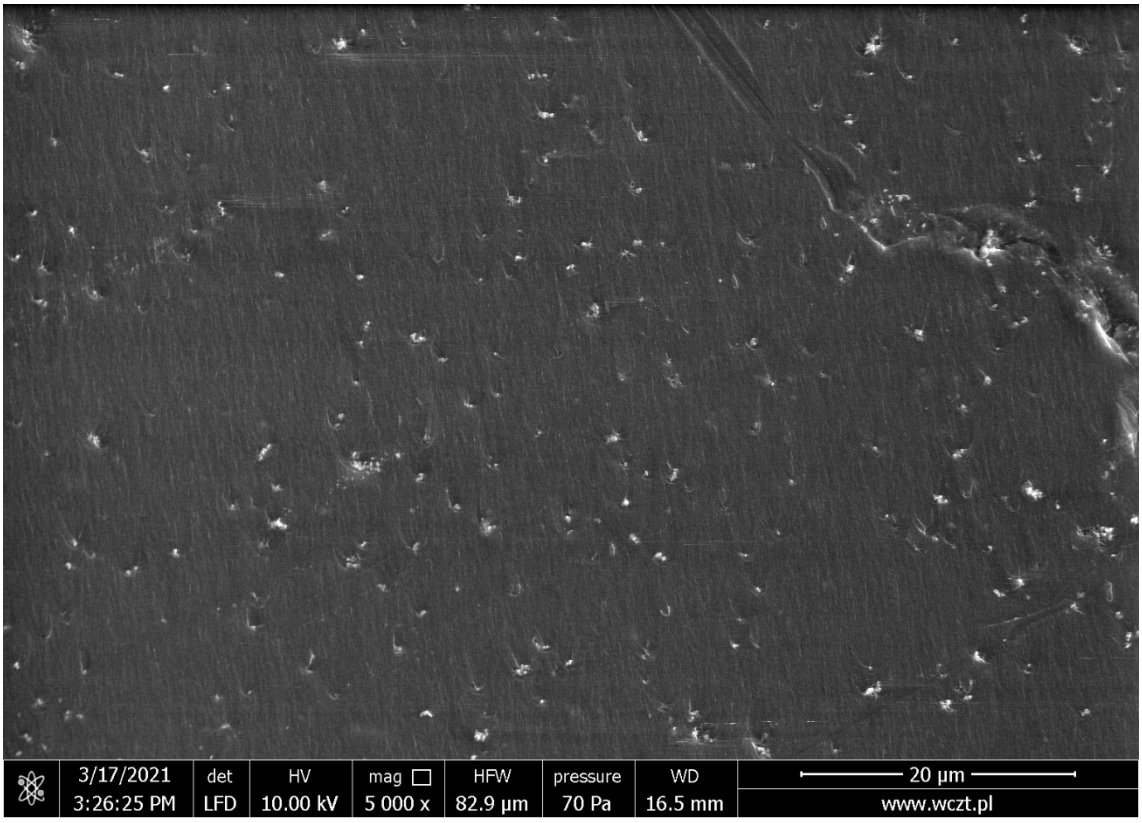
**1%$TiO_2$, 0.5% SS-5GP-3TMOS, mixing pump**

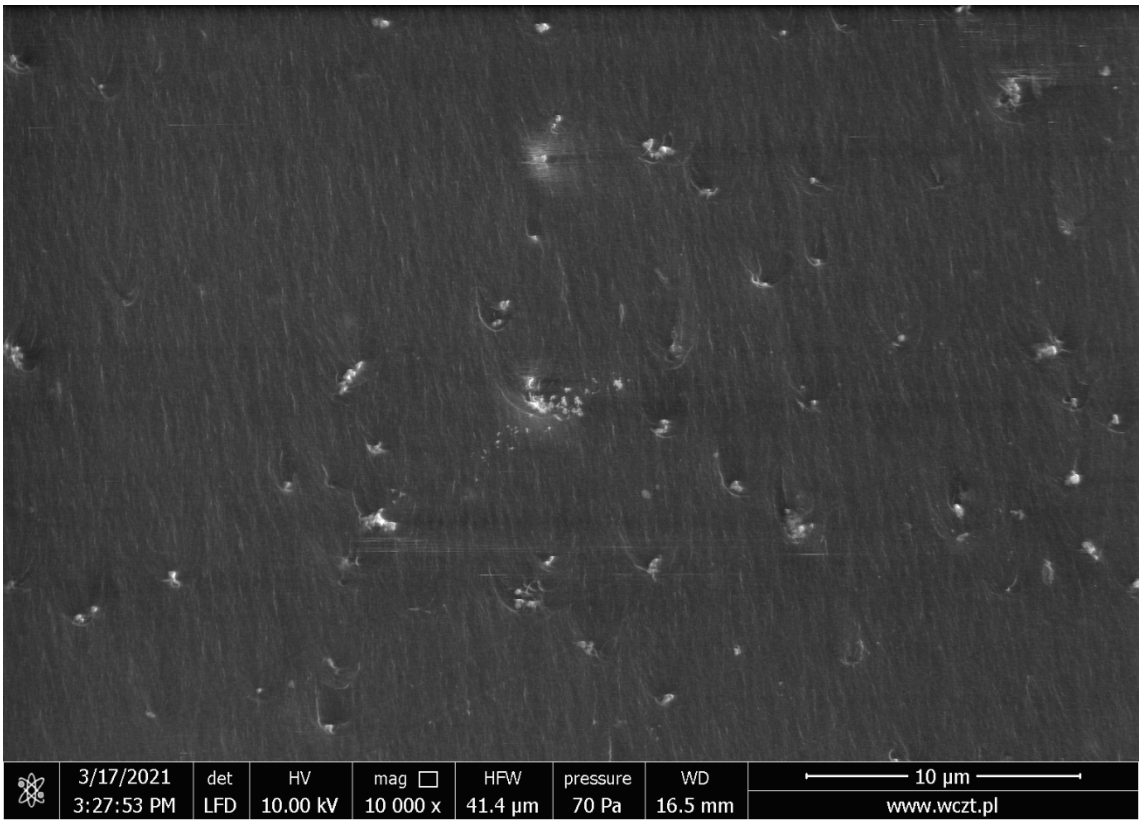


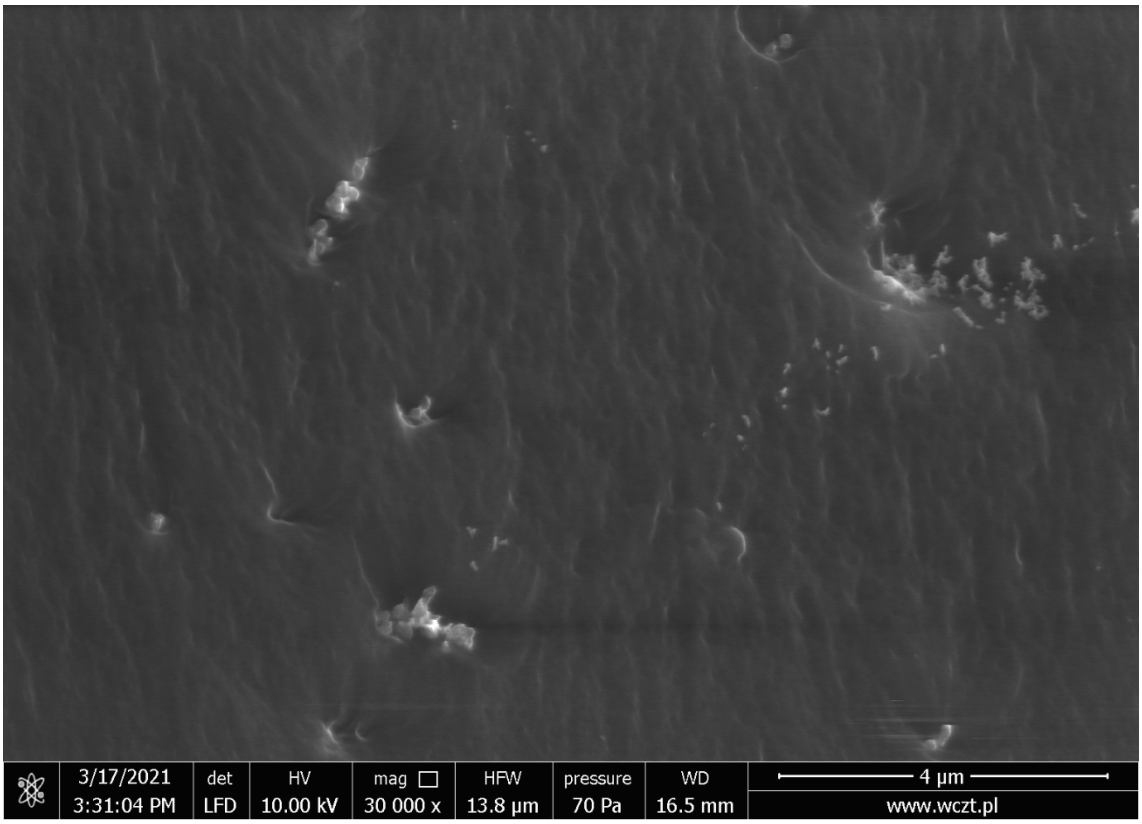




3/17/2021
2:27:40 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
15.3 mm
10 µm
www.wczt.pl

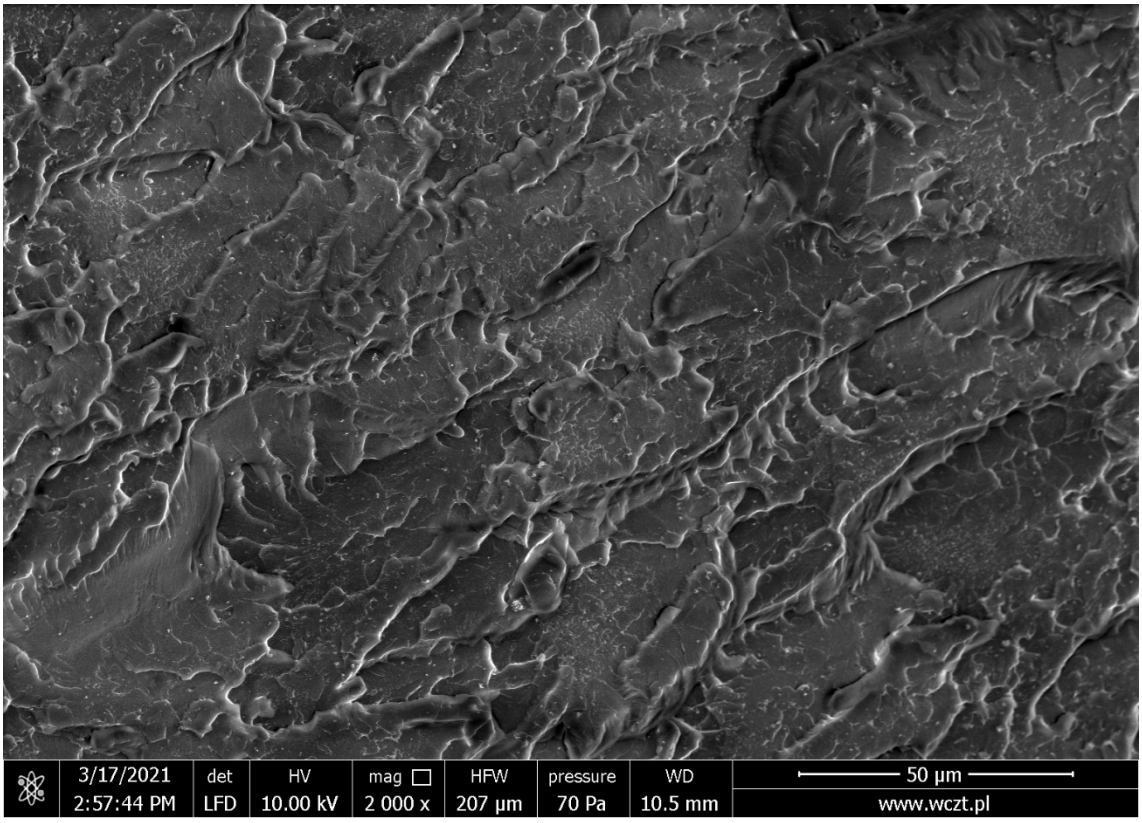
**2%$TiO_2$, 0.5% SS-5GP-3TMOS, mixing pump**

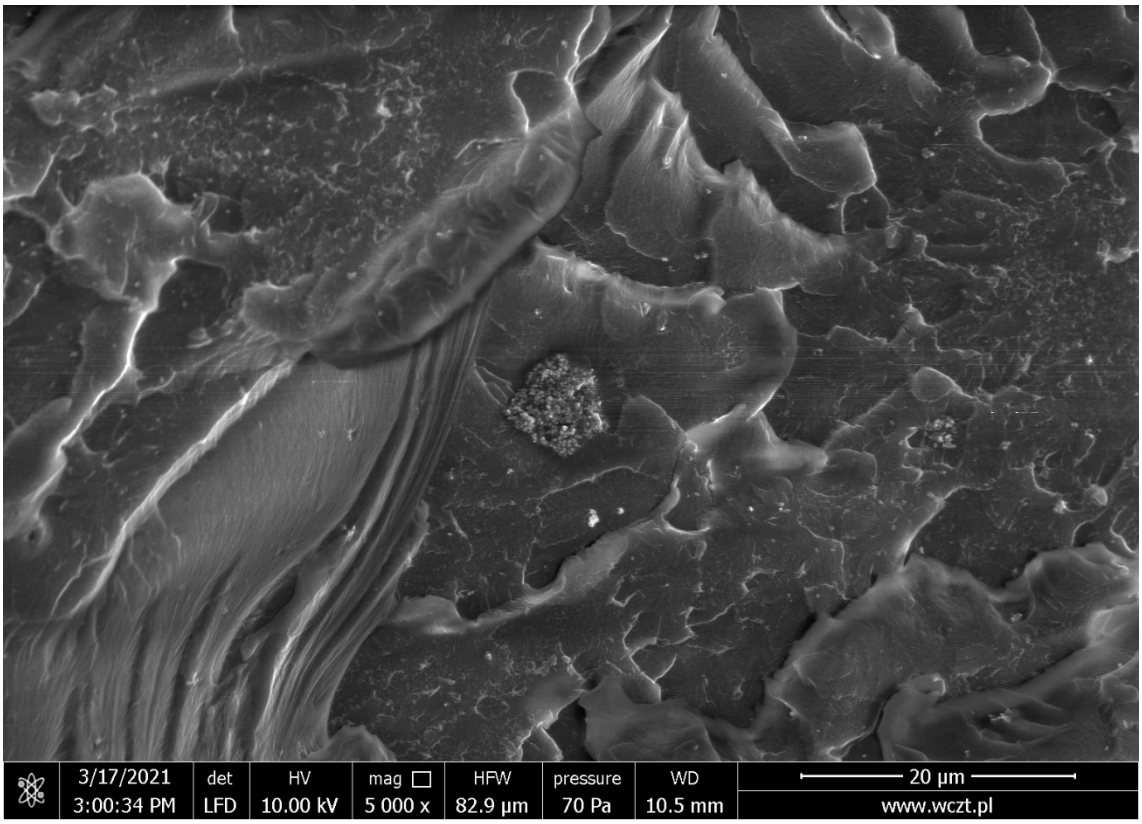


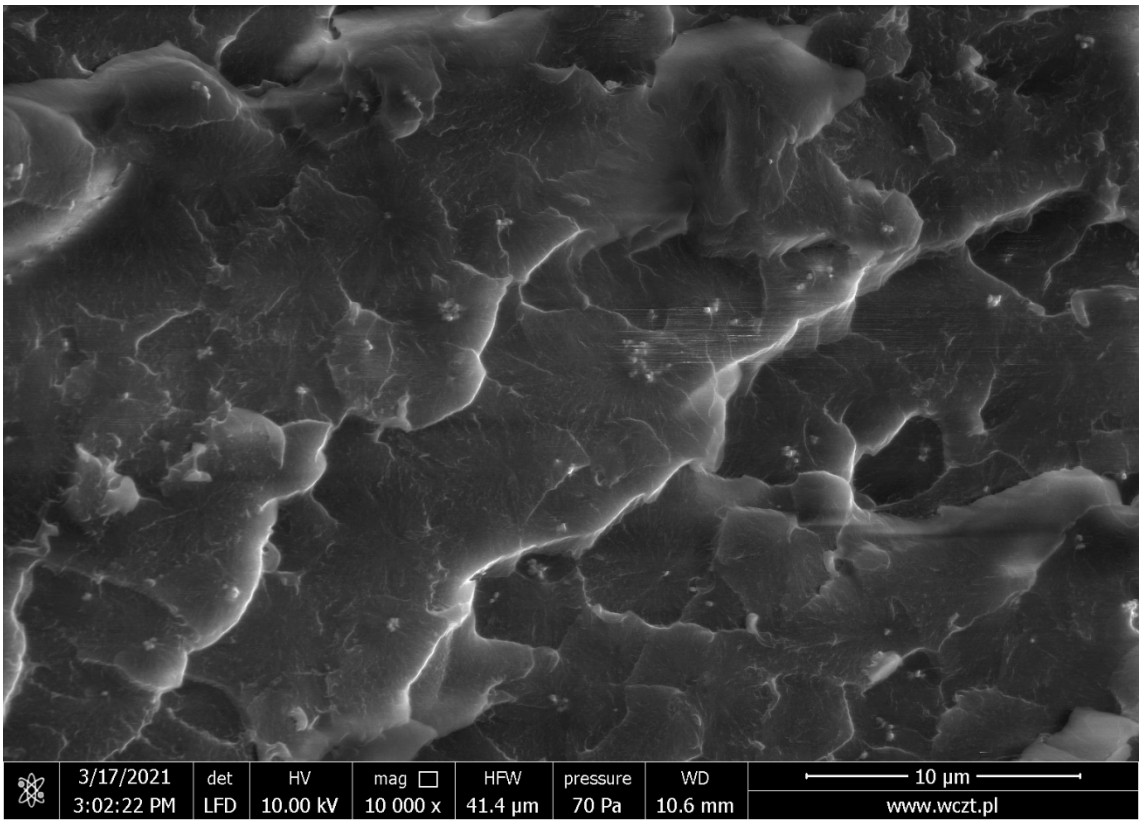




3/17/2021
3:31:04 PM
det
LFD
HV
10.00 kV
mag
30 000 x
HFW
13.8 µm
pressure
70 Pa
WD
16.5 mm
4 µm
www.wczt.pl

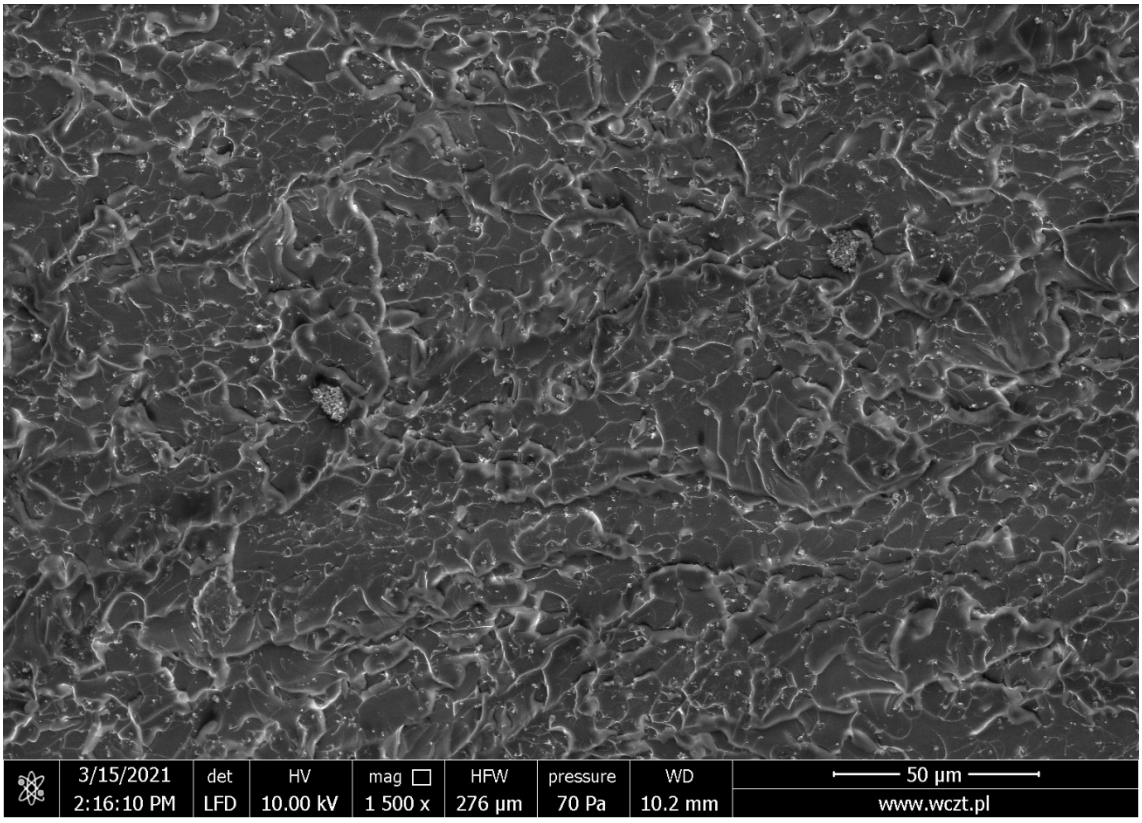
**1%$TiO_2$, 1.5% SS-5GP-3TMOS, mixing pump**

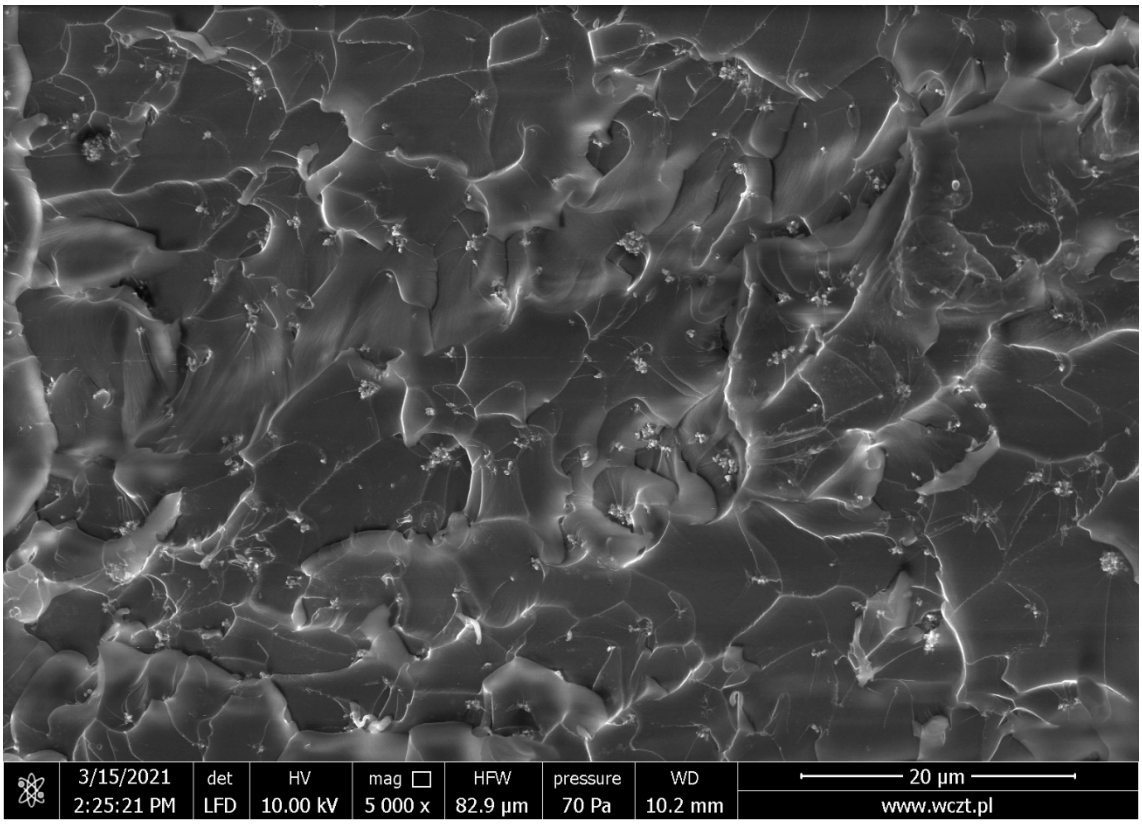


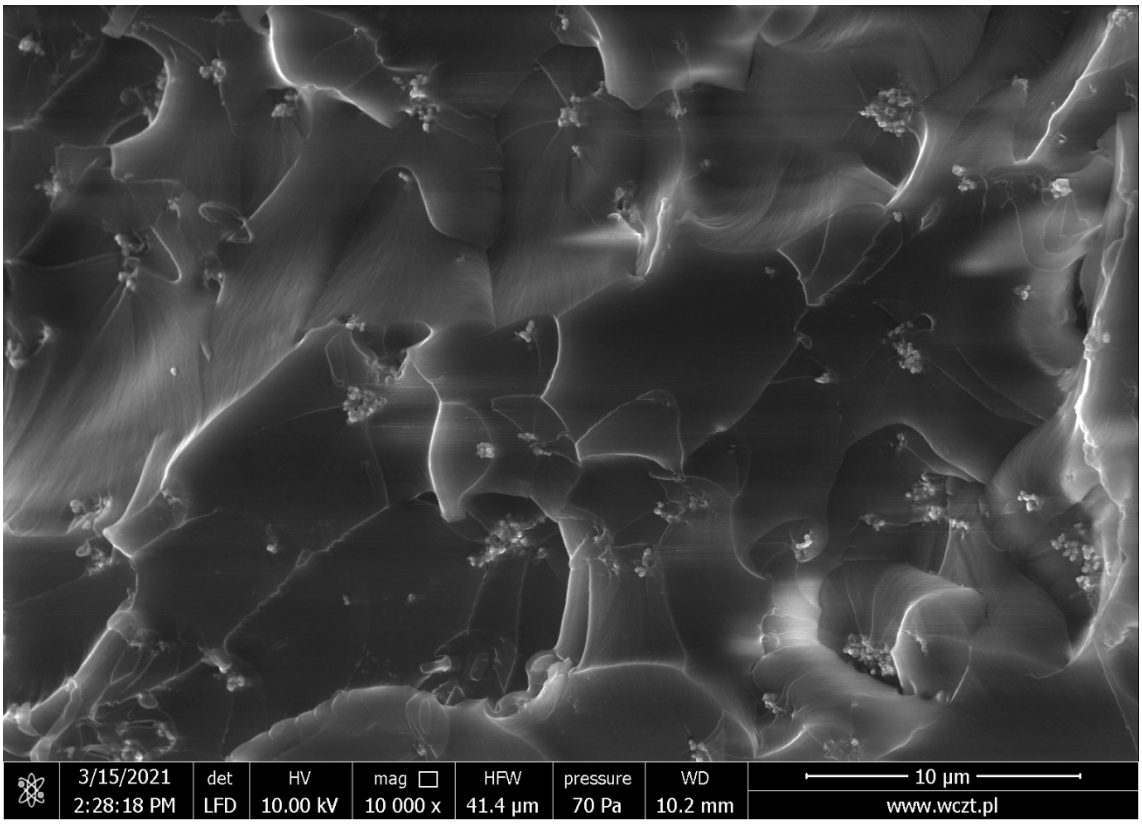




3/17/2021
3:02:22 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.6 mm
10 µm
www.wczt.pl

**2%$TiO_2$, 1.5% SS-5GP-3TMOS, mixing pump**




3/15/2021
2:28:18 PM
det
LFD
HV
10.00 kV
mag
10 000 x
HFW
41.4 µm
pressure
70 Pa
WD
10.2 mm
10 µm
www.wczt.pl