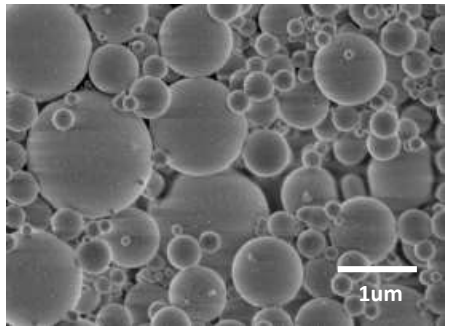
July, 2020
Admatechs Co., Ltd
R&D Division

Admatechs Silica for 3D Printer

Admatechs Co., Ltd.

Contents



1. Company Profile

Overview of Operation

Established February 1990

(History)

July	1994	New plant constructed (within TMC's Myochi Plant)
June	1996	National Commendation for Invention (awarded the Prime Minister Prize)
August	1999	Acquired ISO 9002 certification by the International Organization for Standardization (ISO)
October	1999	Established system with production capacity of 300 tons per month
May	2000	Construction of Technical Center (adjacent to TMC's biotechnology research institute)
October	2001	Relocation of Head Office (from Tokyo to the Technical Center)
October	2002	Acquired ISO 9001:2000 certification

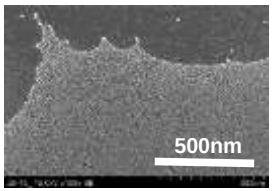
Capital 300 million yen : Toyota Motor Corporation 52.9%, Shin-Etsu Chemical Co., Ltd. 25.6%, Shin-Etsu Quartz Products Co., Ltd.15.4%, Other 6.1%

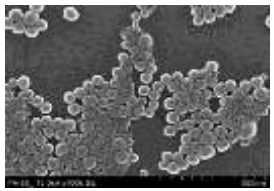
Business activities Manufacture and sale of oxide ceramic powders (silica, alumina, and composite oxides)

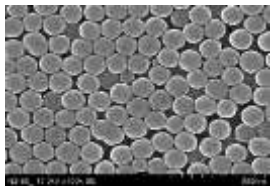
Location **Aichi Prefecture, Japan**

President **Susumu Abe**

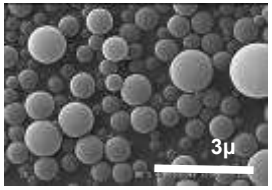
1-1. Admatechs Product Line Up

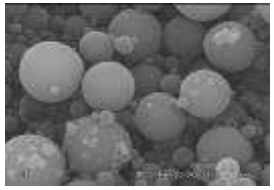


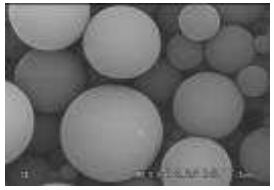




application







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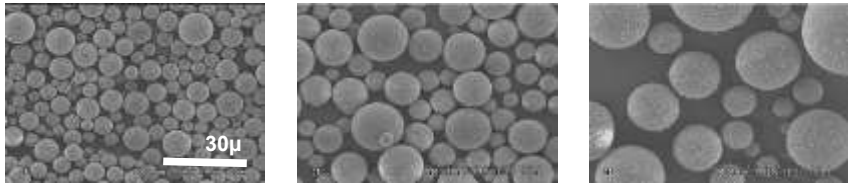


1 nm | 10 nm | 100 nm | 1000 nm (1μm) | 10μm | 100μm

Admanano

Nano sized silica
10 nm～100 nm
High Performance Nano Composite

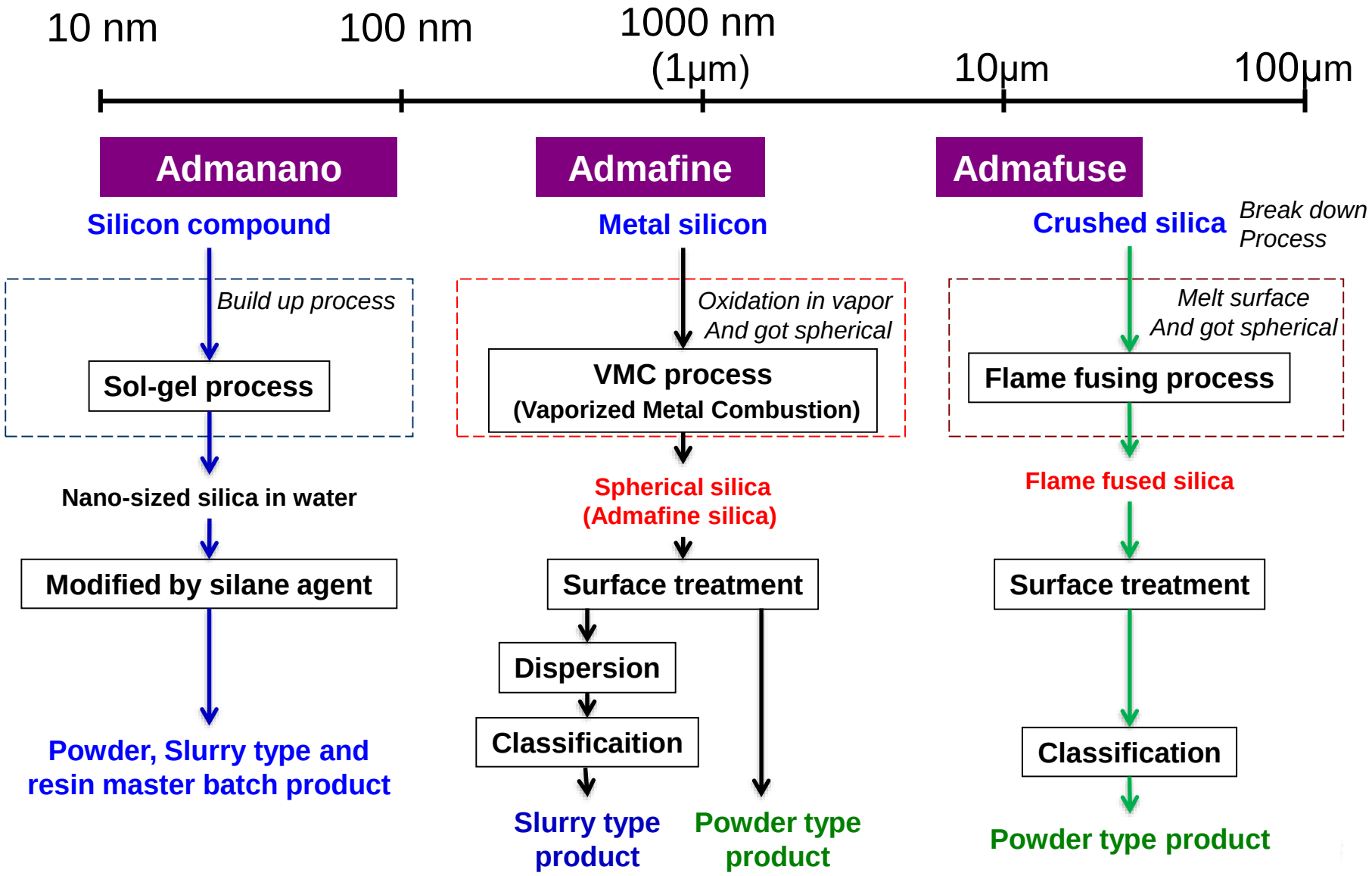
Admafine

VMC silica
0.2 μm～2.0 μm
Liquid encapsulation, sub-particles for EMC

Admafuse

Flame fused spherical silica
5 μm～30μm
Main particles for EMC

1-1. Process Flow of Admatechs Products

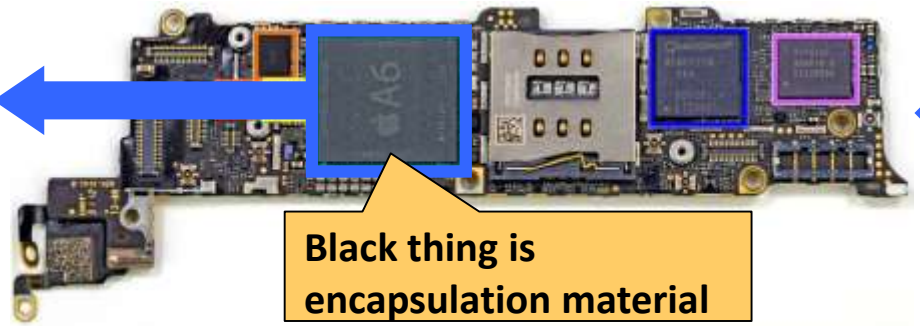


1-1. Application Example of Admatechs Products

Electronic Device

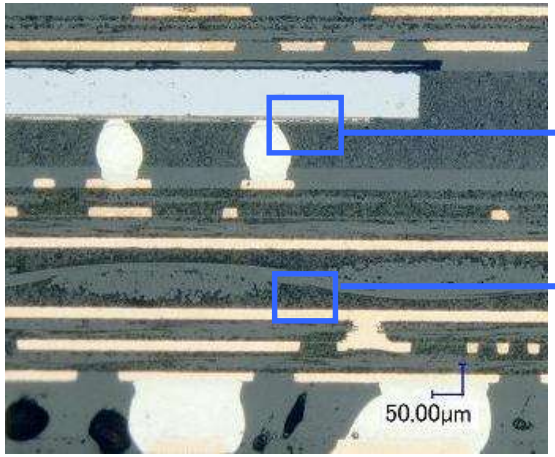
A6 : Application Processer

Cross Section



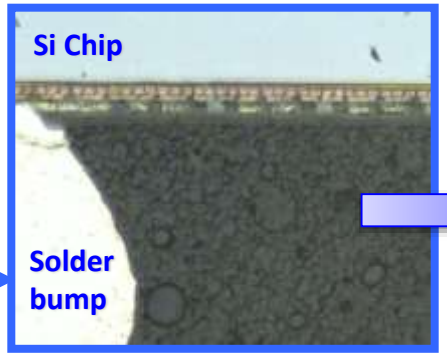
Black thing is encapsulation material

iPhone

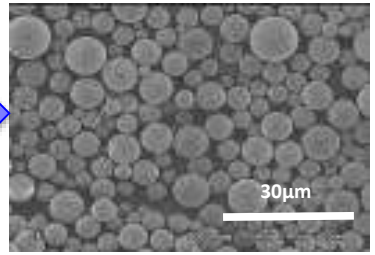


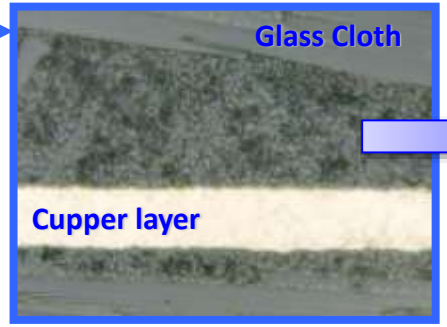
Mold Under Fill

Substrate layer

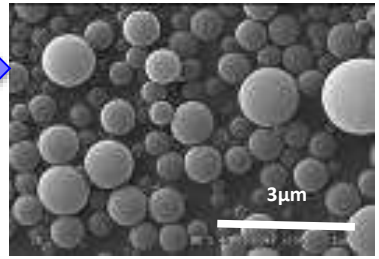


Admafuse : 5um silica





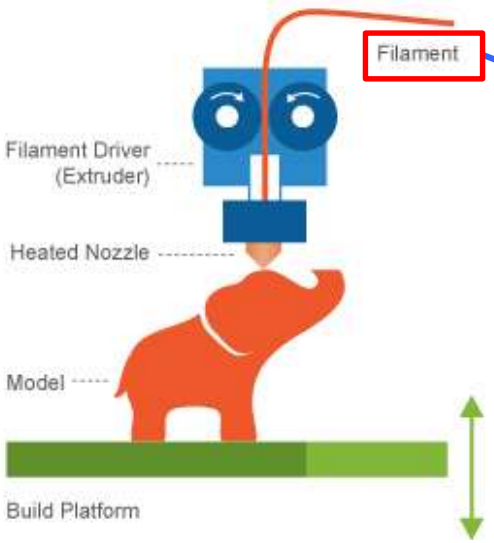
Admafine : 0.5um silica



1-1. Application Example of Admatechs Products

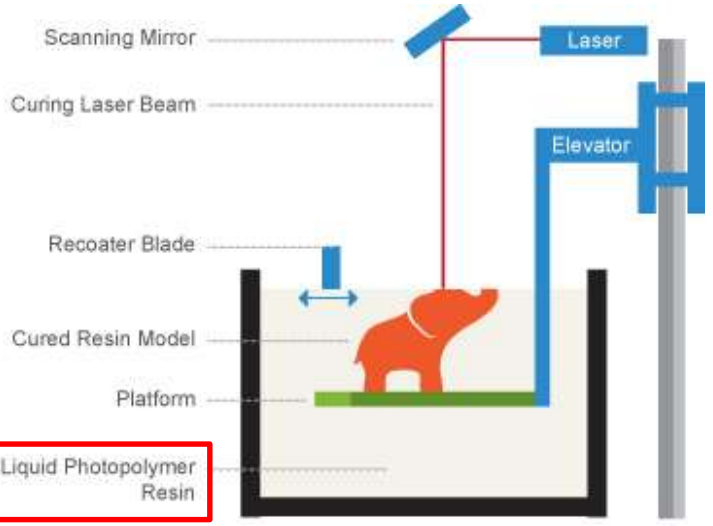
3D Printer

Fused Deposition Modeling (FDM)



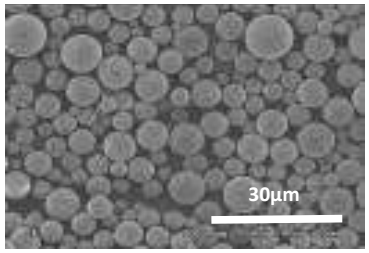
ABS, PLA,
Other resin

Stereo lithography (SLA)

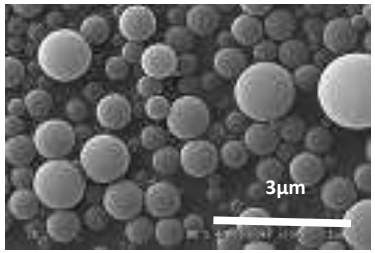


Acryl,
Other Resin

Admafuse : 5um silica



Admafine : 0.5um silica

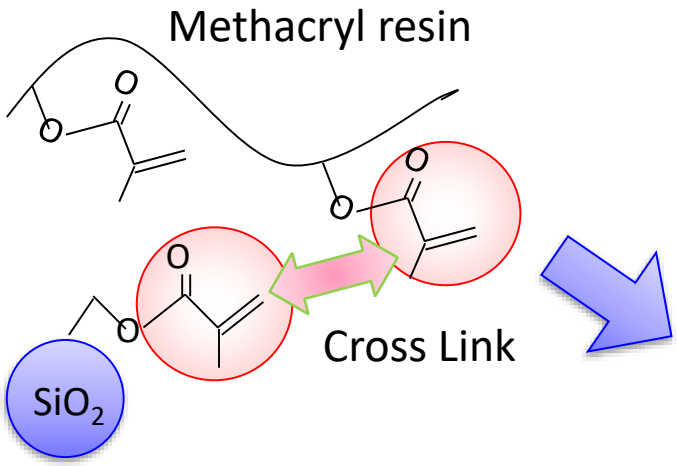


- **Low Viscosity.**
- **Reduce CTE,**
  Improve physical properties.

1-1. Application Example of Admatechs Products

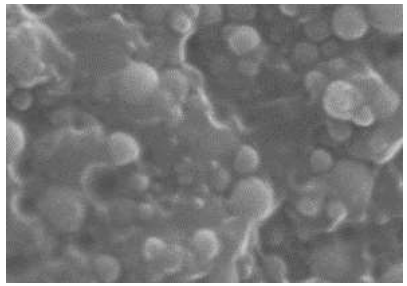
Dental Composite

- Uniformly surface treated nano silica.
- Uniform Dispersion into Methacryl Resin Composite.
- Improve Flexure Toughness with Good Esthetics.



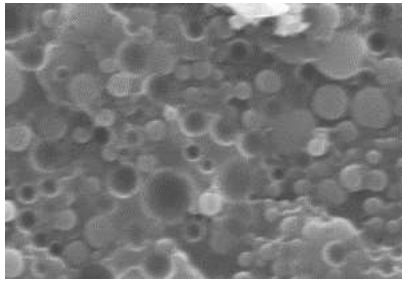
Methacryl treated
Admanano silica

Admanano Silica



Good Compatibility

Ref.. Ordinary silica



Bad Compatibility..

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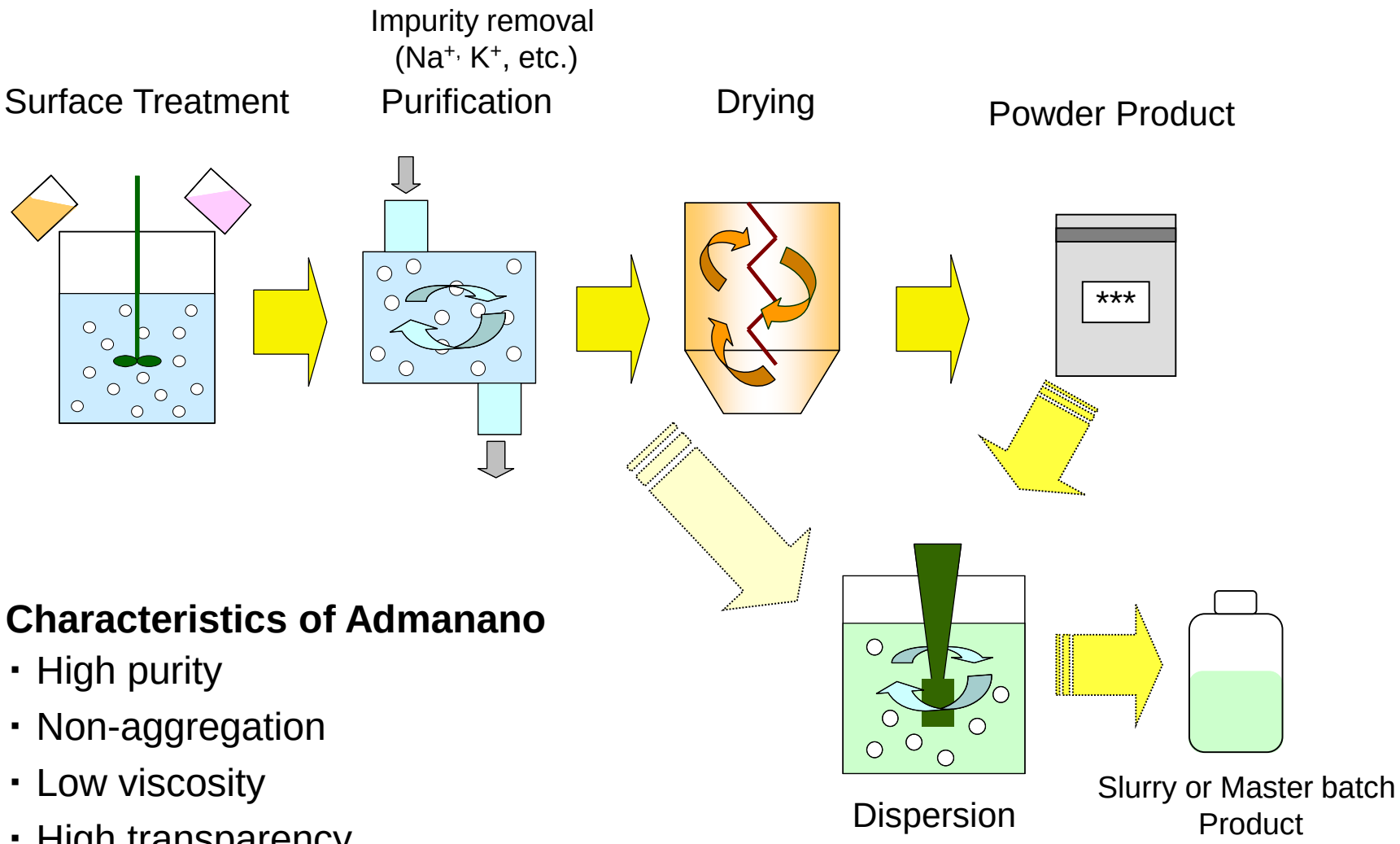
1-2. Various Size Spherical Silica, Alumina

Admanano Manufacturing Process (10 – 100nm)



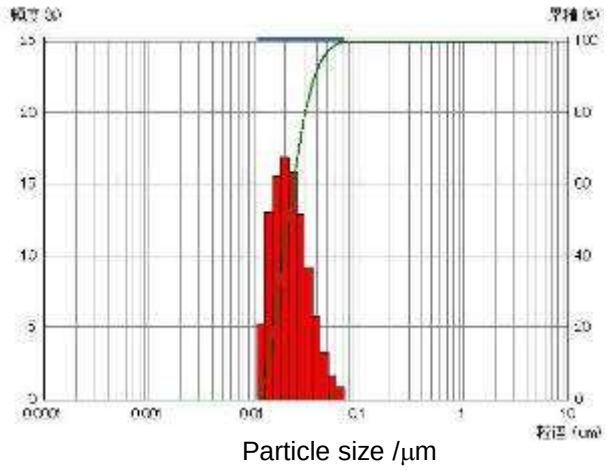
Characteristics of Admanano

- High purity
- Non-aggregation
- Low viscosity
- High transparency

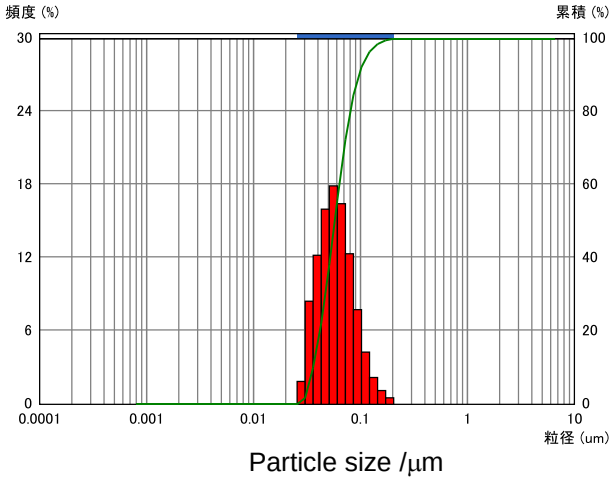
1-2. Various Size Spherical Silica, Alumina

Admanano Silica Line Up

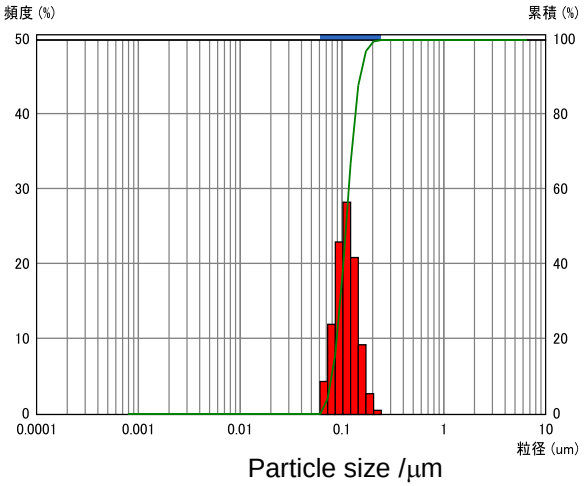
10nm



50nm

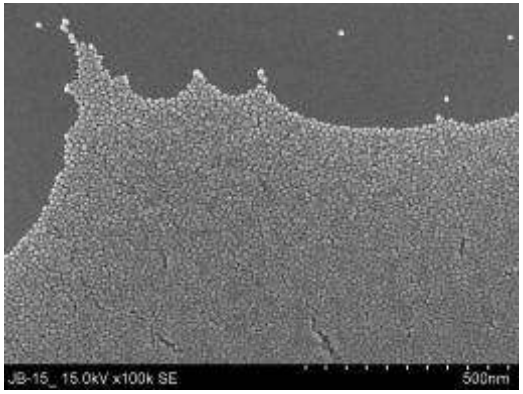


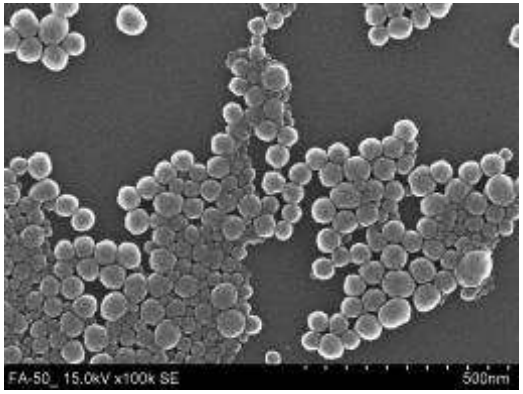
100nm

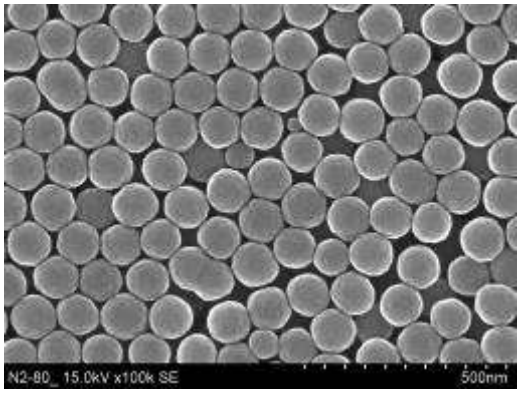


Frequency /%

Accumulation %







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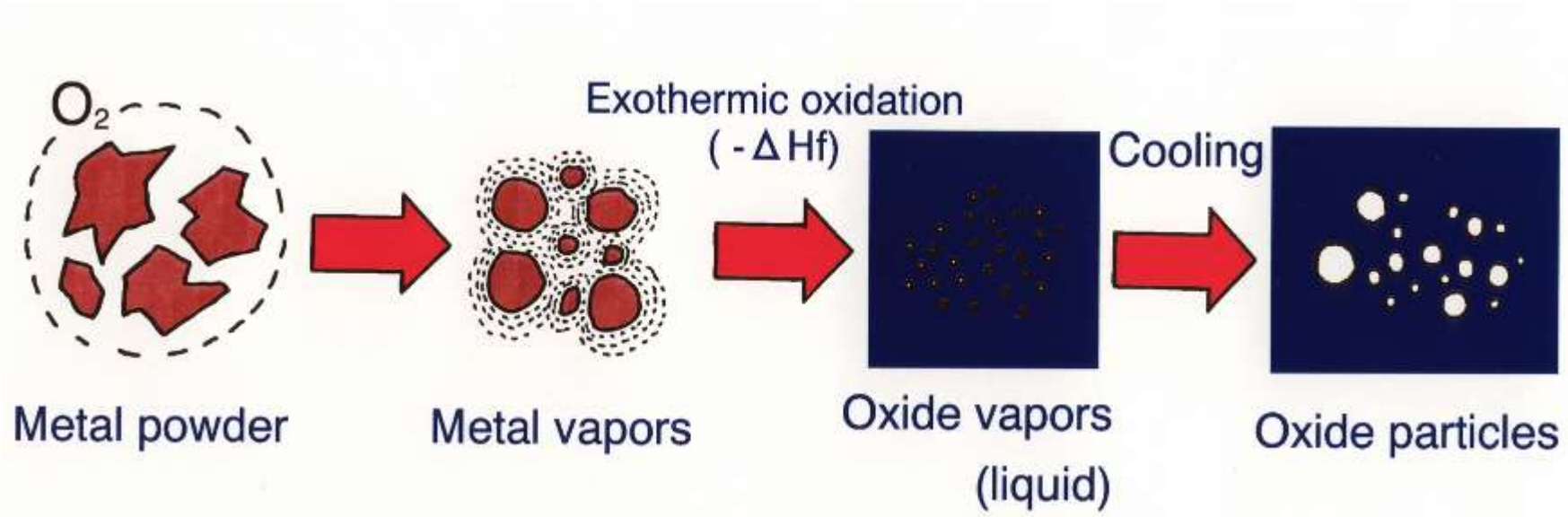
1-2. Various Size Spherical Silica

Admafine Manufacturing Process (0.2 – 2um)

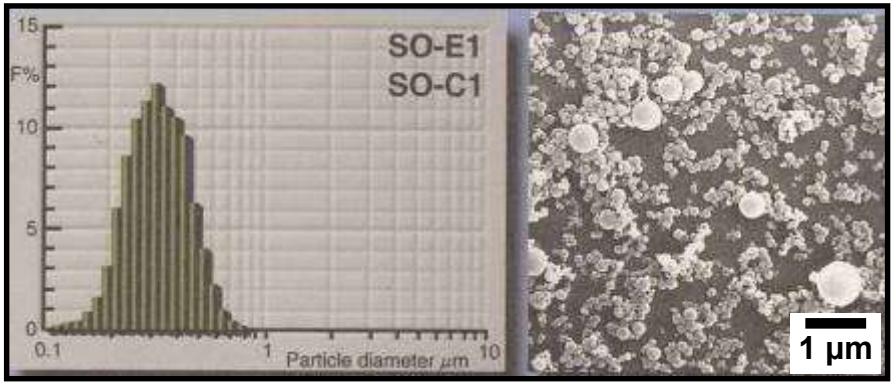
Core technology of ADMATECHS is Vaporized Metal Combustion (VMC) method. The VMC method provides fine spherical silica and alumina particles from metal powder by direct oxidation.



1-2. Various Size Spherical Silica

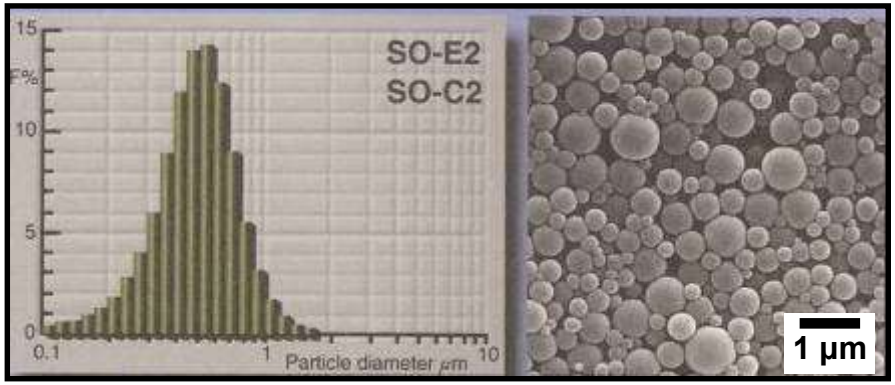
Admafine Silica Product Line Up

Particles size distribution and SEM Images



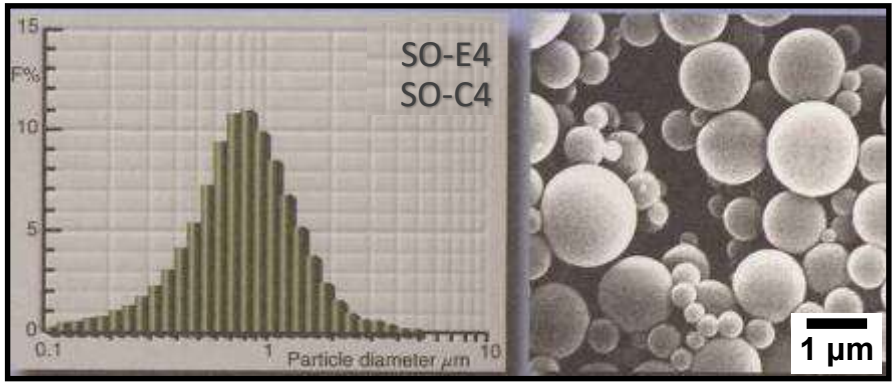
Particle diameter: 0.3 μm

Specific surface area: 10 ~ 20 m^2/g



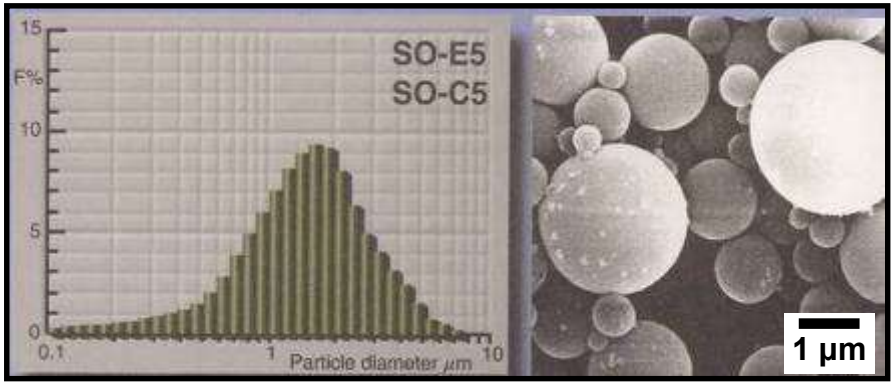
Particle diameter: 0.5 μm

Specific surface area: 5 ~ 9 m^2/g



Particle diameter: 1 μm

Specific surface area: 3 ~ 6 m^2/g



Particle diameter: 1.5 μm

Specific surface area: 2 ~ 5 m^2/g

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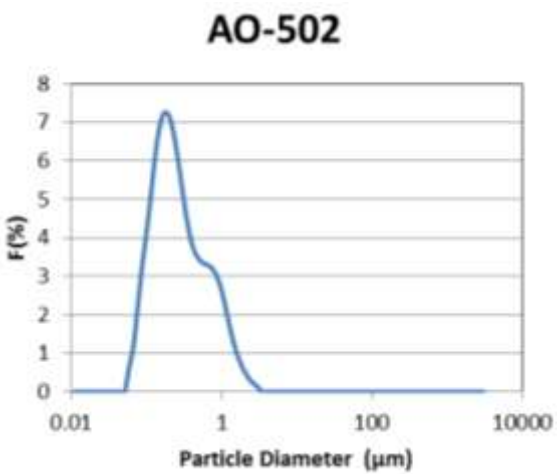
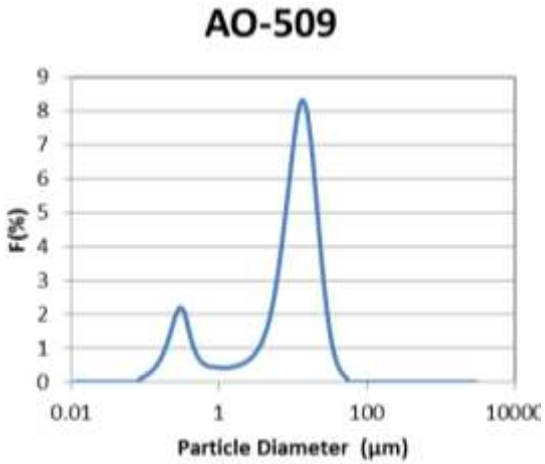
1-2. Various Size Spherical Silica, Alumina
Admafine Alumina Product Line Up

■Particle Size Distribution

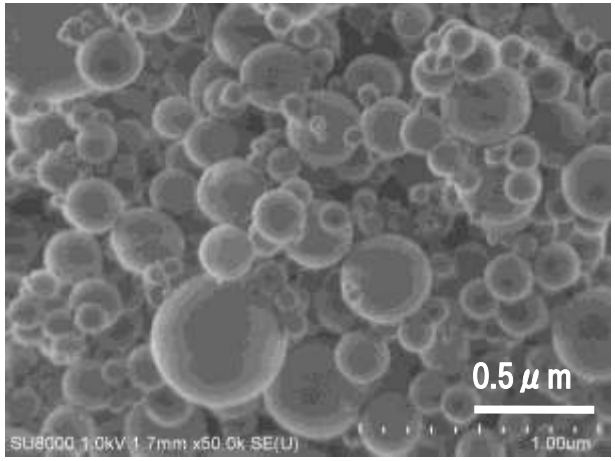


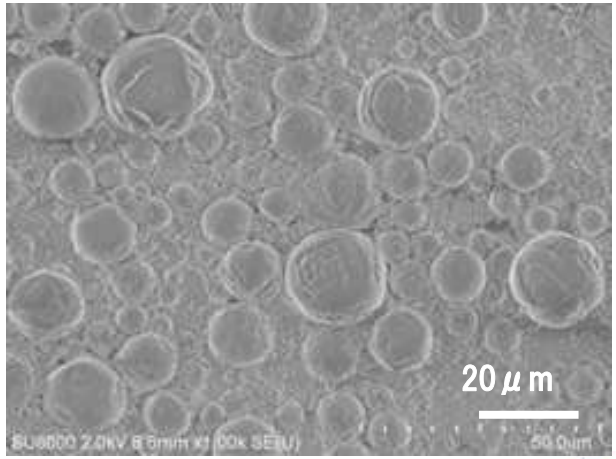
Particle diameter ：0.2 μm



Particle diameter ：10 μm

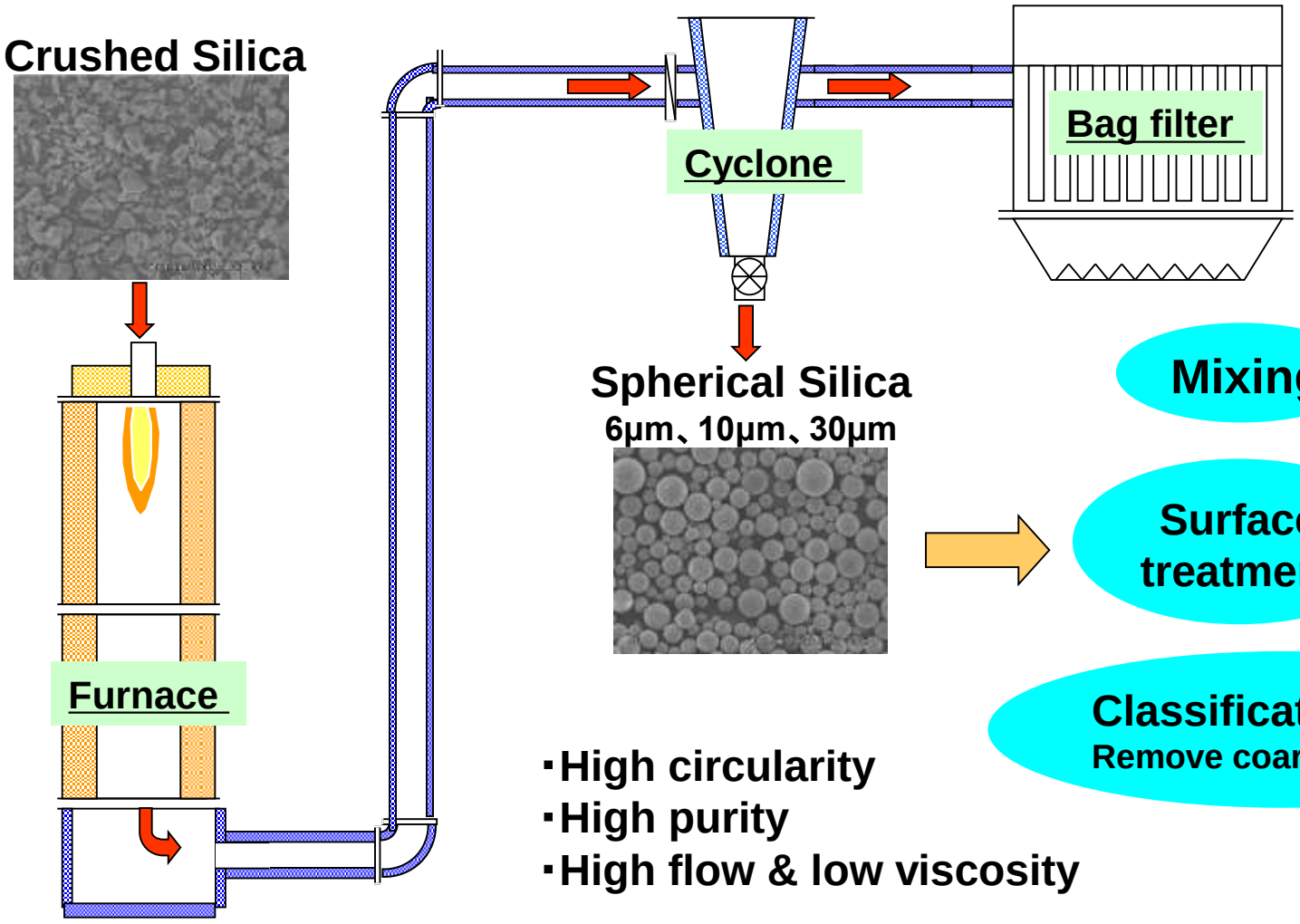
■SEM image





1-2. Various Size Spherical Silica

Admafuse Manufacturing Process (5 – 30um)

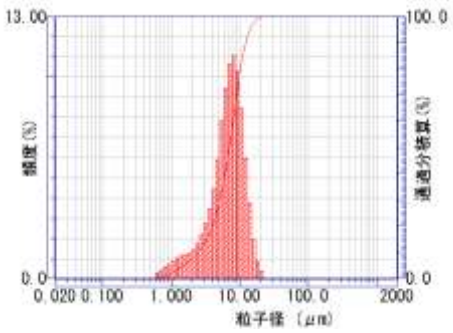
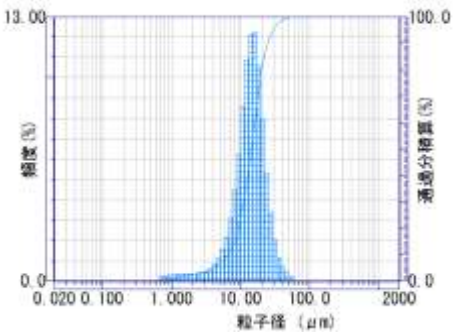
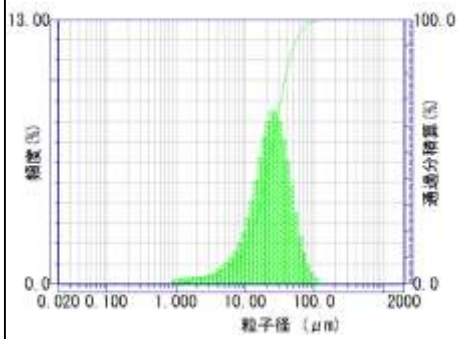
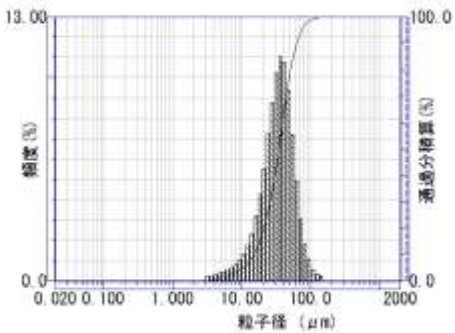
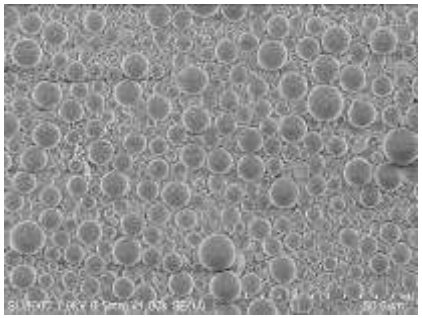
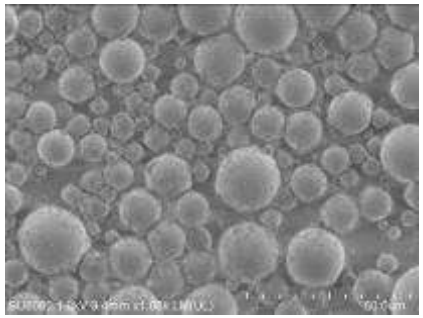
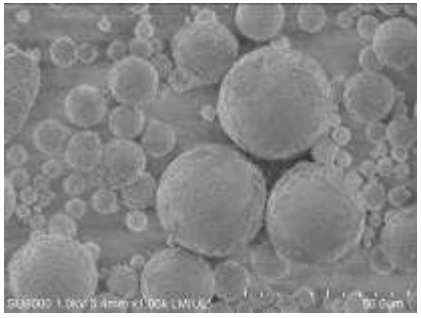
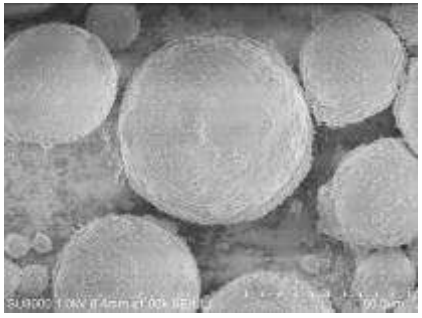


- High circularity
- High purity
- High flow & low viscosity

1-2. Various Size Spherical Silica

Admafuse Product Line Up

Product name

FE9-	FEB-	FED-	FEF-
			
6μm	10μm	20μm	30μm
			

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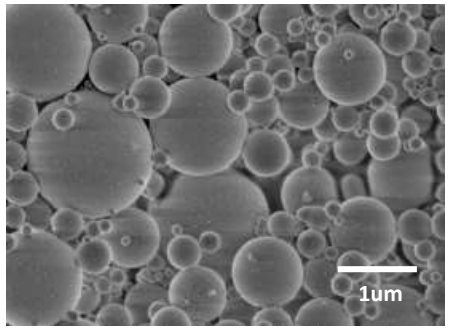
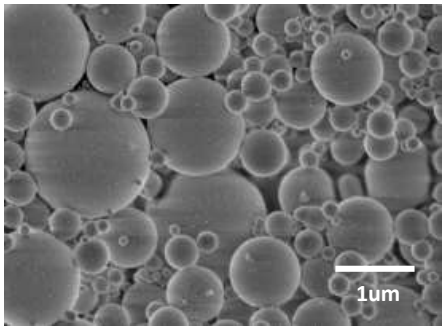
Contents



2-1. Admafine and Admafuse Silica -
Features and Effects of Admafine & Admafuse Silica

Features



- **Sub-micron & Micron Size Spherical Silica**
- **PSD Control Technology** : Low viscosity, High filler loading by closet packing model
- **Surface Treatment Technology** : Various surface treatment agents which meets each resin system are available.
- **Precious Molding** : High precious molding which can't use GF. (Camera Module, Connector, 3D printer..)

Effects

- Improvement of **Abrasion Resistance** and **Anisotropy** with **good flatness**
- Improvement of **Strength, Impact Resistance** and **Modulus**
- **Low Warpage, Good Dimensional Stability**
- **Low Viscosity** Compared to non spherical fillers
- Good **Settling Down Stability**

2-2. Customize Technology
- Surface Treatment Technology, “Layer Concept”.

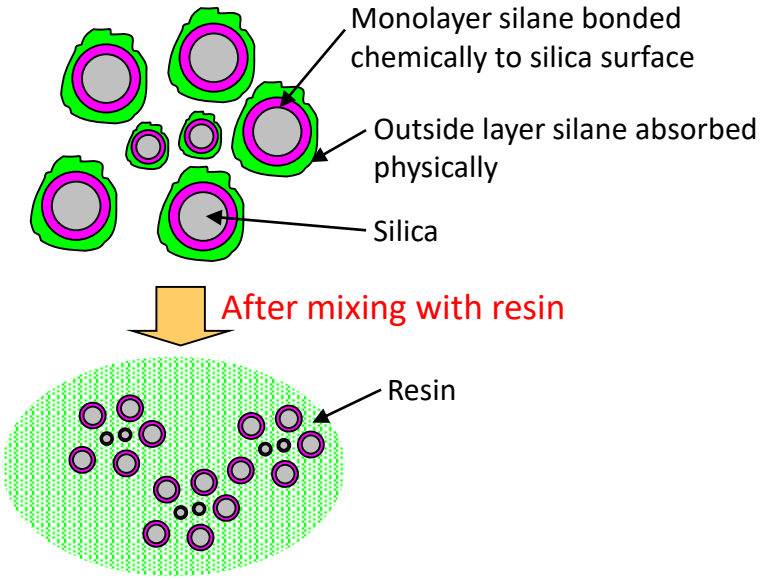
Silica surface modified with silane coupling agent are beneficial for;

(1) Low resin viscosity

(2) Less agglomeration

(3) Better compatibility with epoxy resin

Admatechs Surface Treated Silica

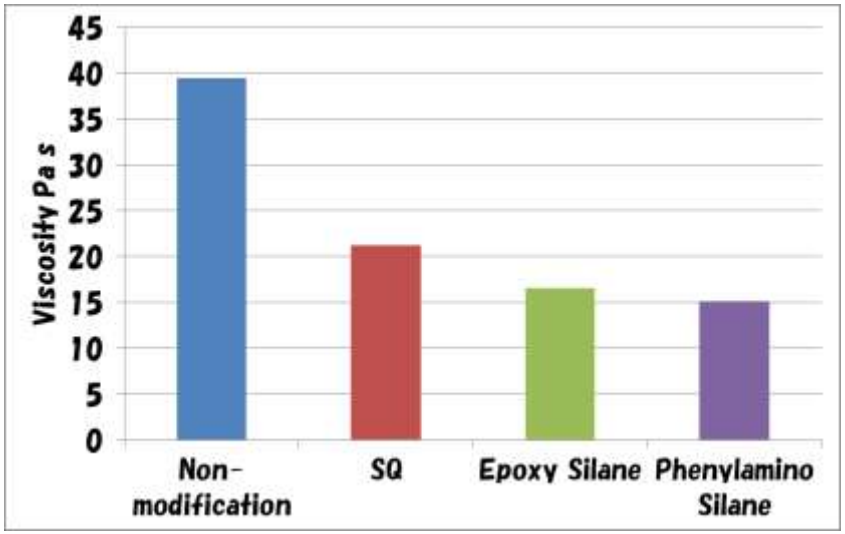


Viscosity Data

Resin : Bis F + Bis A epoxy resin

Silica : 0.5μm silica

Loading : 65wt%



Share rate at 1 (1/sec)

Surface treatment improves the compatibility with resin and reduces the viscosity.

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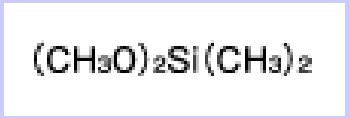
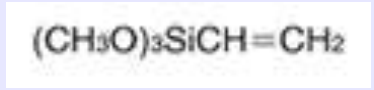
2-2. Customize Technology

Example of Surface Treatment Agents

Silane Coupling Agent	Target Resin System	Silane Coupling Agent	Target Resin System
Dimethyl silane 	-	Epoxy silane 	PPS, Epoxy
Hexyl silane 	-	Phenyl amino silane 	PS, PA, Epoxy
Phenyl silane 	Olefin, LCP, PEEK, PI	Methacryl silane 	Olefin, ABS, Poly Ester, Acryl
Vinyl silane 	Olefin, (PEEK)	Isocyanate silane 	Urethane

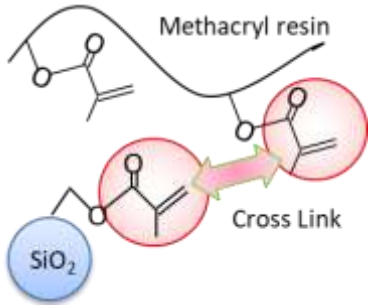
Various surface treatment agents are available.

2-2. Customize Technology

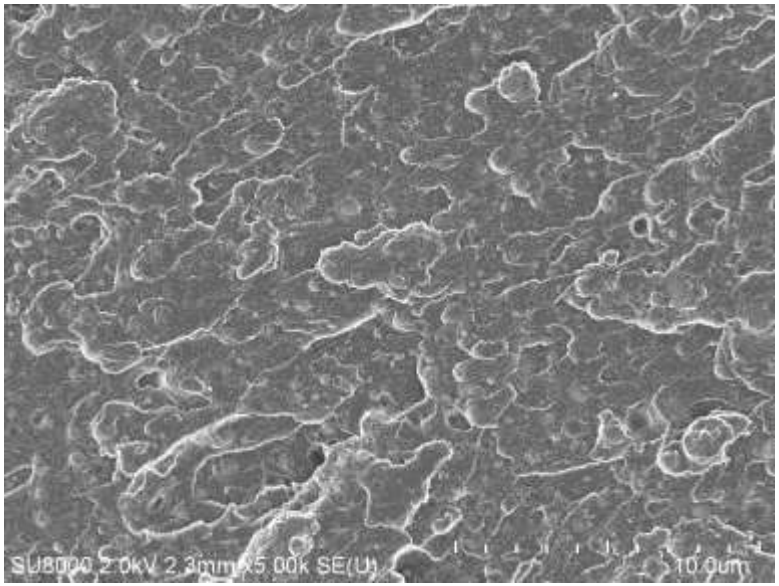
Effect of Surface Treatments

Test Condition

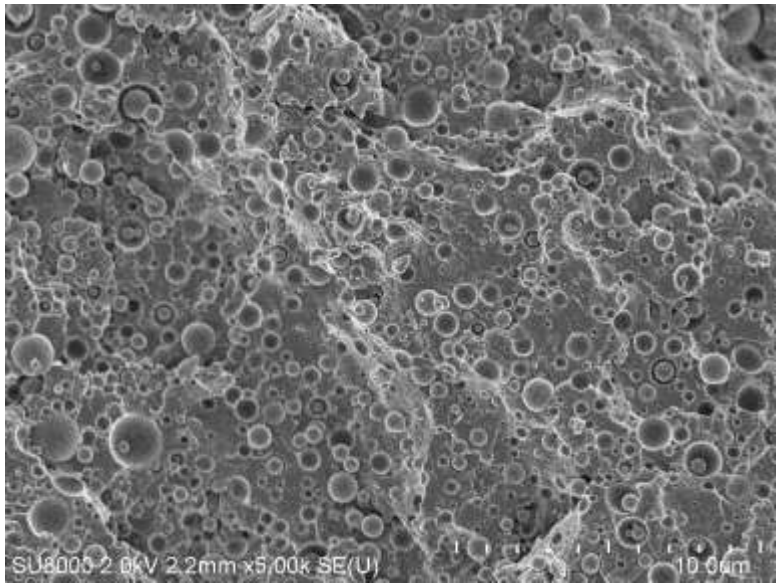
- Silica : 0.5µm silica with various surface treatment
- Resin : Urethan Methacryl resin + Radical Polymerization Initiator
- 3D Printing : DLP type 3D Printer “ML-100”made by MUTOH INDUSTRIES LTD.
- Evaluation : Observation of fracture surface after curing by SEM



Methacryl Treated Silica



Methacryl Treated Silica



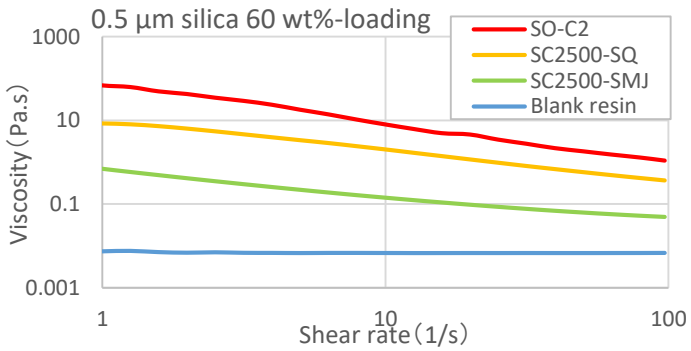
No Treatment, or Phenyl Treated Silica

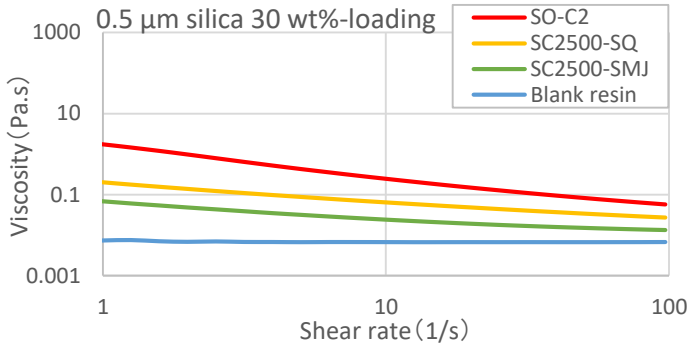
Surface treatment improves the adhesion between silica surface and resin.
This result improves physical properties of compounds.

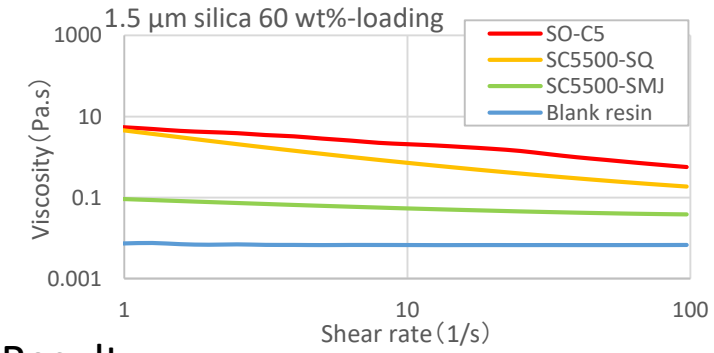
2-2. Customize Technology
- Surface Treatment Technology, Viscosity Data.

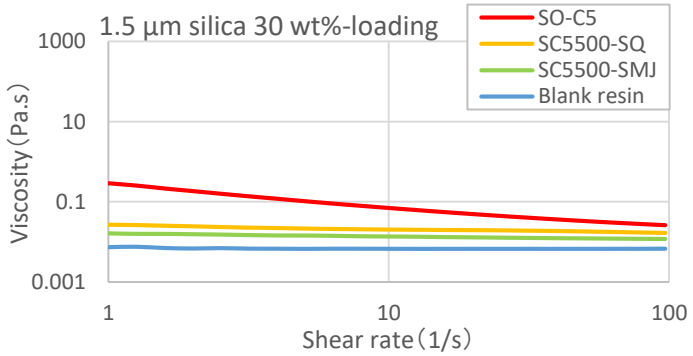
Viscosity Data

Resin :Acrylic resin
Silica :0.5 & 1.5μm silica
Surface treatment : non(SO-C2,SO-C5),SQ(SC2500-SQ,SC5500-SQ),methacryl silane(SC2500-SMJ,SC5500-SMJ)
Loading : 30 & 60 wt%
Measurement temperature : 25℃









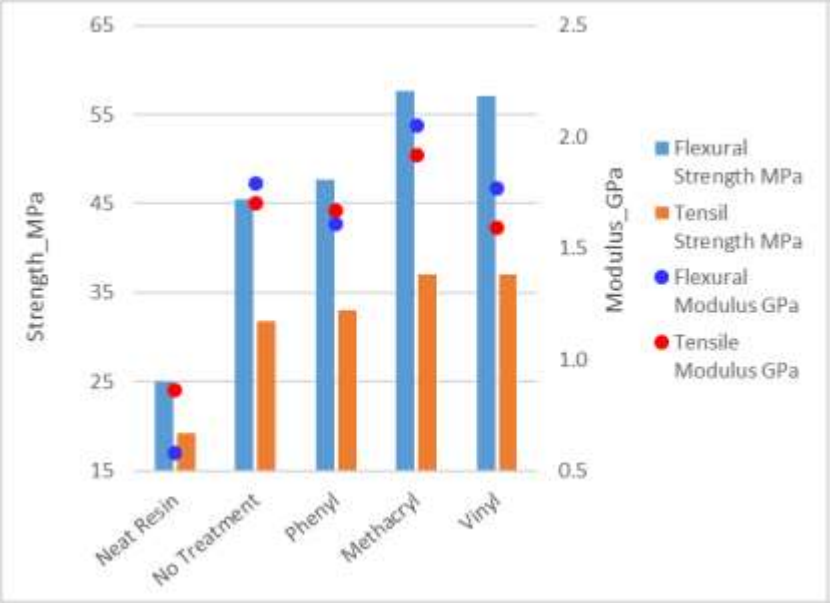
Result

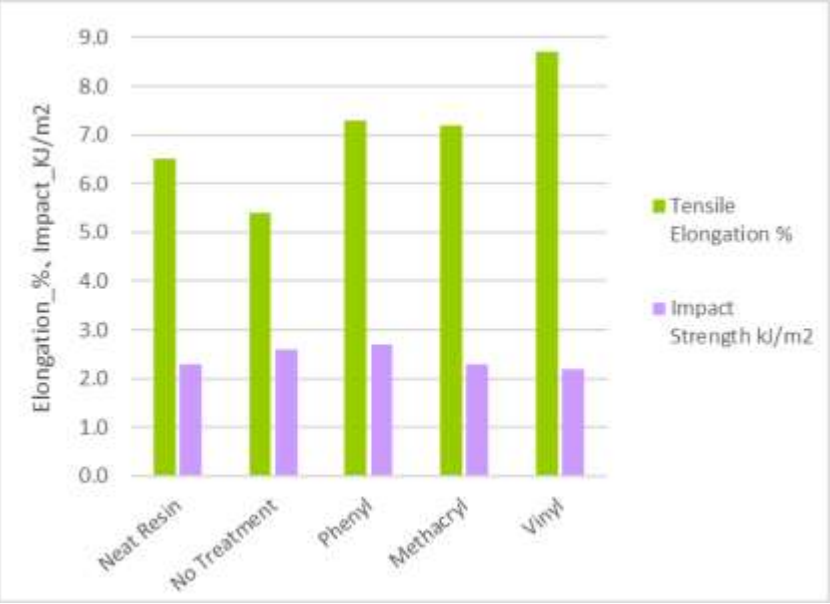
- In any case, surface treatment reduced the viscosity.
- Methacryl silane treatment was particularly effective at high filling.

Physical Properties - Surface Treatments

Physical Properties Data

Note	Surface Treatment	Loading Ratio	Flexural Strength	Flexural Modulus	Tensil Strength	Tensile Modulus	Tensile Elongation	Impact Strength
			MPa	GPa	MPa	GPa	%	kJ/m2
	Neat Resin	0%	25	0.6	19	0.9	6.5	2.3
	No Treatment	30%	46	1.8	32	1.7	5.4	2.6
	Phenyl	30%	48	1.6	33	1.7	7.3	2.7
++	Methacryl	30%	58	2.1	37	1.9	7.2	2.3
+	Vinyl	30%	57	1.8	37	1.6	8.7	2.2



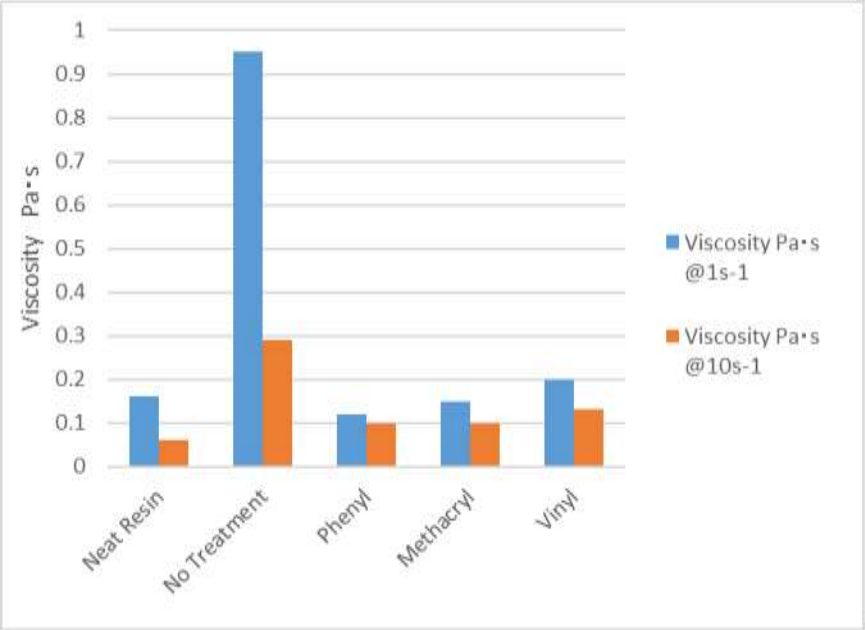


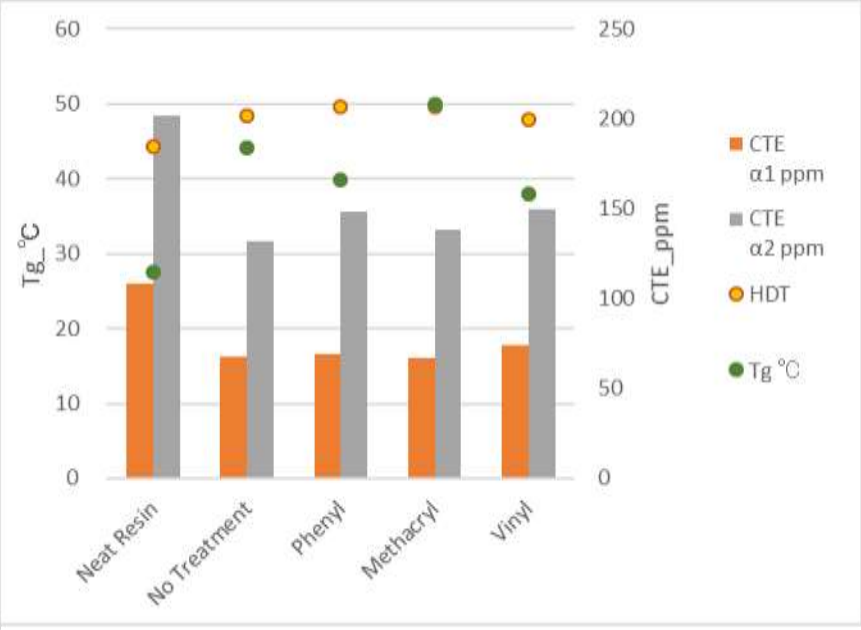
- Methacryl surface treated products performed best.
- In regards to impact strength, Phenyl and No Treatment products showed the largest improvement.
  →There is a possibility that the gaps between surfaces due loose attachment are mitigating the impact.

Viscosity, Thermal Properties - Surface Treatments

Viscosity, Thermal Properties Data

Note	Surface Treatment	Loading Ratio	Viscosity		HDT	Tg	CTE α1	CTE α2
			Pa·s @1s^{-1}	Pa·s @10s^{-1}	℃	℃	ppm	ppm
	Neat Resin	0%	0.16	0.06	44	28	108	202
	No Treatment	30%	0.95	0.29	48	44	68	132
	Phenyl	30%	0.12	0.10	50	40	69	148
++	Methacryl	30%	0.15	0.10	50	50	67	138
+	Vinyl	30%	0.20	0.13	48	38	74	150



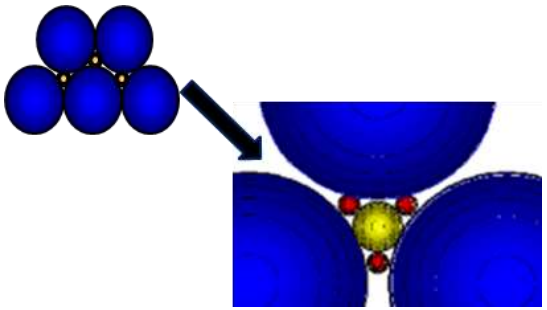


- **Methacryl surface treated products have low viscosity which is almost same as Neat Resin.**
- **Thermal properties (HDT, Tg, CTE) is increased because of adding silica.**

2-2. Customize Technology

Control of Particle Size Distribution

<Closest Packing Concept>



1) Combination of bigger particle and smaller particle

2) Submicron size & Spherical shape

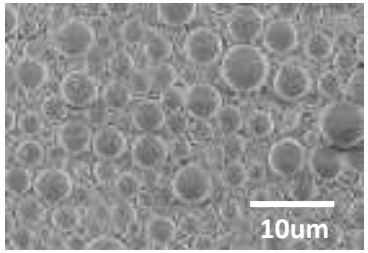
Resin Viscosity

Resin : Liquid Epoxy resin （BisA ＆ BisF mixed）

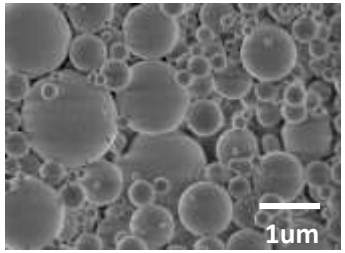
Filler : 5um silica

: 0.5um silica]

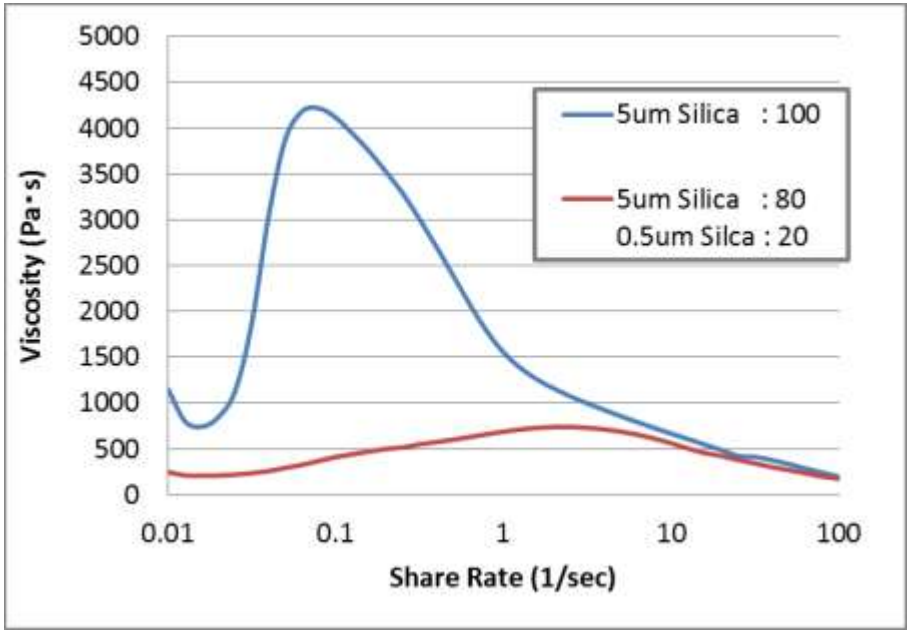
Loading : 80wt%



5um silica (FE975A)



0.5um silica (SC200G-SQV)

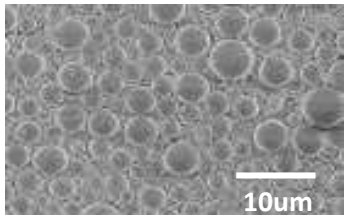


Closest Packing can improve the compound viscosity.

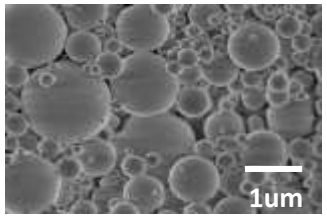
2-3. Admafine and Admafuse Silica - Evaluation of Viscosity and Settling Down Stability

Silica Samples

- **Admafuse , 5um silica**
  - ①Original PSD (Only 5um)
  - ②Optimized PSD (5um + 0.5um)
  - ③Optimized PSD (5um + 0.5um), + Methacryl Treatment.



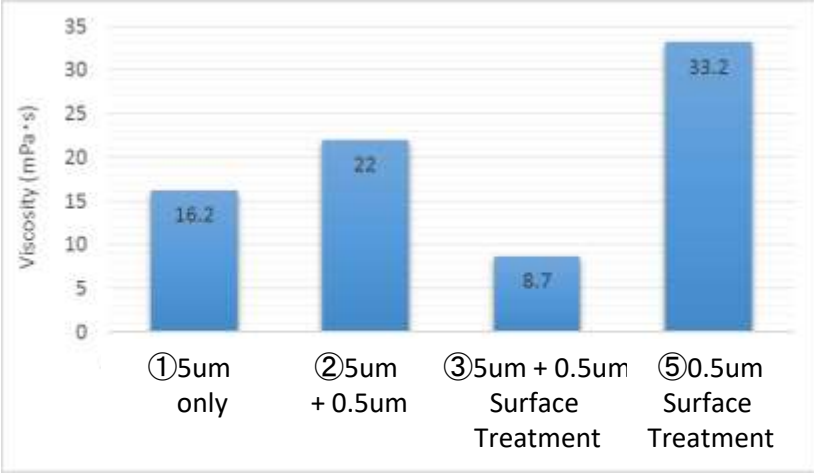
- **Admafine , 0.5um silica**
  - ④No Surface Treatment
  - ⑤Methacryl Treatment



Viscosity Evaluation Results

- **Procedure**
  - Silica (70wt%) + MMA (30wt%) was dispersed using ultra sonic wave.
  - Viscosity was measured using rheometer.

Samaple		Average Diameter (μm)	SSA (m2/g)	Viscosity (mPa･s)
Admafuse (FE975A) 5um silica	① 5um only	6.8	2.1	16.2
	② 5um + 0.5um	5.5	2.8	22.0
	③ 5um + 0.5um Methacryl	5.5	2.8	8.7
Admafine (SO-C2) 0.5um silica	④ 0.5um	0.5	6.3	No Dispersion
	⑤ 0.5um Methacryl	0.5	6.3	33.2

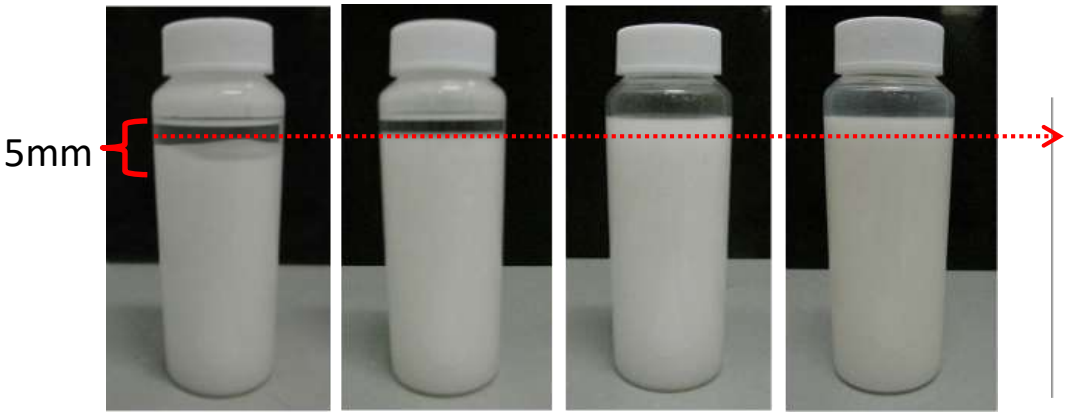


"Controlling PSD & methacryl treatment" is effective for viscosity of MMA composite.

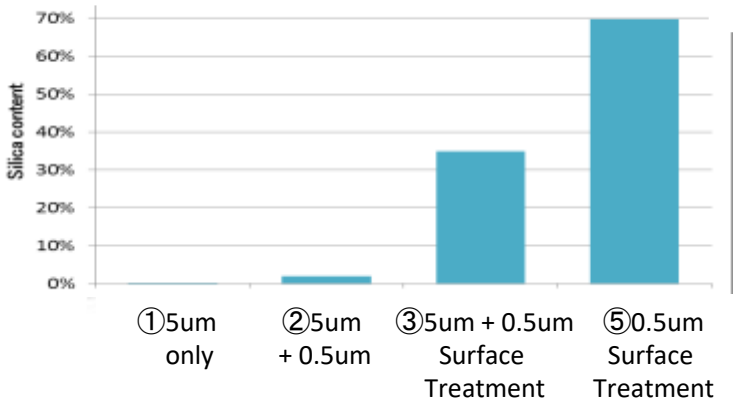
2-3. Admafine and Admafuse Silica - Evaluation of Viscosity and Settling Down Stability

Settling Down Evaluation Results

- **Procedure**
  - Silica (70wt%) + MMA (30wt%) was dispersed using ultra sonic wave.
  - The MMA dispersions were put into vessels, then keep them for 12hrs.
  - Check the level of settling down by eye, then measure the silica concentration which is under 5mm from the top of dispersion.



Silica concentration under 5mm from the top



- Methacryl treated samples were no layer separation.
- "Admafuse Optimized PSD + Methacryl treatment" had concentration gradient, but "Admafine + Methacryl treatment" had no settling down after 12hrs.

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2-4. Product Line Up for 3D Printer

3D Printer Type		SLS	SLA, MJ	SLA, SLS,	SLA, FFF
Resin Type		Thermoplastic LCP, PC, PEEK …	Acryl	Epoxy, PA	Urethane
Surface Treatment		Phenyl $(CH_3O)_3SiC_6H_5$ Vinyl $(CH_3O)_3SiCH=CH_2$	Methacryl $(CH_3O)_3SiC_3H_6OC(=O)C(CH_3)=CH_2$	Epoxy $(CH_3O)_3SiC_3H_6OCH_2CH(O)CH_2$ Phenyl Amino $(CH_3O)_3SiC_3H_6NH$–C$_6$H$_5$	Isocyanate $(C_2H_5O)_3SiC_3H_6N=C=O$
Silica Particle Size	5um, All in One	※	※	※	※
	2 um	※	※	○ Epoxy	※
	1.5 um	※	○ Methacryl	※	※
	1 um	※	※	※	※
	0.5 um	○ Phenyl ○ Vinyl	○ Methacryl	○ Epoxy ○ Phenyl Amino	○ Isocyanate
	0.3 um	※	○ Methacryl	※	※

○ : Commercialized ※ : No commercialized yet, However, they are available.

- Summary -

- **Various Size Silica Fillers and Customize Technology**

  Admatechs can supply various customized silica filler based on demand.

- **Surface treated Admafine and Admafuse silica**

  Surface treated silica can improve the viscosity and settling down property.

  In addition, they can improve the physical and thermal properties.

Thank you!

Admatechs

Admafine Silica Line Up

Particle size [μm]	Specific surface area [m^2/g]	Surface treatment	Slurry	
			Max filler loading [wt%]	Solvent
0.3	10-20	Regular(SQ) Epoxy Vinyl Phenyl-amino Methacryl Phenyl , etc.	～65	MEK MIBK CHN PGMAC , etc.
0.5	4-7		～75	
1.0	3-6		75	
1.5	3-5		75	
2.0	1.5-2.5			

*Several cut points are available.

Purity	SiO_2 [%]	Moisture [%]	Na+ [ppm]	Cl- [ppm]	Fe [ppm]	Al [ppm]	U [ppb]	α-ray count [$c/cm^2 \cdot h$]
Regular grade	> 99.8	< 0.05	< 1	< 1	< 500	< 700	11	0.006

※Data on this sheet are NOT guaranteed value.

Admafine Alumina Line Up

Base Material	Particle Size [μm]	Specific Surface Area [m^2/g]	Top Cut [μm]					
			75	45	25	15	10	5
AO-502	0.2	7.5	○	—	○	—	—	○
AO-509	10	1.5	○	○	○	○	—	

*Note: This table includes development grade.

Purity	Al_2O_3 [%]	Moisture [%]	Na+ [ppm]	Cl- [ppm]	Fe [ppm]	Si [ppm]
Regular grade AO-5 Type	> 99.8	< 0.3	< 1	< 2	< 1500	< 500

※Data on this sheet are NOT guaranteed value.

AdmaFuse Silica Line Up

Base Material	Particle size [μm]	Specific surface area [m^2/g]	Top cut [μm]				Surface Treatment
			75	45	25	20	
FE9	~8	~2	○	—	○	○	Epoxy Vinyl Phenyl-amino Methacryl Phenyl , etc.
FEB	~15	~2	○	—	○		
FED	~25	~2	○	○			
FEF	~35	~2	○				

Purity	SiO_2 [%]	Moisture [%]	Na+ [ppm]	Cl- [ppm]	Fe [ppm]	Al [ppm]	U [ppb]	α-ray count [$c/cm^2 \cdot h$]
High purity grade (Low α-ray)	> 99.9	< 0.1	< 1	< 1	< 300	< 100	< 1	< 0.002

※Data on this sheet are NOT guaranteed value.

Admanano Silica Line Up

Particle size [nm]	Specific surface area [m^2/g]	Surface treatment	Slurry		Resin master batch
			Filler loading [wt%]	Solvent	
10	300	Methacryl Vinyl Phenyl Phenyl-amino	20～30	MEK MIBK CHN PGMAC , etc.	Resin : Epoxy Acrylic Urethane , etc.
50	60		50		
100	30		60		

*Note: This table includes development grade.

Purity	SiO_2 [%]	Moisture [%]	Na+ [ppm]	Cl- [ppm]	Fe [ppm]	Al [ppm]	U [ppb]	α-ray count [$c/cm^2 \cdot h$]
Regular grade	> 95	< 2	< 10	< 10	< 1000	< 2000	-	-

※Data on this sheet are NOT guaranteed value.