Improvement of Water-Repellency Homogeneity by Compound Fluorine-Carbon Sprayed Coating and Silane Treatment

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Abstract:

To improve the water-repellency of materials, a composite coating of fluorine-carbon has been developed in this study. A thermal sprayed coating produced by using a compound fluorine-carbon cored wire exhibits excellent water-repellency. However, the contact angles of water of the coating surface show remarkable scatters since the fluorine is usually difficult to be distributed uniformly on the coating surface. To improve the homogeneity of the water-repellency of the thermal sprayed coating, a surface modification using silane solution was further processed. Optimal processing conditions were investigated. The results show that highly cross-linked polymers characterized with water-repellency were formed on the sprayed coating, and the scatter of the contact angle is decreased. Empirically, the contact angle of the coated surface was 130±5º for water.

Keywords:

Water-repellency homogeneity, Thermal sprayed coating, Silane treatment, Fluorine-carbon.

1. Introduction

In cold areas, there is always a critical problem of how to decrease the adhesion of water/ice or make the adhered ice easily removed from constructions under low temperature environments. Since if the materials have good water-repellency, it also has the advantage of lubricity and separating characteristics, many structures used for out-doors are required to be made with high water-repellency materials. In recent years, various functional coating materials have been developed instead of bulk materials. Utilizing these functional coatings, various additional functions beyond the substrate material can be gained. Thus how to make a high water-repellency coating becomes important.

As a coating method, thermal sprayed coating has been characterized by high coating speed, and independence of the material property, shape and size of the substrate. It has been widely used in various fields of industry. On the other hand, the sol-gel coating process is a technology for forming a thin solid film with nano-structure from a liquid raw material using a chemical reaction. Sol-gel processes using a silane agent are thought to be a promising resolution for surface modification, that is, improving surface properties of various materials including glass **[1-3]** and ceramic **[4,5]** to gain a uniform film.

Fluorine-carbon is a kind of white powder that is gained after the coal pitch-based carbon reacts with the fluorine directly. Its mean powder size is approximately 1.2μm. It exhibits a contact angle as large as 145° to water drops, a water-repellency coating thermal sprayed by compound fluorine-carbon cored wire has been investigated **[6,7]**. The contact angle of the coating formed using this method was highly increased. However, it was also shown that fluorine is hard to distribute on the coating uniformly. The contact angle has a great scatter within the sprayed coating surface. Due to this problem, adhesion of water/ice will initiate from the spots having low contact angles and grow to larger scale. To improve the uniformity of the water-repellency, several techniques are considerable. For example, to find a suitable compound wire capable of making the fluorine-carbon deposited uniformly on the surface, or to perform post uniformity treatment after thermal sprayed coating. The former are sometimes difficult due to that fluorine-carbon will evaporate because of high temperature during the thermal spraying process. Thus the latter, a chemical method using silane treatment, is proposed for gaining a uniform hydrophobic property.

In this study, a composite coating was first thermal sprayed by the compound fluorine-carbon cored wire. The fluorine dispersion on the thermal sprayed coating surface was examined, and the surface modification was performed to improve the water repellency homogeneity of the sprayed coating. It has been confirmed that by dipping the samples into the silane solution, hydrolysis and subsequent poly-condensation, highly cross-linked polymers having high water-repellency and homogeneity can be formed.

2. Experimental Procedures

2.1 Preparation of sprayed coating

The as-received substrates were aluminum plates. To prepare the water-repellency coating by wire flame spraying method, a compound cored wire was first made by adding fluorine-carbon into an aluminum tube with a weight rate of 3:5, since the melting point of the fluorine-carbon is relatively low (573K) for thermal spraying applications. The cross section of the aluminum tube is a circle. While wire flame spraying, fluorine-carbons are protected from over-heating under the shield of an aluminum tube, until they will run into the substrate with aluminum particles together after the tube is heated to spray. Under the conditions shown in **Table 1**, a thermal sprayed coating was formed on an aluminum plate by using the compound fluorine-carbon cored wire. The thermal sprayed coating was observed by a scanning electron microscope (SEM). An electron probe micro analyzer (EPMA) was also used to examine the constituent of the coating surface.

2.2 Processing procedure of silane solution

After the thermal sprayed coating became stable, the strips were cut from the thermal sprayed plate in a size of 75×25mm. The contact angles to water were measured on the surface by the liquid drop method at an interval of 5×5mm, thus 75 points were measured for each strip. For surface modification, various kinds of silanes were prepared in the experiment, the chemical name, empirical formula and designation of which are listed in **Table 2**. Ethanol, 1.0 N-hydrochloric acid (HCl) and distilled water were used to prepare a silane solution without further purification. Conventionally, the reaction is liable to be conducted in a water system, for it is a reaction in which hydroxyl groups participate. An alcohol-water mixing solvent system was prepared and then silane was added to make a solution. HCl was subsequently added as a catalyst for rapid hydrolysis. The hydrolysis reaction between silane and distilled water react for a short time under acid conditions at 323K, before a strip is dipped into the solvent for hydrated oxide surface reaction and polymerization. After such a process, the resulting strip was well rinsed and dried at 403K for 8 hours to make the chemical film stabilized for the purpose of increasing the durability of the chemical film. The contact angles of the processed strip were then measured again. The procedure of the chemical process for the strips is shown in **Fig. 1**. However, processing conditions such as concentration of the silane solution, hydrolysis reaction time and the surface reaction time in the Fig. 1 should be optimized for gaining well effect of surface modification. It was determined by comparing the contact angles measured before and after the chemical treatment. Infrared (IR) spectra were recorded in diffused reflection mode with a FT-IR spectrometer (JASCO Corp, Model FT/IR-410).

3. Results and discussion

3.1 Distribution of the sprayed coating

Figure 2 is the SEM micrograph of the thermal sprayed coating surface, in which the thickness of the film is 300μm. To examine the water repellency of the coating surface, the distribution of the fluorine on the coating is examined by EPMA analysis. As shown in **Fig. 3**, the white areas indicate the fluorine contents, while the black areas indicate the aluminum. The relation between the fluorine content percentage and its area shows that the area where the fluorine content percentage is below 0.12 wt% takes about 97.5% of the total sprayed coating. It can be seen that fluorine can hardly be distributed on the coating uniformly. Therefore it is aluminum rather than the fluorine mainly occupies the coating surface, where ice is easy to be adhered because of its small contact angles. To eliminate the scatter of the contact angles of the surface, it is necessary to improve the contact angles of the area where is deficiency of fluorine.

3.2 Hydrophobic film formed by silane process

MTEOS solutions were first used as a hydrophobic treatment. A mixture of 22.5g of ethanol and 37.5g of distilled water was used as solvent. When MTEOS solutions are varied in concentration, the surface brightness of the processed strips is observed to decrease with increasing MTEOS concentration, indicating that the reactivity between MTEOS and water increase with increasing MTEOS concentration. The contact angles of water are measured on each processed strip. The scatter of the contact angles of the processed strips is noticed to be lower than that before processing for all the tested strips. Also, it is observed that the scatter of the contact angles decreases with increasing MTEOS concentration. The homogeneity in contact angle on the surface shows to have been improved compared with that prior to processing. The average of 75 degrees for a strip is considered as its average contact angle. The consequent contact angles of processed strips various with the silane concentration are shown in **Fig. 4**. The contact angles before processing are also shown in the figure for comparison. The contact angle shows a peek value at 6 wt.% MTEOS concentration, and then decreases with increasing concentration until it shows a tendency to be a constant at higher concentrations. Moreover, the contact angles after processing are lower than those before processing, except that the contact angles after processing at 6 wt.% MTEOS concentration is higher than the value before processing. This phenomenon can be explained by the fact that the water repellency of the coating surface after being treated by MTEOS solution is affected by the silane concentration. Since the coating thermally sprayed by the compound fluorine-carbon cored wire exhibits hydrophobic behavior on spots enriched with fluorine, the coating surface could not contact with silane solution uniformly. When a strip is chemically processed in a low concentration silane solution, chemical film is expected to prioritize at the surface deficiency with fluorine, and increase to occupy the main aluminum surface with increasing silane concentration to a certain extent. As a result, the water-repellency of the surface mainly occupied by the aluminum is improved; also the high water-repellency is maintained on spots enriched with fluorine. However in case of processing the strip in a higher silane concentration, it is supposed that the reactivity becomes so high that the polymer film increases to cover the spots even with high fluorine content. Thus the surface water-repellency of the processed strips is attributed only to the chemical film, but not the dispersion of fluorine. This supposition agrees well with the results that when increasing silane concentration higher than 10 wt.%, the spots with high contact angles that where enriched with fluorine before processing decrease significantly after processing. Moreover, the mean contact angle tends to be constant, showing that the surface water-repellency is attributed to the chemical film.

FT-IR absorption spectra for the chemical films formed in various concentrations of silane solutions are shown in **Fig. 5**. The absorption bands between 1080 and 1229 cm^{-1} correspond to the asymmetric Si-O stretching variation. The bands around 1272 cm^{-1} are related to Si-CH_3 deformation vibration modes, and the bands between 2876 and 2960 cm^{-1} are assigned to C-H stretching of -CH_3. These results indicate that a chemical film was successfully formed on the thermal sprayed coating from the solution of MTEOS. Moreover, it is observed in Fig. 5 that the deformation variations of -CH_3 increase with increasing MTEOS concentration. However, the stretching vibration of asymmetric Si-O shows a change from high wave number to low wave number, which indicates Si-O bonding energy decreased.

This result is thought to be attributed to that the structural formula of the polymer film formed on the thermal sprayed coatings varies with silane concentration. **Process 1(a)** shows that MTEOS react with water to form hydrolyzed $RSi(OH)_3$ in acidic condition. Further, as shown in **Process 1(b)**, the hydrolyzed $RSi(OH)_3$ on the surface of thermal sprayed coating proceed through a poly-condensation reaction. The effect of silane concentration on the results of the polycondensation reaction is shown in **Process 2.** Process 2(a) shows that the polymer film is expected to form a cross-linked structure in case of low concentration. While with increasing the concentration to a high value, it is suggested to form a structure as shown in Process 2(b). Parts of asymmetric Si-O bonds are enclosed in the inner, orienting toward the sprayed coating, Si-O bonding energy is therefore decreased for its hydrogen combination, as indicated in Fig. 5. From the results shown in Fig. 4 and Fig. 5, it can be said that the silane concentration affects the chemical films on the reactivity degree and structure. Considering that the cross-linked polymers film is expected for high hydrophobic property, low silane concentration such as 6 wt.% is preferred to the higher one for surface modification.

Furthermore, the surface modification was made by varying the hydrolysis reaction time 0, 5, 10, 15, 20 and 45 minutes, respectively. The contact angles of the processed strips comparing with the previous values are shown in **Fig. 6**. Five minutes is the optimal time for the hydrolysis reaction, because the mean value is increased from 120° to 130°. The contact angles are increased for the spots having low contact angles, and the high contact angles are also maintained after processing. However, the subsequent contact angle decreases with increasing hydrolysis reaction time longer than 5 minutes indicating that poly-condensation reaction occurs before a strip is dipped in, thus cross-linked film can hardly be formed on the sprayed coating surface. Also, the hydrated oxide surface reaction time was determined by examining the subsequent contact angles of the coating surface. The contact angles show an increase with reaction time until 3 hours. The thermal sprayed coating strips were therefore processed using the optimum conditions. **Figure 7** shows an example of the subsequent contact angles measured for the surface of chemical processed strip, compared with the previous value before MTEOS process. The scatter of the contact angles for water at 75 spots of the processed strips has been diminished, and the contact angles are also highly increased compared with that of the thermal sprayed coatings. This indicates that the improvement of water-repellency homogeneity could be gained for the thermal sprayed coating surface by silane treatment.

3.3 Hydrophobic films formed by various silane solutions

Besides the MTEOS, other silane solutions as listed in Table 2 are also used to process the thermal sprayed strips. The silanes are similar in empirical structural formula to that of MTEOS, therefore the mechanism of the silanes reacting with the sprayed coating surface are thought similar to that of the MTEOS, as shown in Process 1 and 2. Using approximate processing conditions that are optimized by the MTEOS, the contact angles are increased for the processed thermal sprayed coatings by various silane solutions. The results of surface modification by the various silanes are compared in **Fig. 8**. Among the silanes employed, propyltriethoxysilane shows a higher hydrophobic property, the contact angle for water reaches 135° after processing. It can be said that the scatter of the contact angles significantly decreased by the silane chemical treatment.

4. Conclusions

The coating thermally sprayed by compound fluorine-carbon cored wire on an aluminum substrate has been known to have good water-repellency. However, the contact angles of water on the sprayed coating surface varied in a wide range, because fluorine is difficult to be distributed uniformly on the coating surface. In this study, a surface modification method using silane solution was proposed for processing the thermal sprayed coating. After chemical processed by the silane solutions using the optimized processing conditions, the water-repellency of the thermal sprayed coating was significantly improved and the scatter of the contact angles is decreased. Empirically, contact angles of 130±5° were obtained.

References

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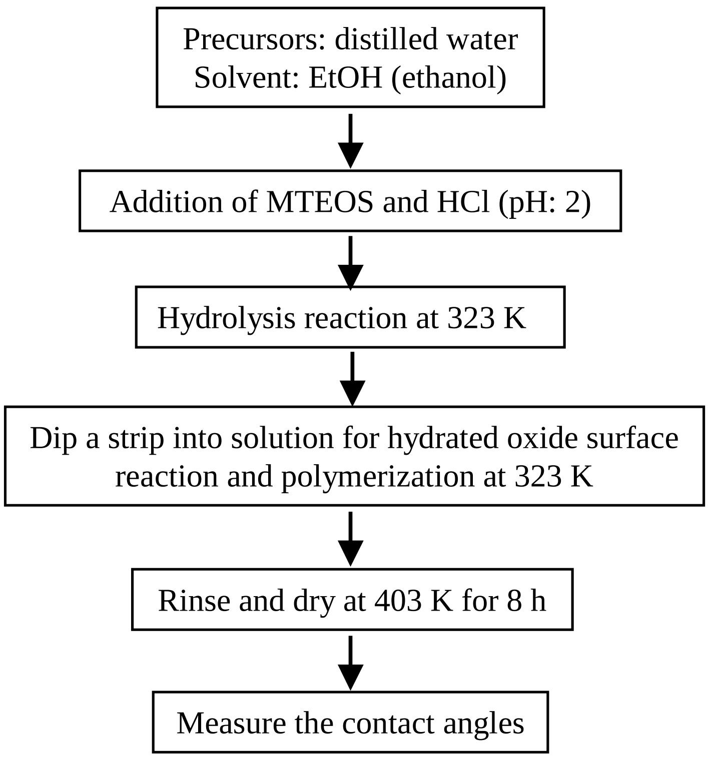
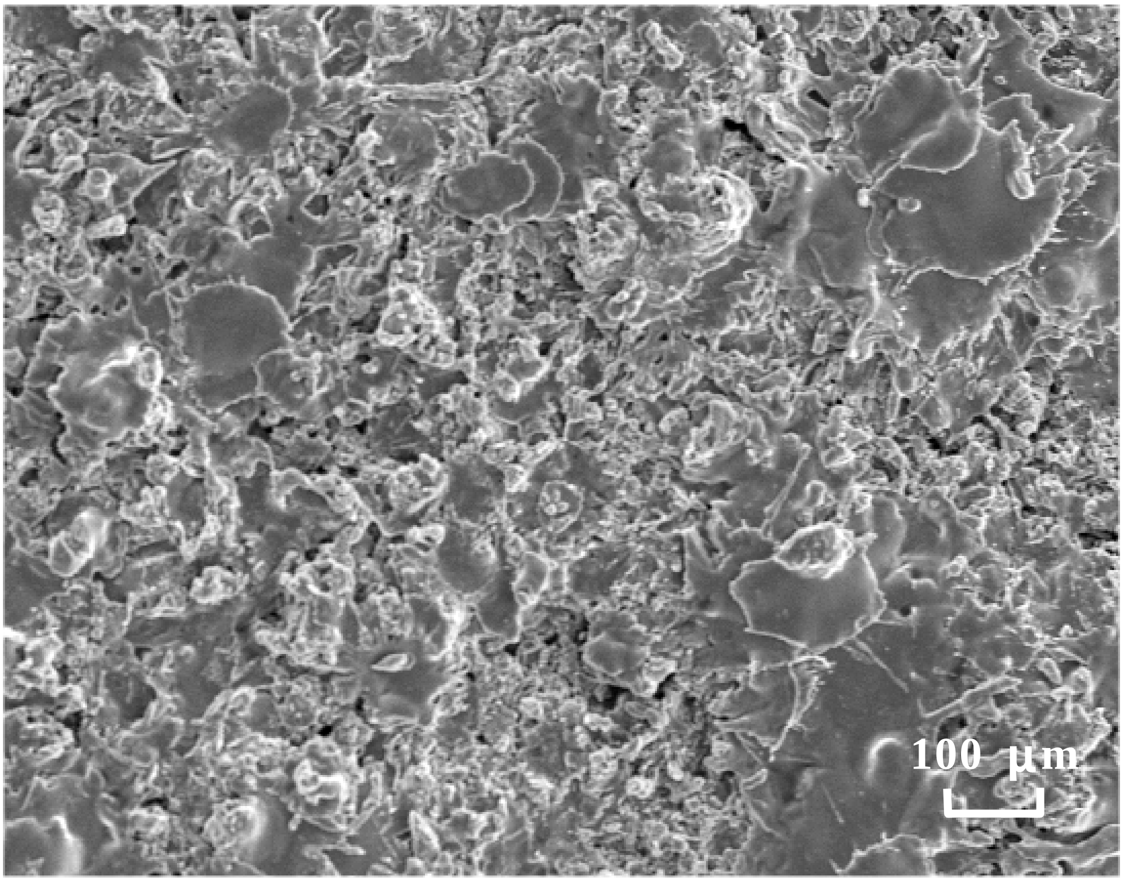
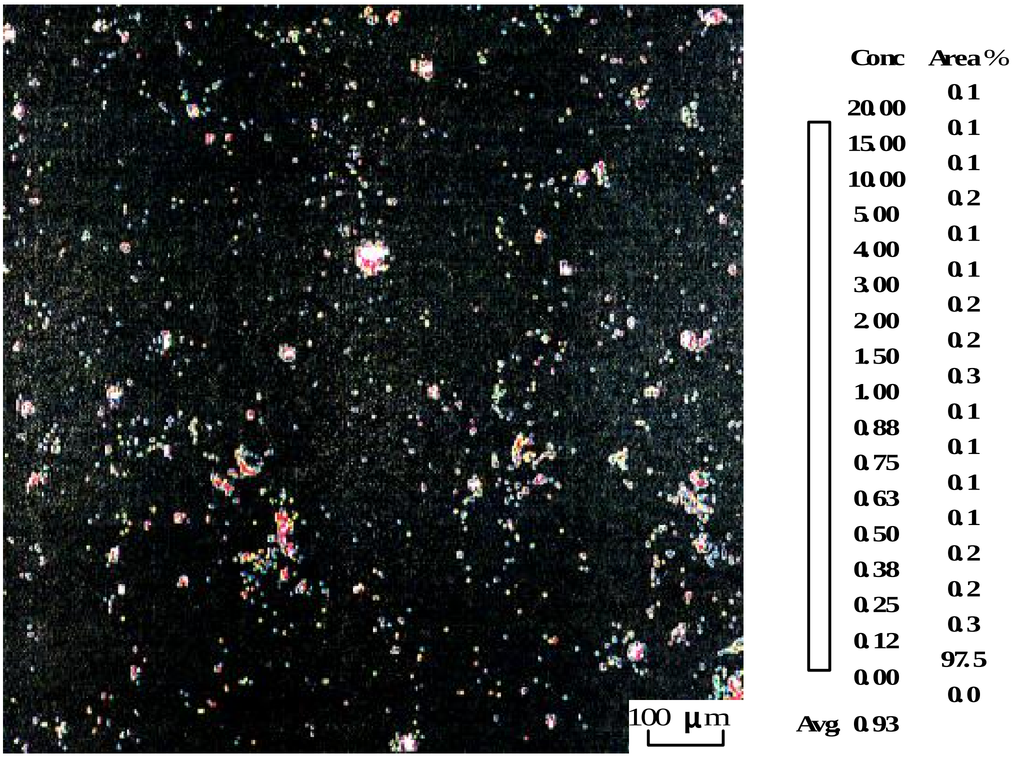
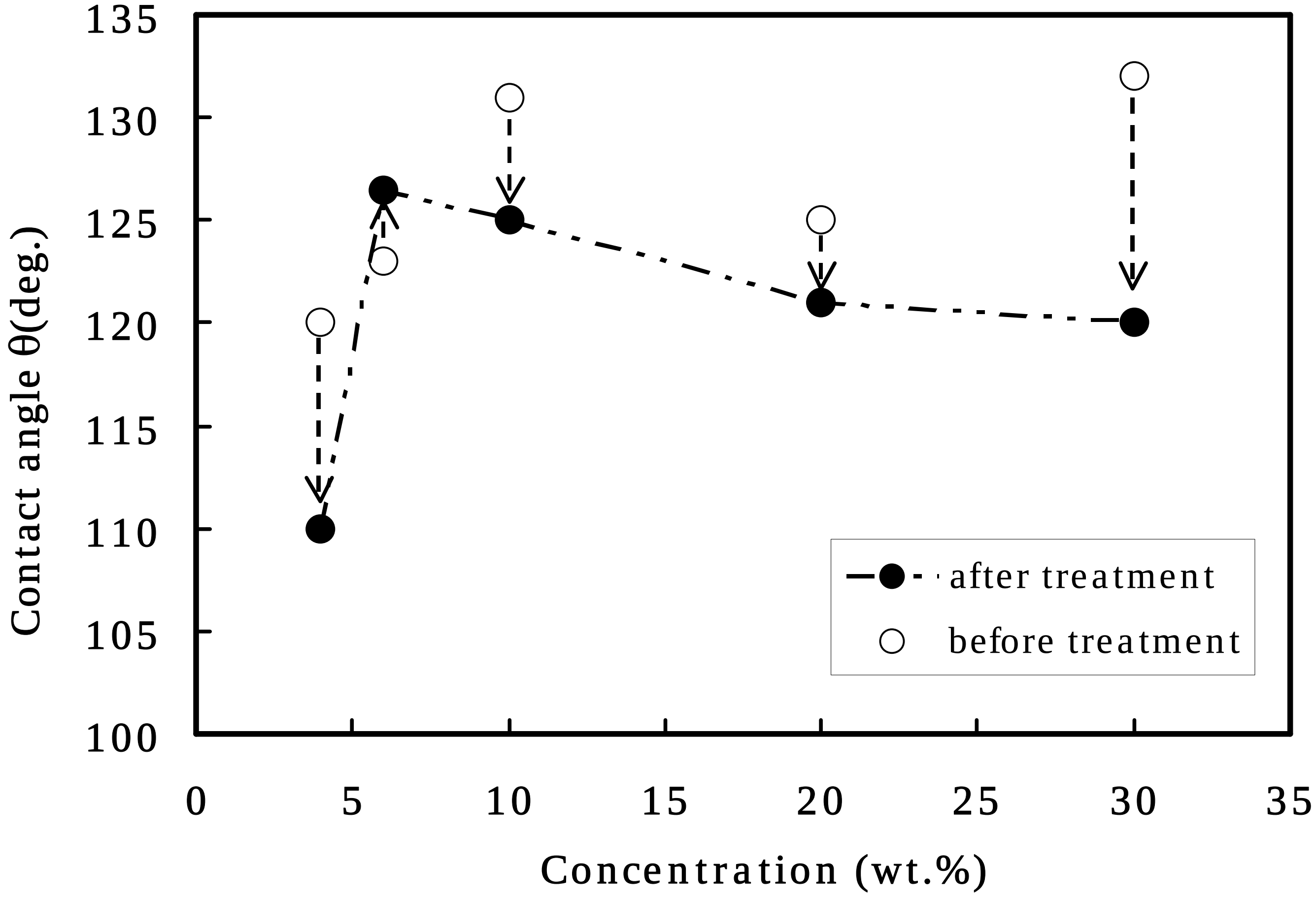

Precursors: distilled water
Solvent: EtOH (ethanol)
Addition of MTEOS and HCl (pH: 2)
Hydrolysis reaction at 323 K
Dip a strip into solution for hydrated oxide surface reaction and polymerization at 323 K
Rinse and dry at 403 K for 8 h
Measure the contact angles

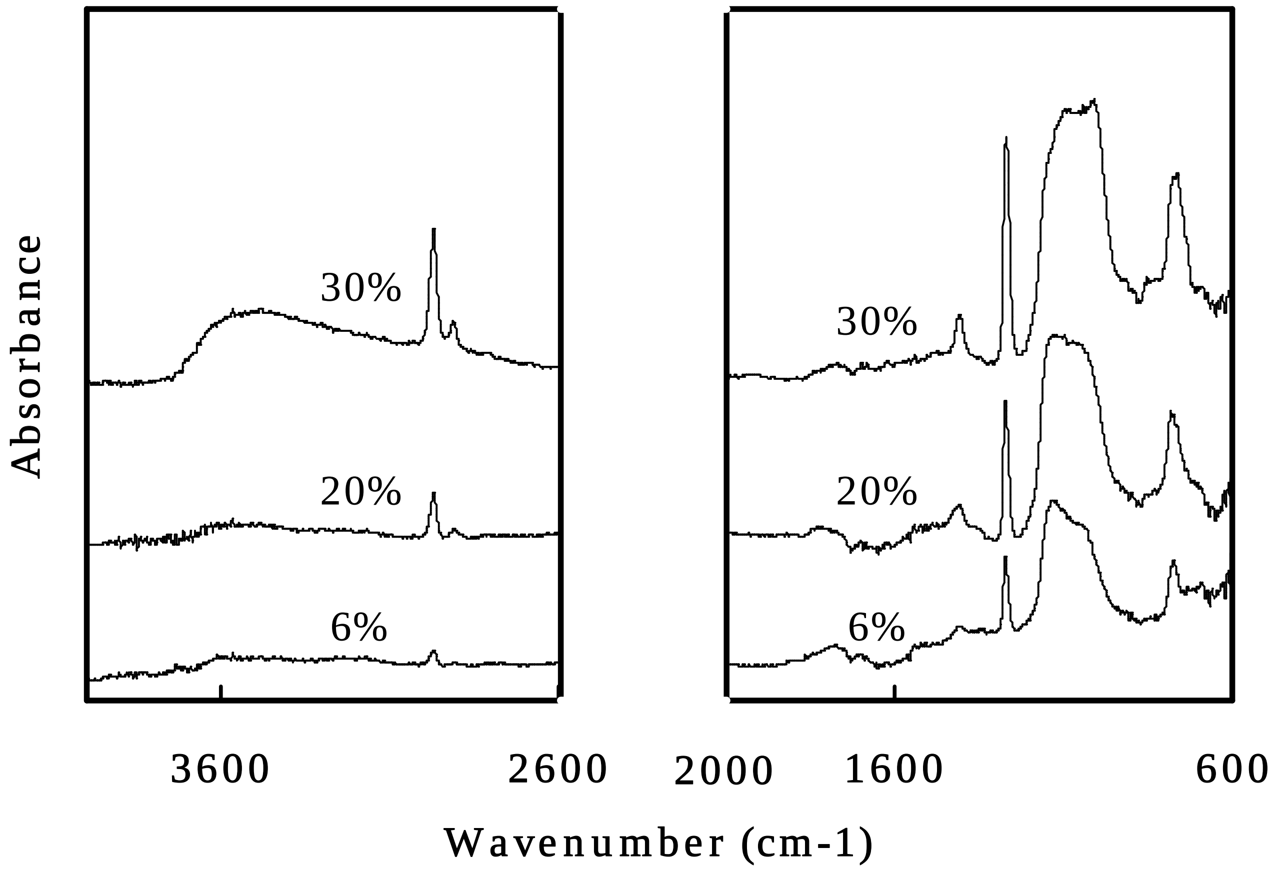

100 µm



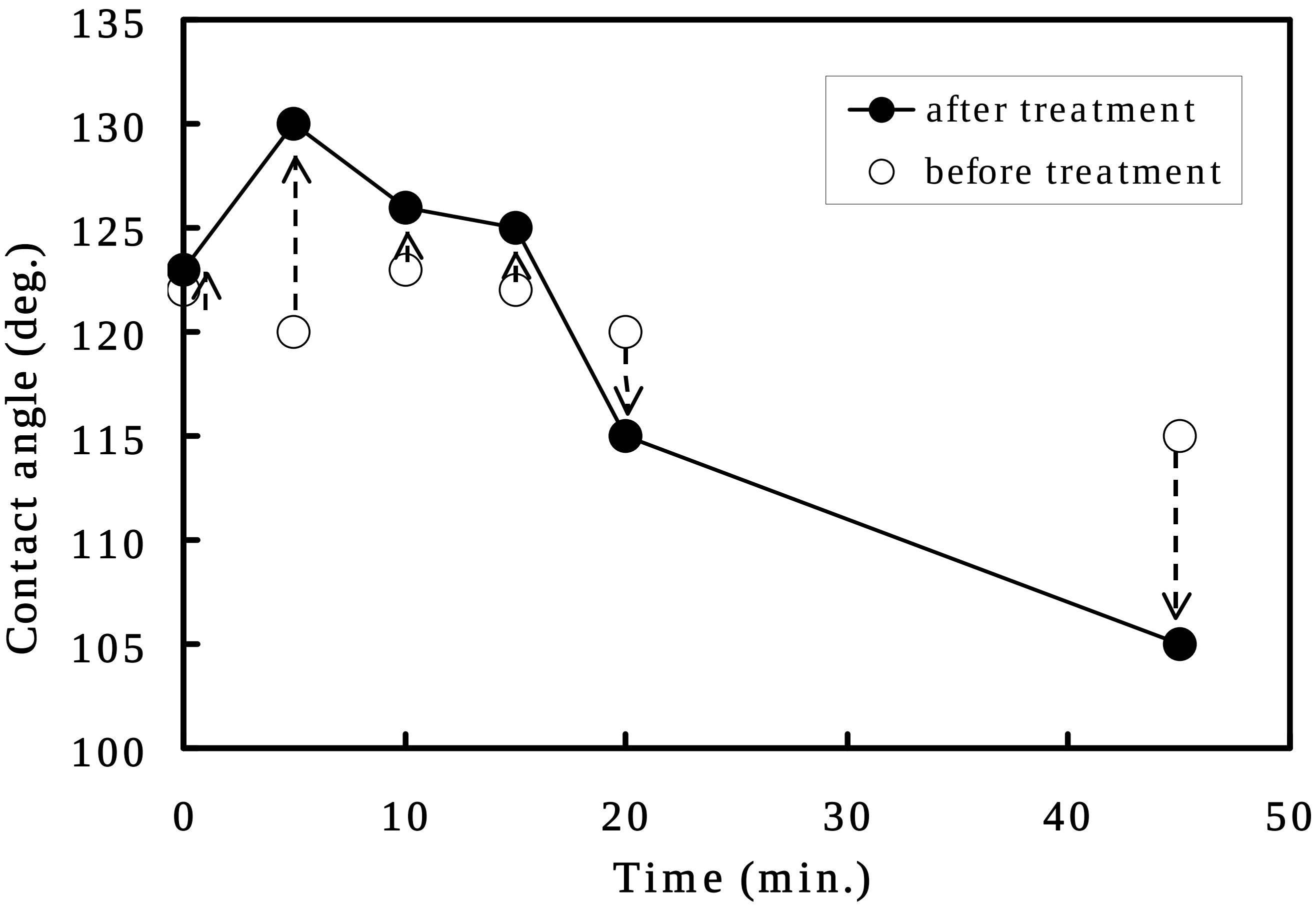
100 μm
Conc
Area%
20.00
15.00
10.00
5.00
4.00
3.00
2.00
1.50
1.00
0.88
0.75
0.63
0.50
0.38
0.25
0.12
0.00
0.1
0.1
0.1
0.2
0.1
0.1
0.2
0.2
0.3
0.1
0.1
0.1
0.1
0.2
0.2
0.3
97.5
0.0
Avg. 0.93



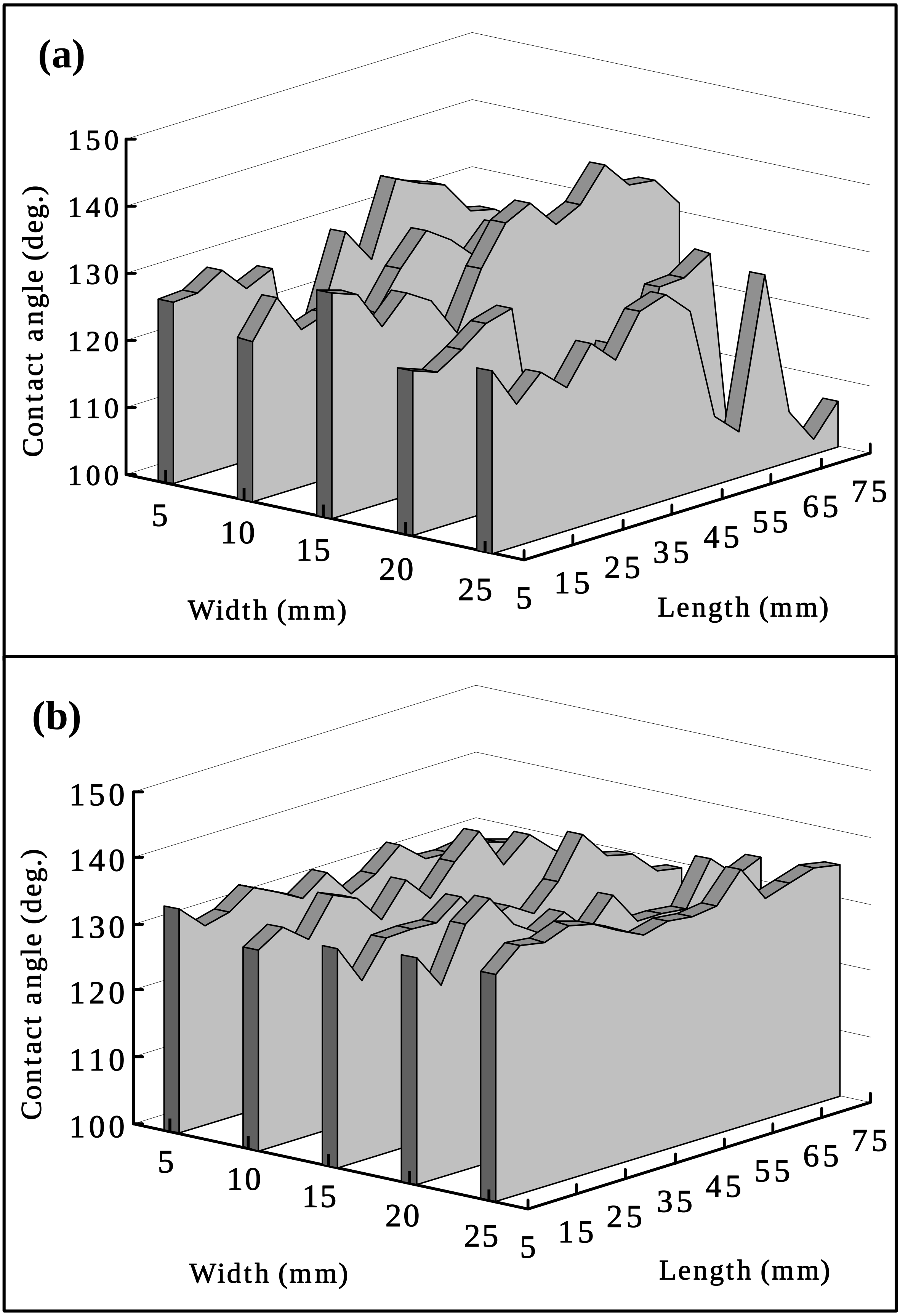
135
130
125
120
115
110
105
100
Contact angle θ(deg.)
0
5
10
15
20
25
30
35
Concentration (wt.%)
after treatment
before treatment



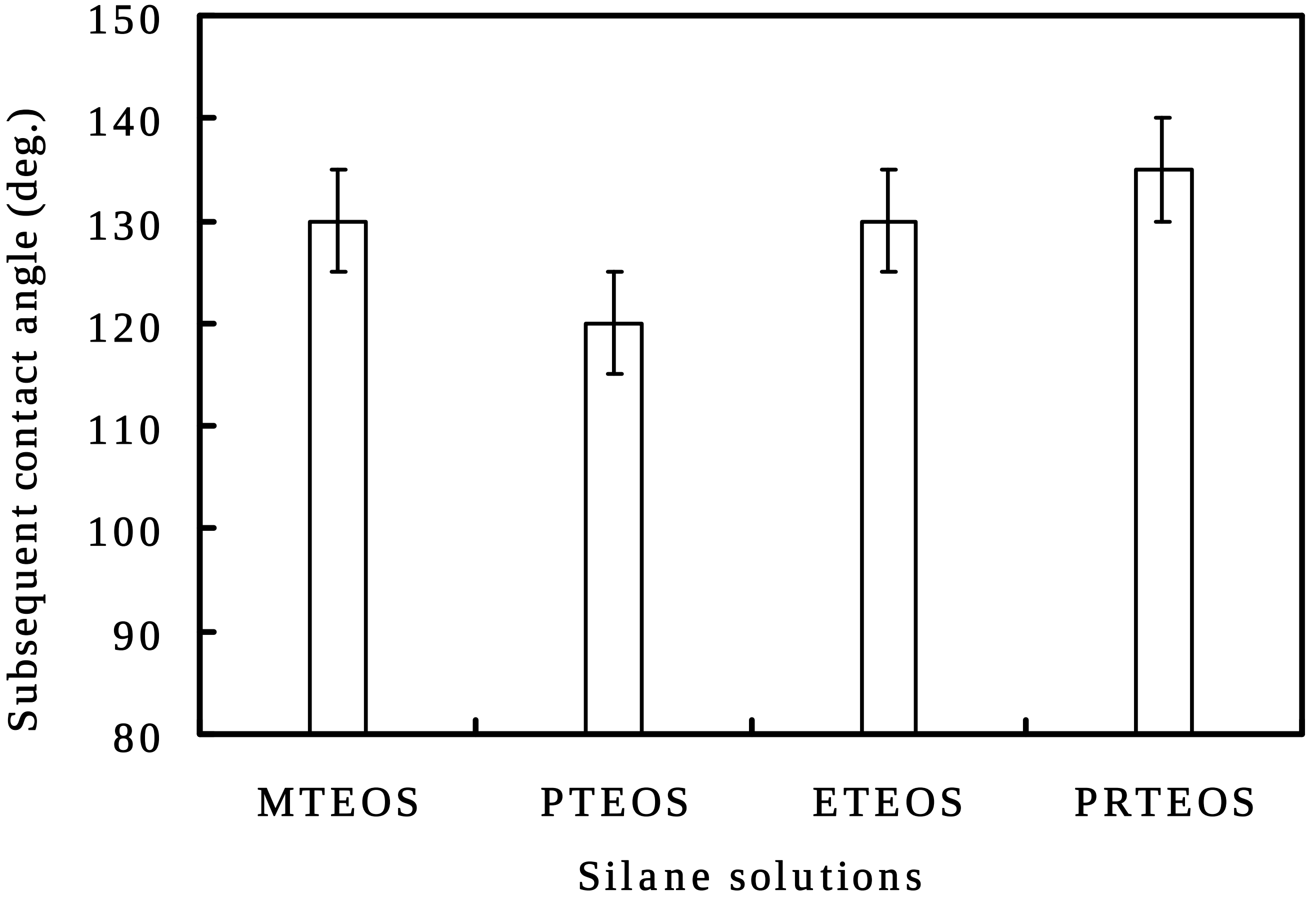
Absorbance
30%
20%
6%
30%
20%
6%
3600
2600
2000
1600
600
Wavenumber (cm-1)

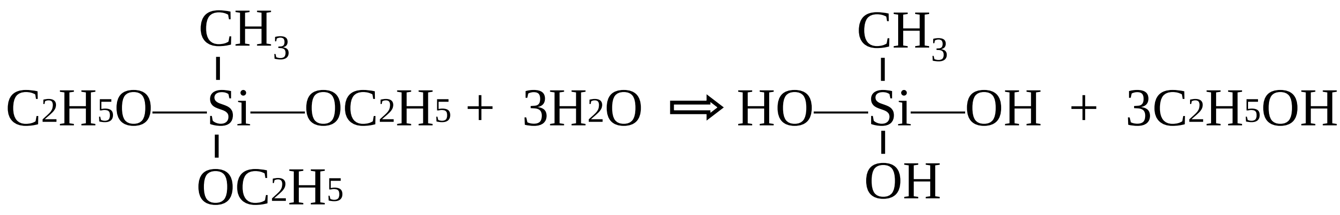


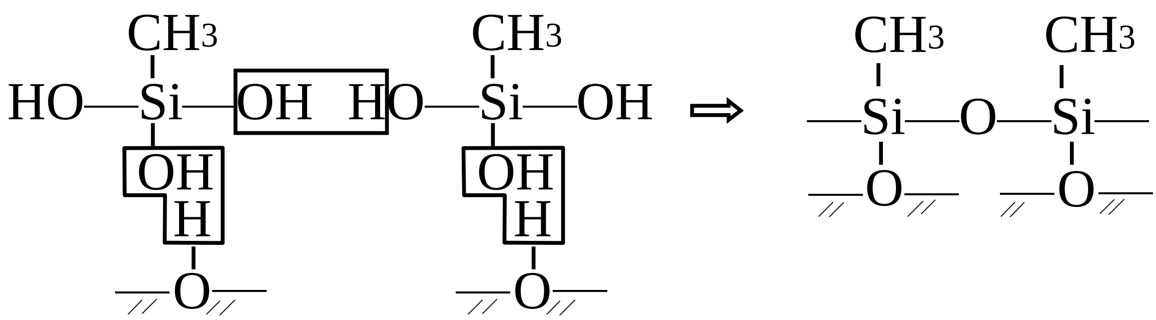
135
130
125
120
115
110
105
100
Contact angle (deg.)
0
10
20
30
40
50
Time (min.)
after treatment
before treatment

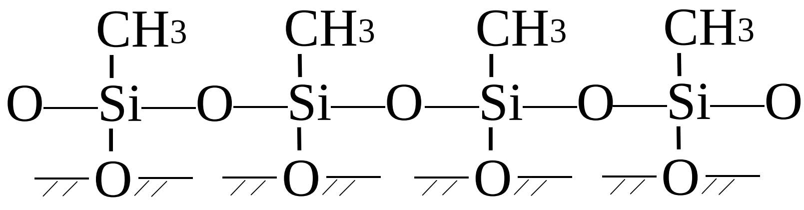


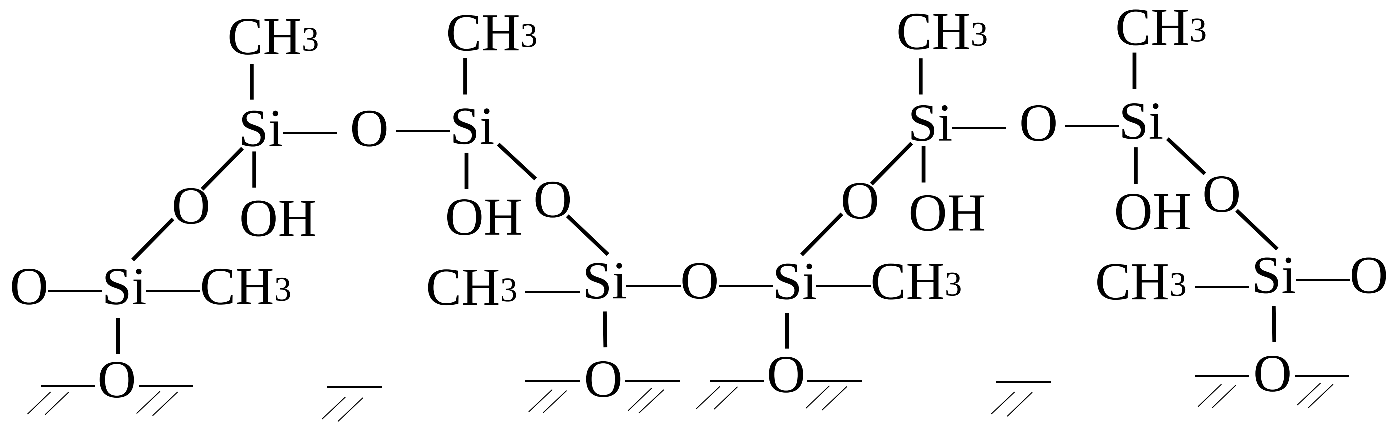
(a)
Contact angle (deg.)
150
140
130
120
110
100
5
10
15
20
25
Width (mm)
5
15
25
35
45
55
65
75
Length (mm)
(b)
Contact angle (deg.)
150
140
130
120
110
100
5
10
15
20
25
Width (mm)
5
15
25
35
45
55
65
75
Length (mm)

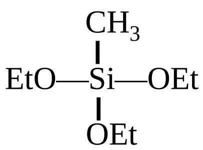
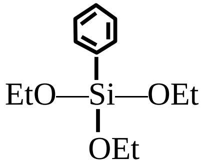
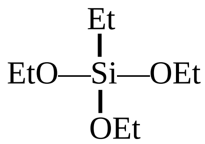
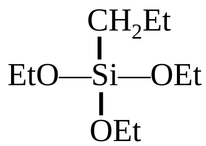

150
140
130
120
110
100
90
80
Subsequent contact angle (deg.)
MTEOS
PTEOS
ETEOS
PRTEOS
Silane solutions






CH3
O
Si
OH


CH3
O
Si
OH

Designation	MTEOS	PTEOS	ETEOS	PRTEOS
Chemical name	Methyltriethoxy silane	Phenyltriethoxy silane	Ethytriethoxy silane	Propyltriethoxy silane
Empirical formula	$C_7H_{18}O_3Si$	$C_{12}H_{20}O_3Si$	$C_8H_{20}O_3Si$	$C_9H_{22}O_3Si$
Structure formula Et: CH_2-CH_3				

Gas pressure (MPa)			Gas flow rate ($\times 10^{-3} m^3/s$)			Spraying distance (mm)	Traveling speed (m/s)	Wire feed rate (mm/s)
O_2	C_2H_2	Air	O_2	C_2H_2	Air	150	≈0.7	60
0.21	0.10	0.48	0.64	0.31	13.3			