UV Curable Polysiloxane-acrylic Hybrid Resins

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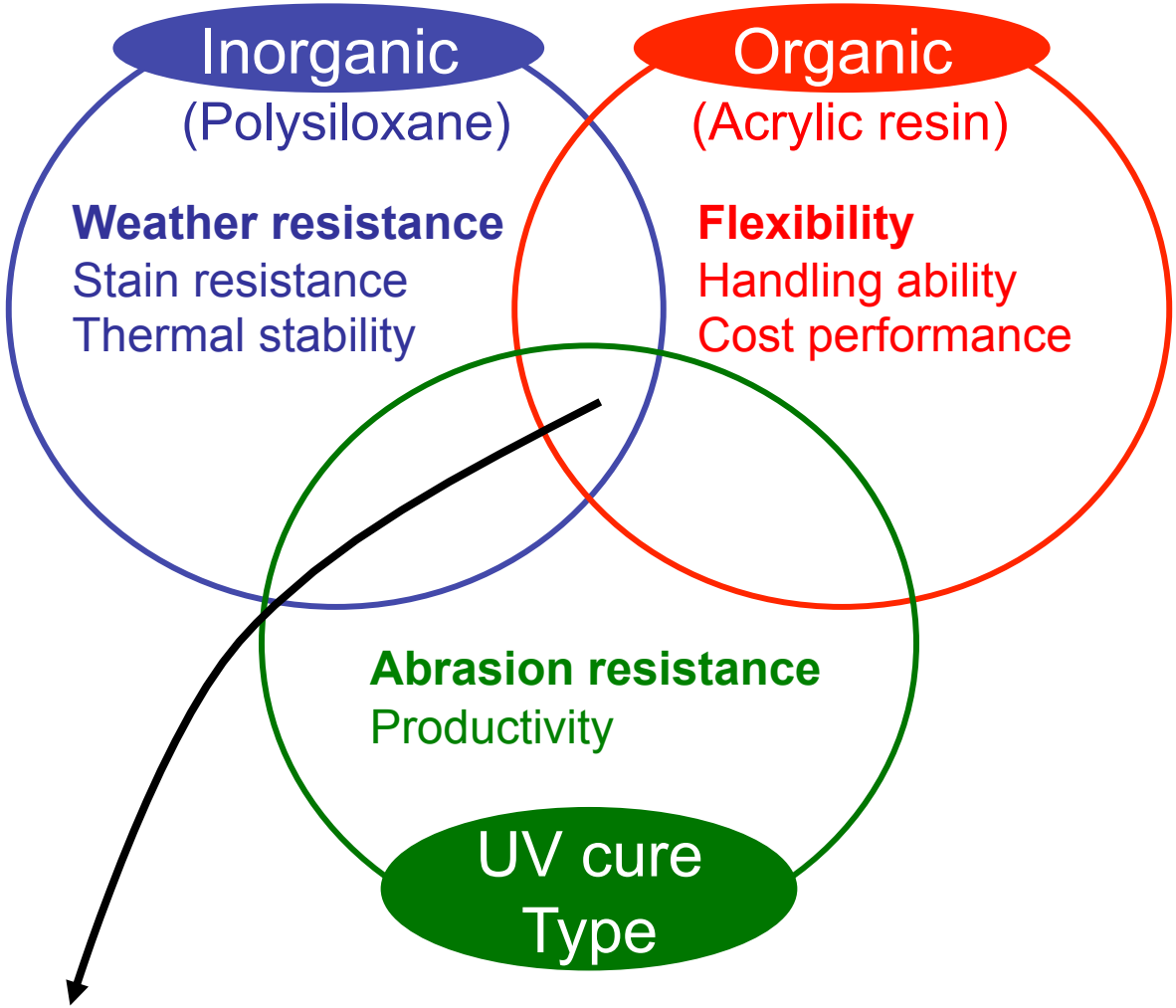
Development concept in this work



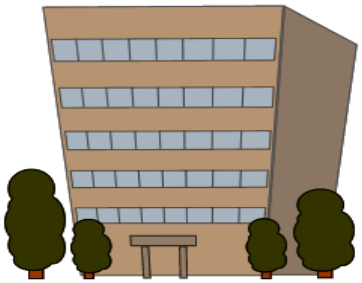
Next functional coating.

Expected coating field in this work

《Application Fields & Demands》

- *Automotives*
  - *・・・ Abrasion resistance and weather resistance for plastics*
- *A*rchitectural materials
  - *・・・ Weather resistance and self-cleaning effect*
- *Aero*
  - *・・・ Weather resistance and self-cleaning effect*

Automotives



Architectural materials

Aero

Contents

Registered patent

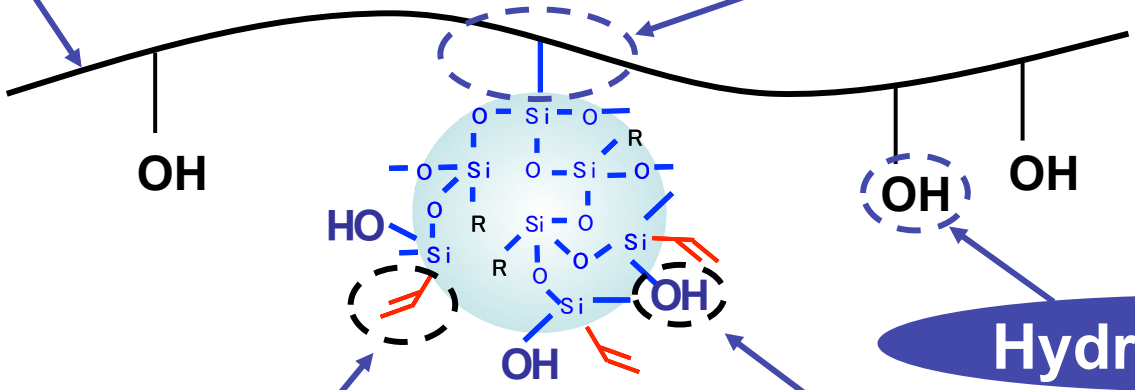
Concept of UV curable Polysiloxane-Acrylic Hybrid Resin

Excellent transparency

Weather resistance

Acrylic chain

Chemical bond



Hydroxyl group

Unsaturated double bond

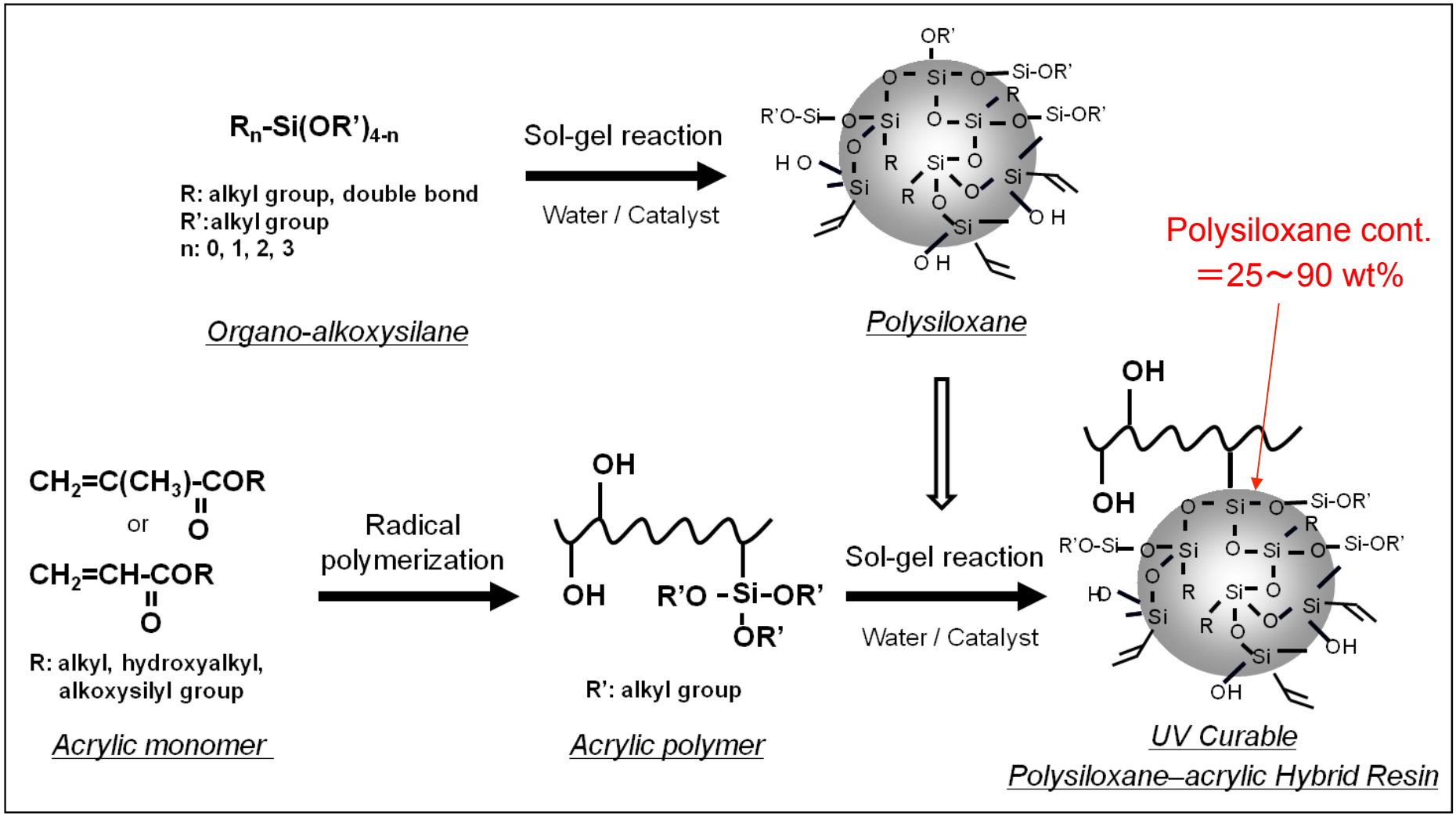
Polysiloxane

UV-curable
(Copolymerizable with multifunctional acrylates)
Hard coating

Weather resistance

Registered patent

Synthetic process of UV curable Polysiloxane-Acrylic Hybrid resin



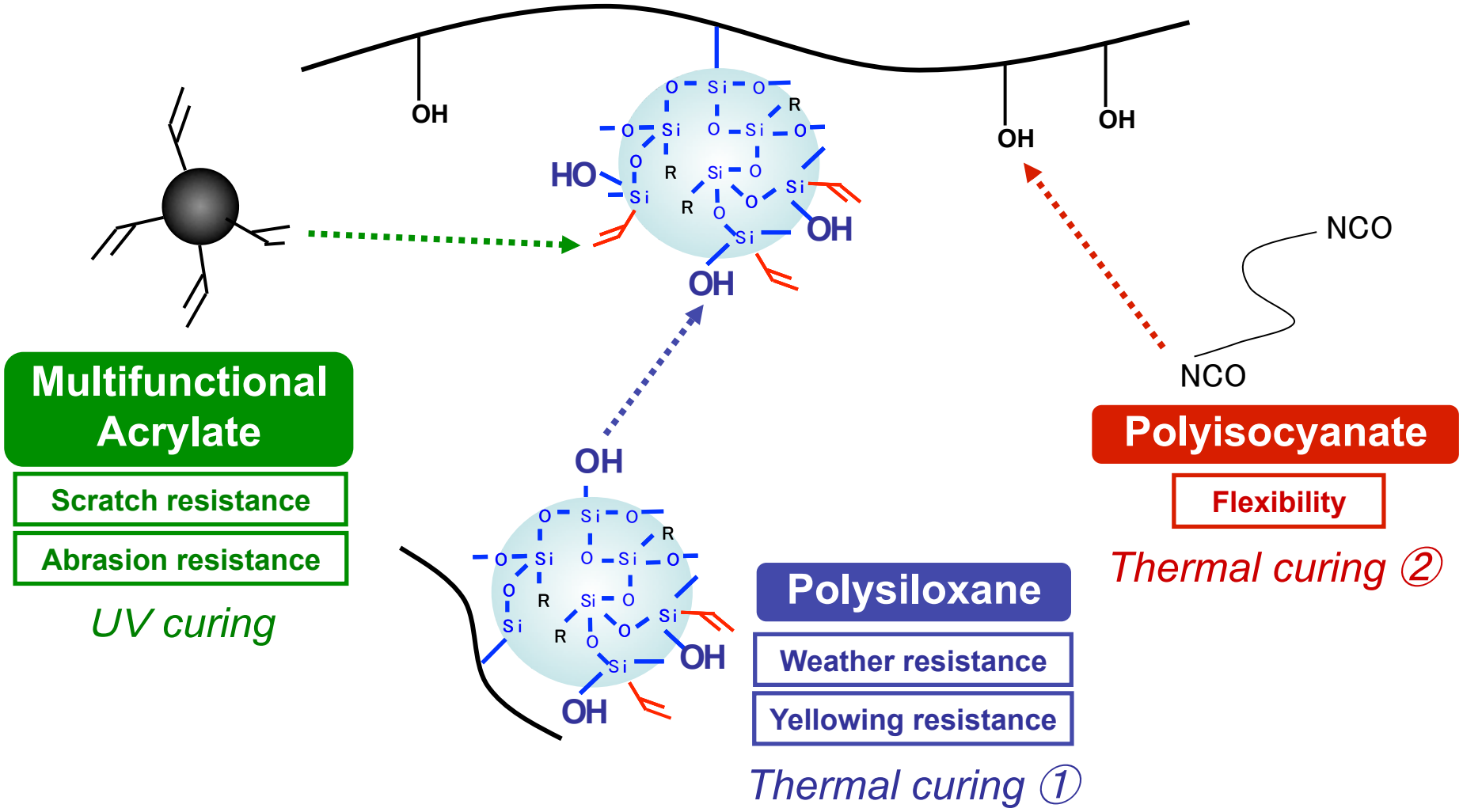
Bonding energy of polysiloxane(-Si-O-Si-)

	bonding energy (Kcal/mol)		ionicity (%)		bond distance (Å)	
	C	Si	C	Si	C	Si
C	85	75	0	11	1.5	1.9
Si	75	51	11	0	1.9	2.3
O	81	106	23	51	1.4	1.6

Ultraviolet energy: 95Kcal/mol (λ=300nm)

Concept of the cross-linking

UV Curable Polysiloxane – Acrylic Hybrid Resin



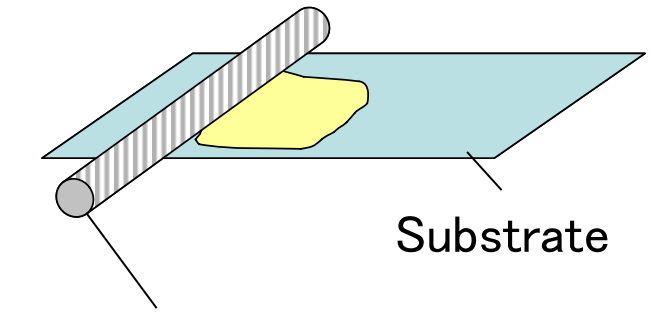
Coating formulations of the hybrid resin

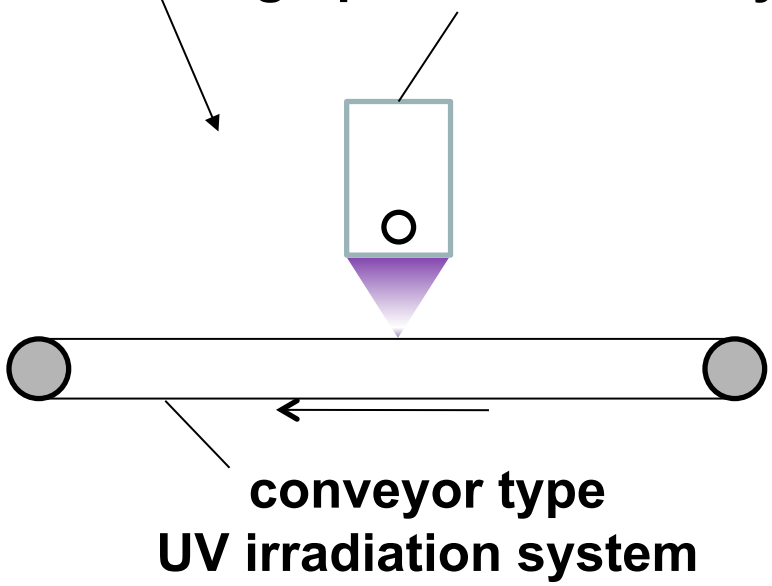
Sample No.	UV curable hybrid resin		Acrylate monomer Cont. [%]	Polyisocyanate Cont. [%]
	Polysiloxane Cont. [%]	Acrylic polymer Cont. [%]		
SD-1	30	30	20	20
SD-2	15	15	50	20
SD-3	30	30	40	0
SD-4	0	0	100	0

Preparation of UV cured films

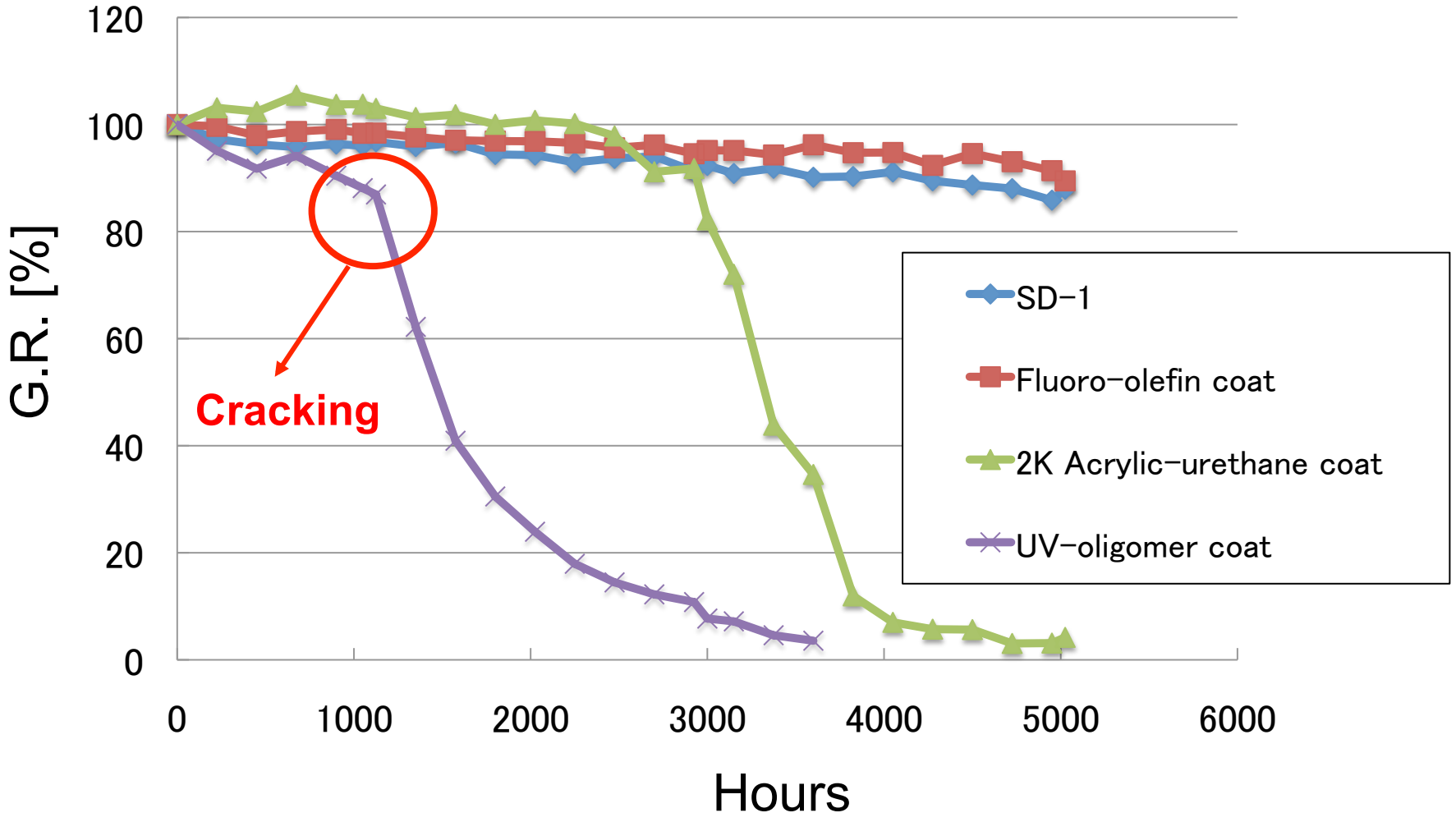
Coating → Drying → UV irradiation → Curing → Samples

UV curing *Thermal curing*

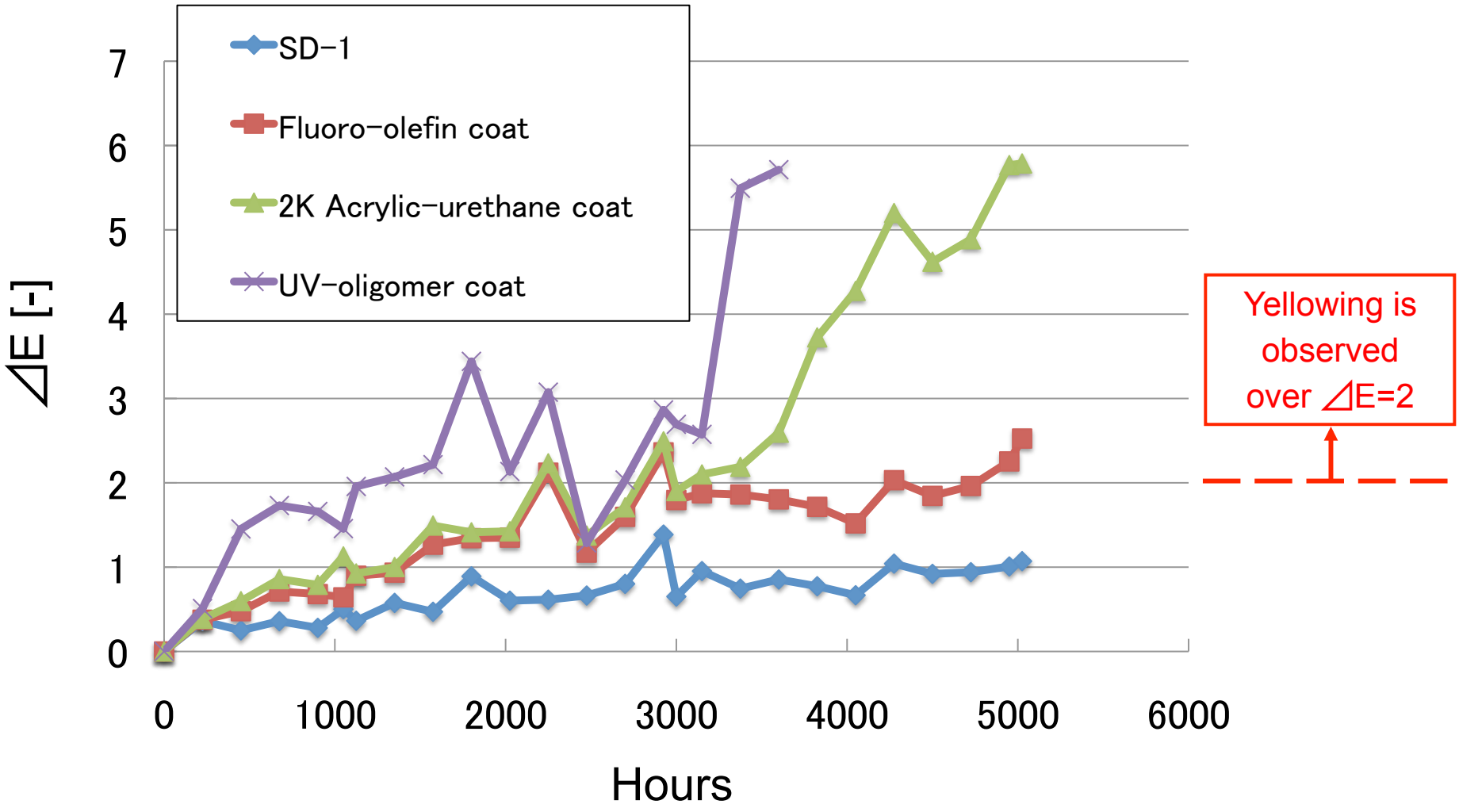




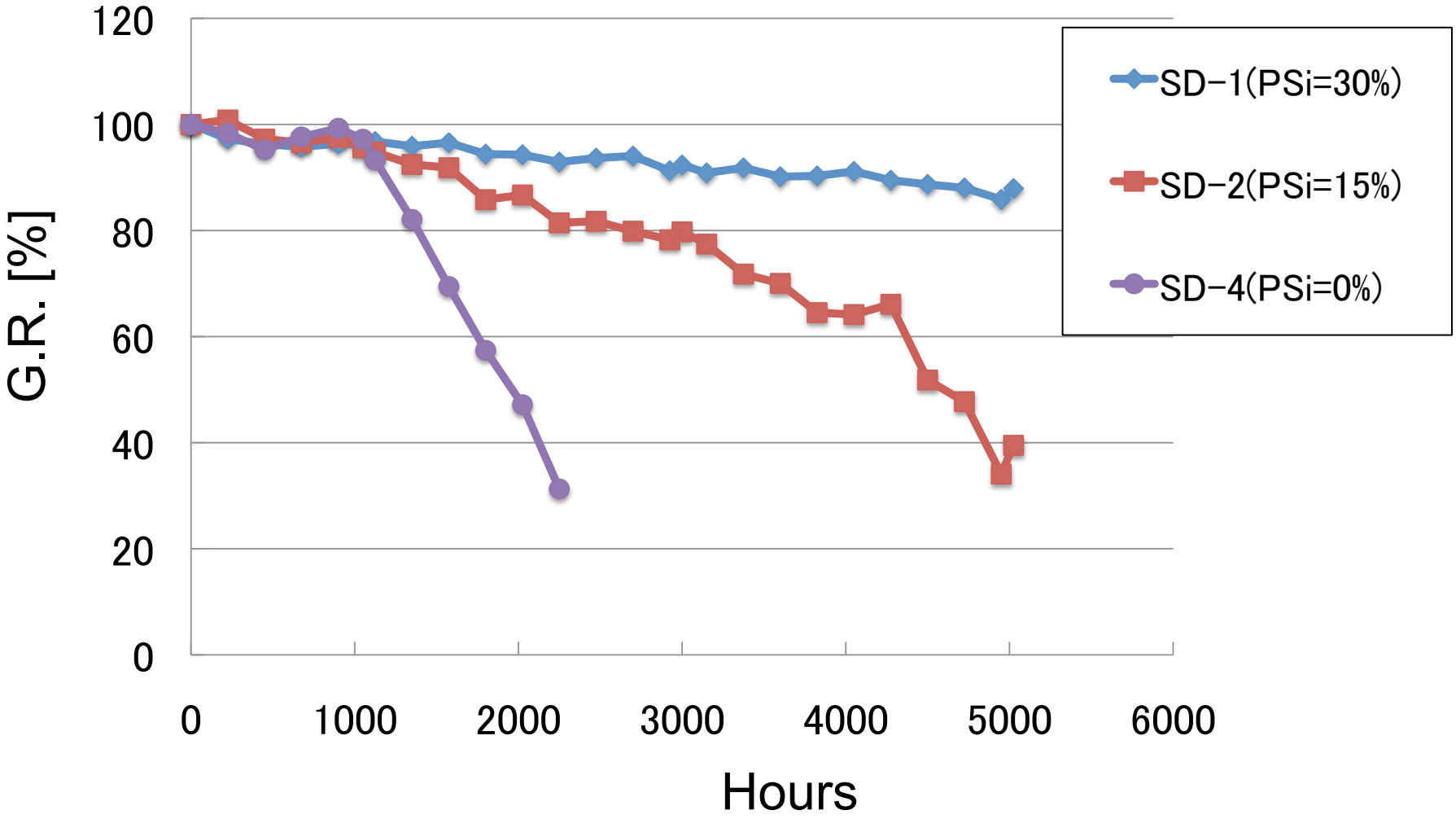
Result of Accelerated exposure test (SWOM)
－Gloss retention－



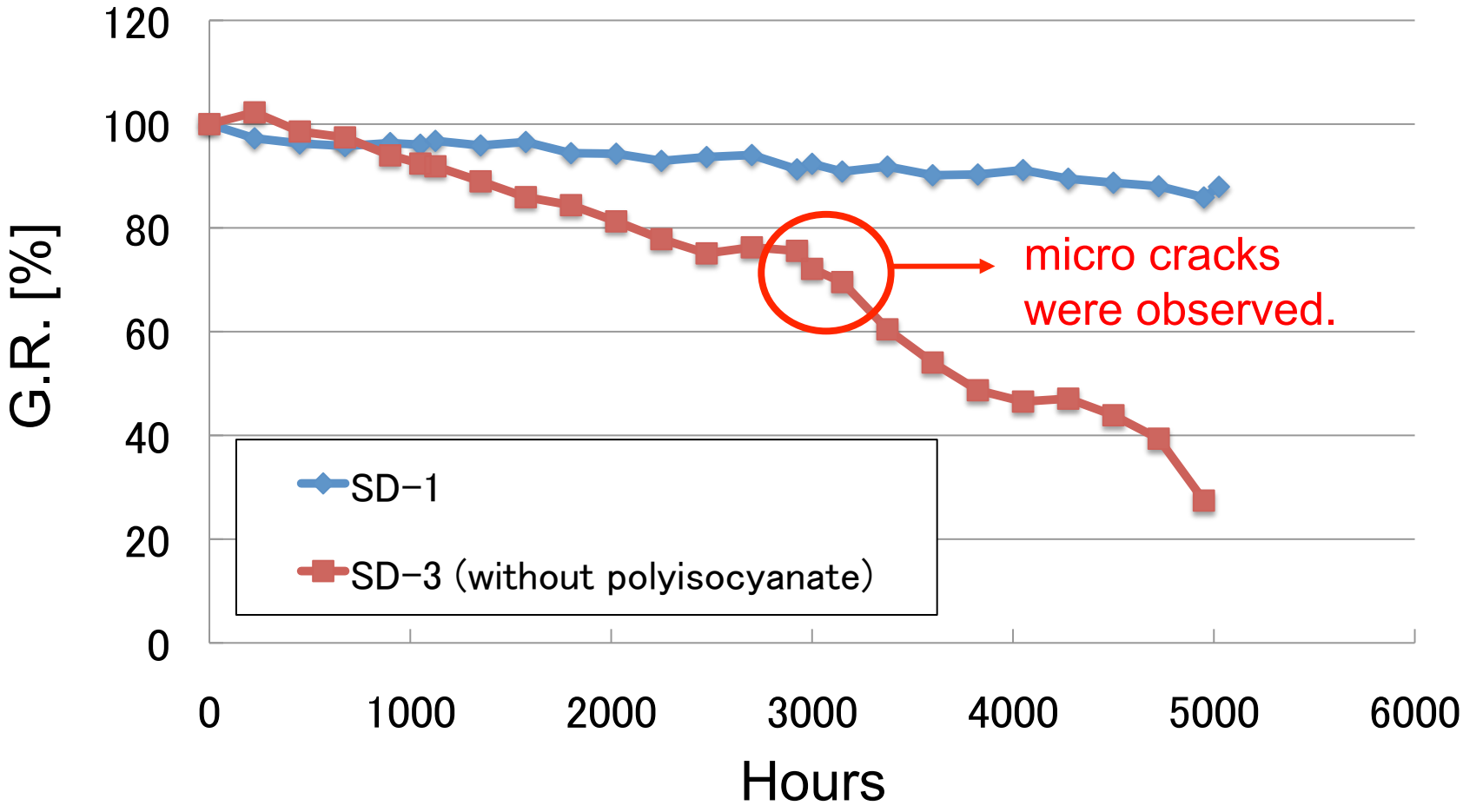
Result of Accelerated exposure test (SWOM)
－Yellowing－



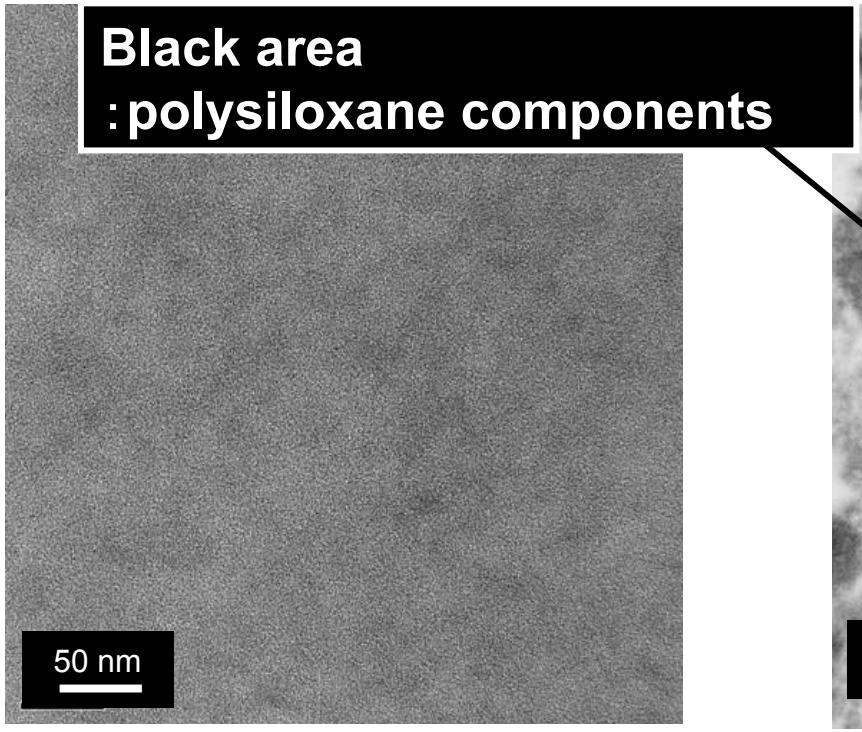
Effect of polysiloxane content for gloss retention (SWOM)



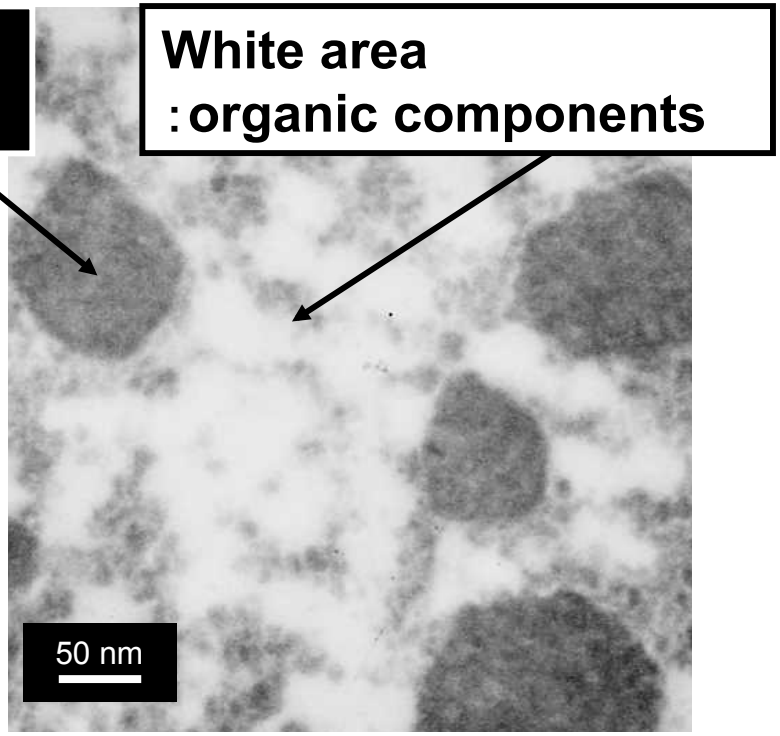
Need for urethane linkage for gloss retention (SWOM)



Morphology analysis of SD-1 cured film



A. SD-1 UV cured film.



B. Polysiloxane/acrylic-polymer blended resin coat .

＜Observation of the cured films by using TEM＞

- Polysiloxane formed matrix homogeneously on the molecular level in the hybrid film.

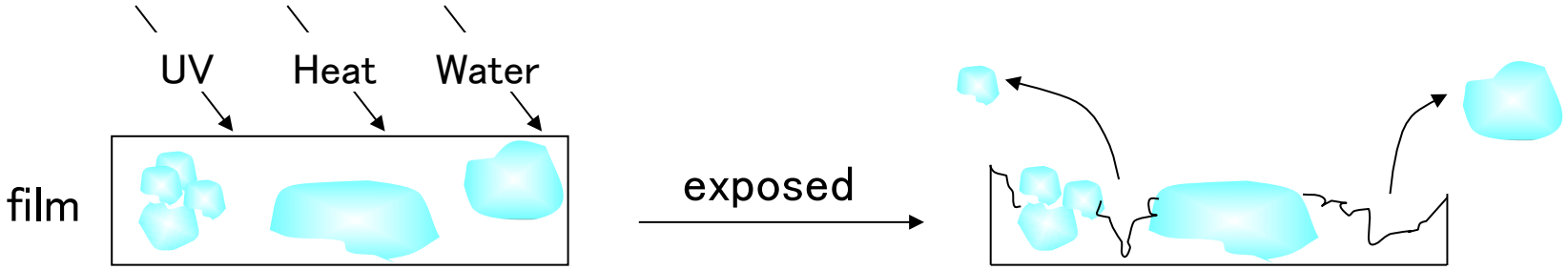
Mechanism for weather resistance of the film

Polysiloxane-acrylic hybrid resin coat.

Polysiloxane components and organic components are dispersed homogeneously.

Surface organic components degrade, but underlying polysiloxane components stop degradation.

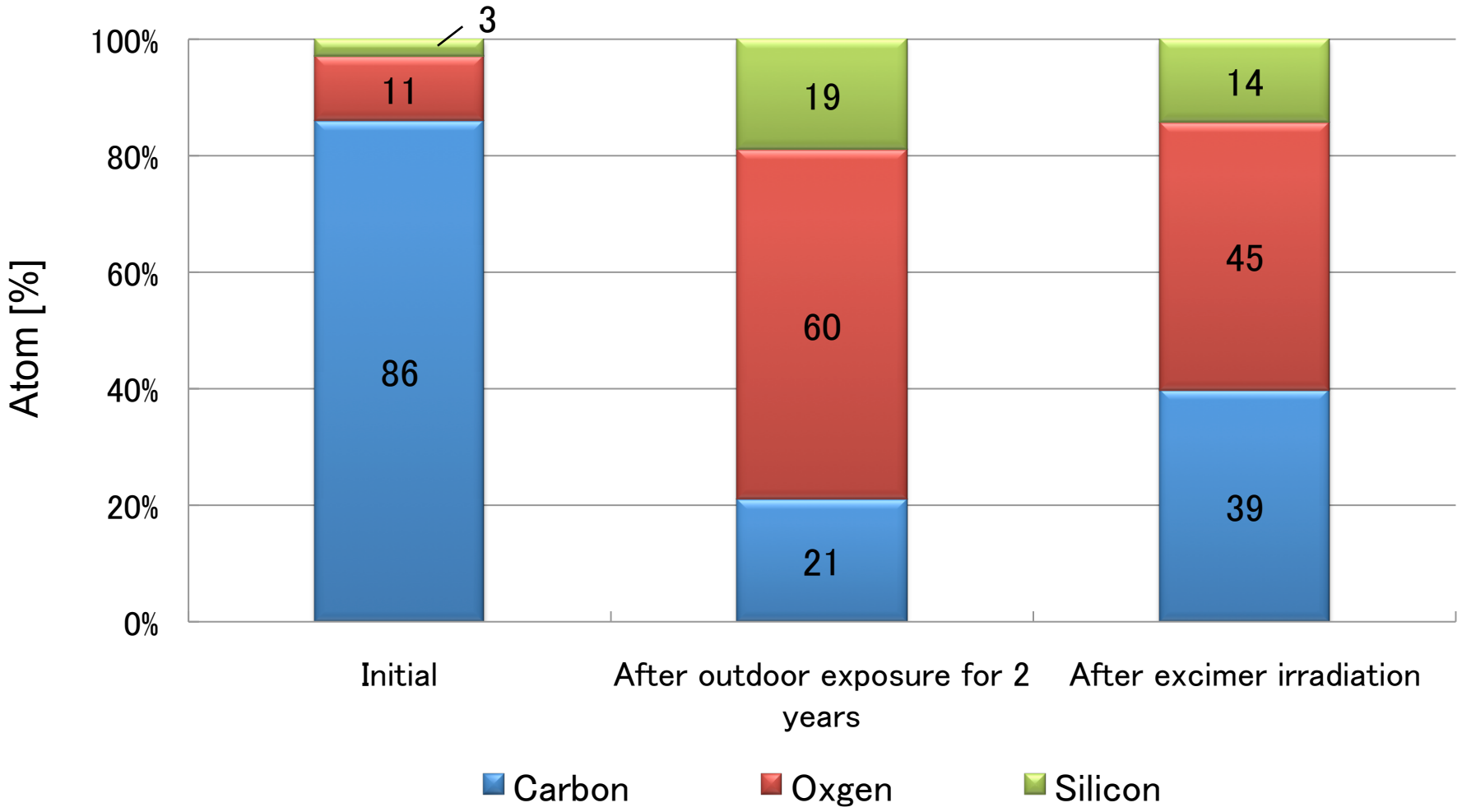
Polysiloxane/acryl polymer blended resin coat.



Polysiloxane components are dispersed heterogeneously, because of aggregation.

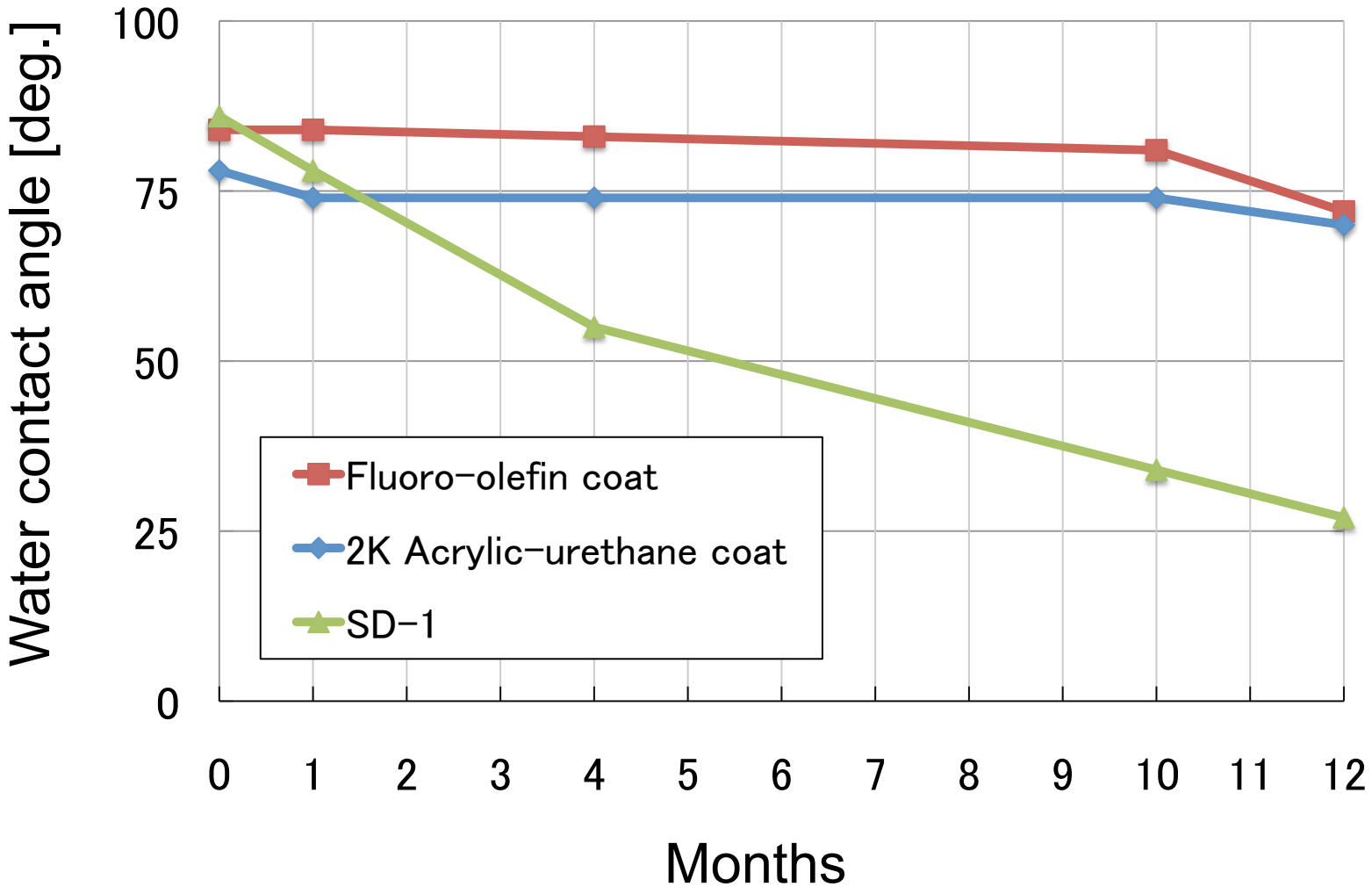
By degradation of organic components, the film are damaged and polysiloxane components drop out.

Surface analysis of the film by XPS



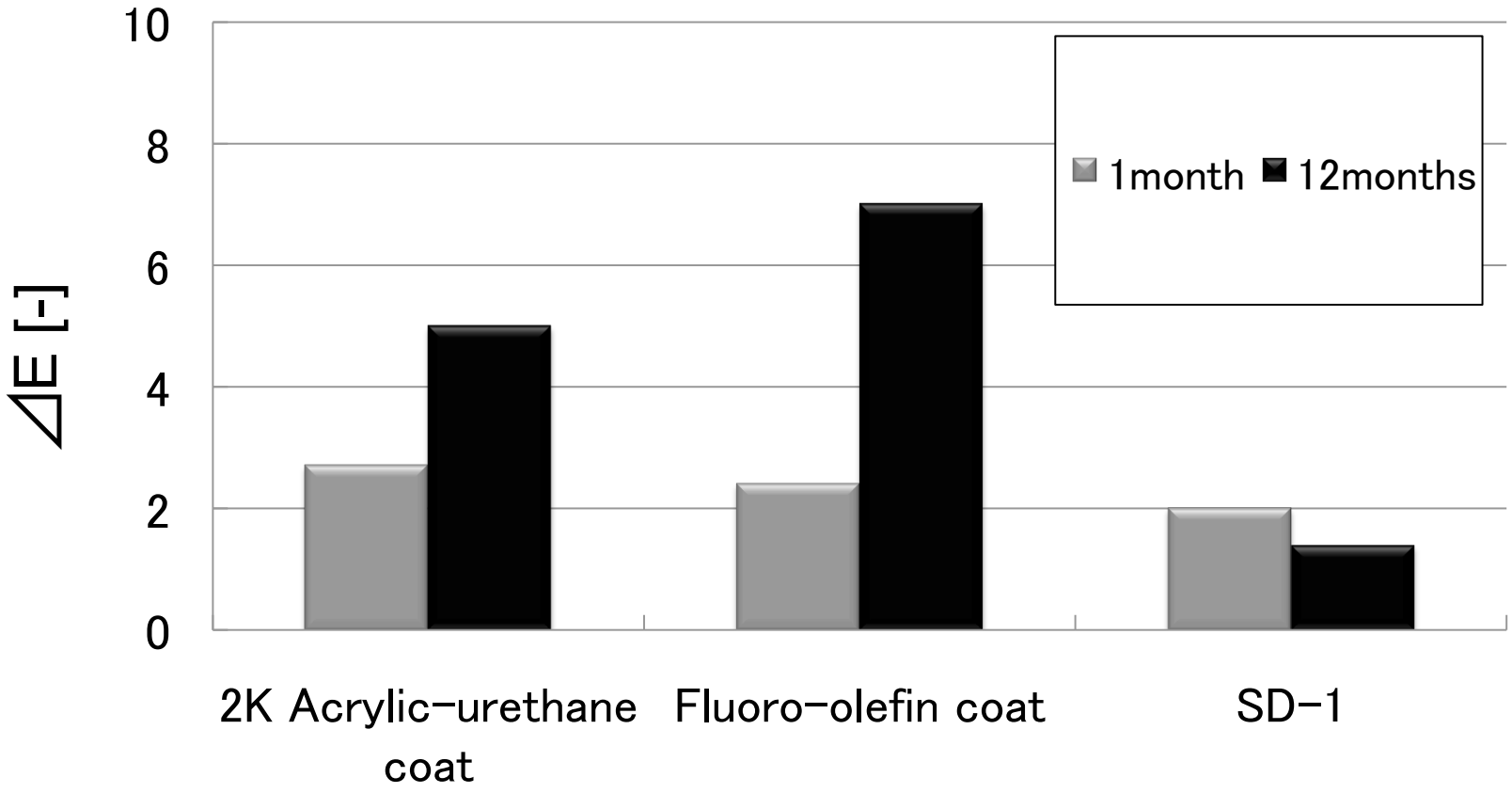
Element Components of the SD-1 film surface
at the initial time, after exposed outdoor, and after excimer irradiation

Self-cleaning effect



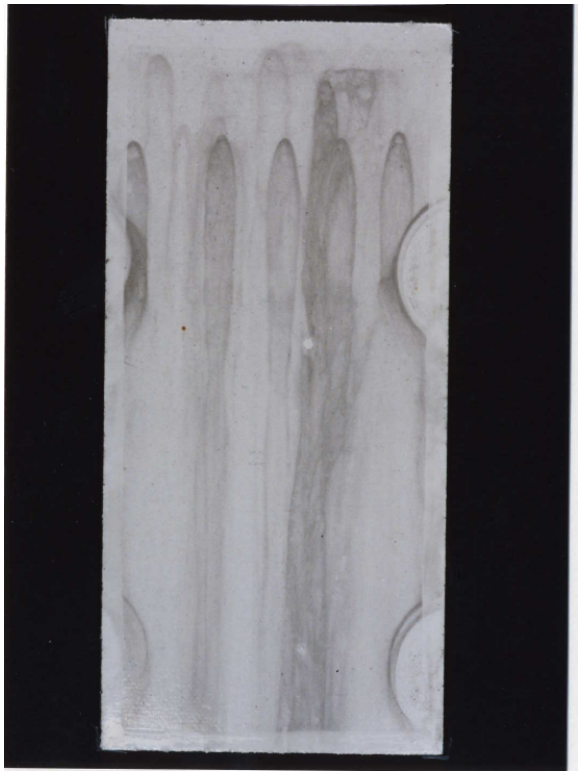
Self-cleaning effect

Stain resistance test of 2K acrylic-urethane coat and fluoro-olefin coat and SD-1 after exposure for 1 year in Osaka, Japan.

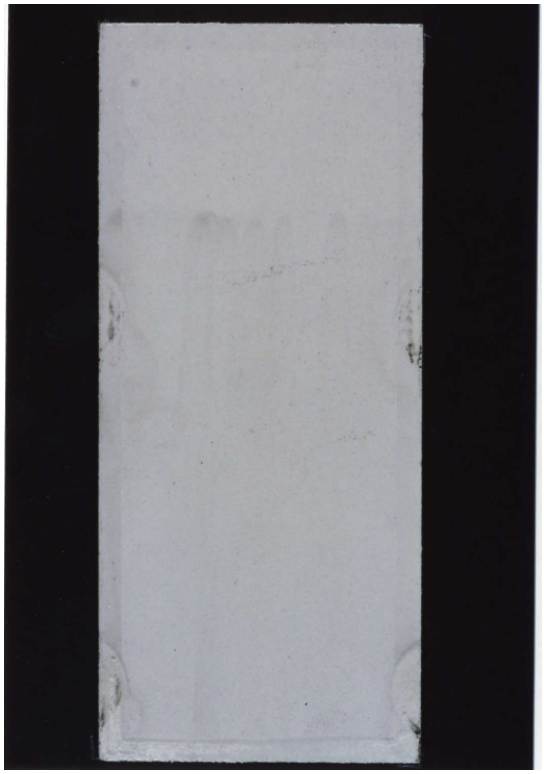


Self-cleaning effect

These are photo images of 2K acrylic-urethane clear coat and SD-1 clear coat after exposure for 1 year in Osaka, Japan.



2K Acrylic-urethane coat



SD-1

Primer : 2K Acrylic-urethane white enamel
Substrate : Aluminum plate (chromate treated)

Abrasion resistance of the clear coat film

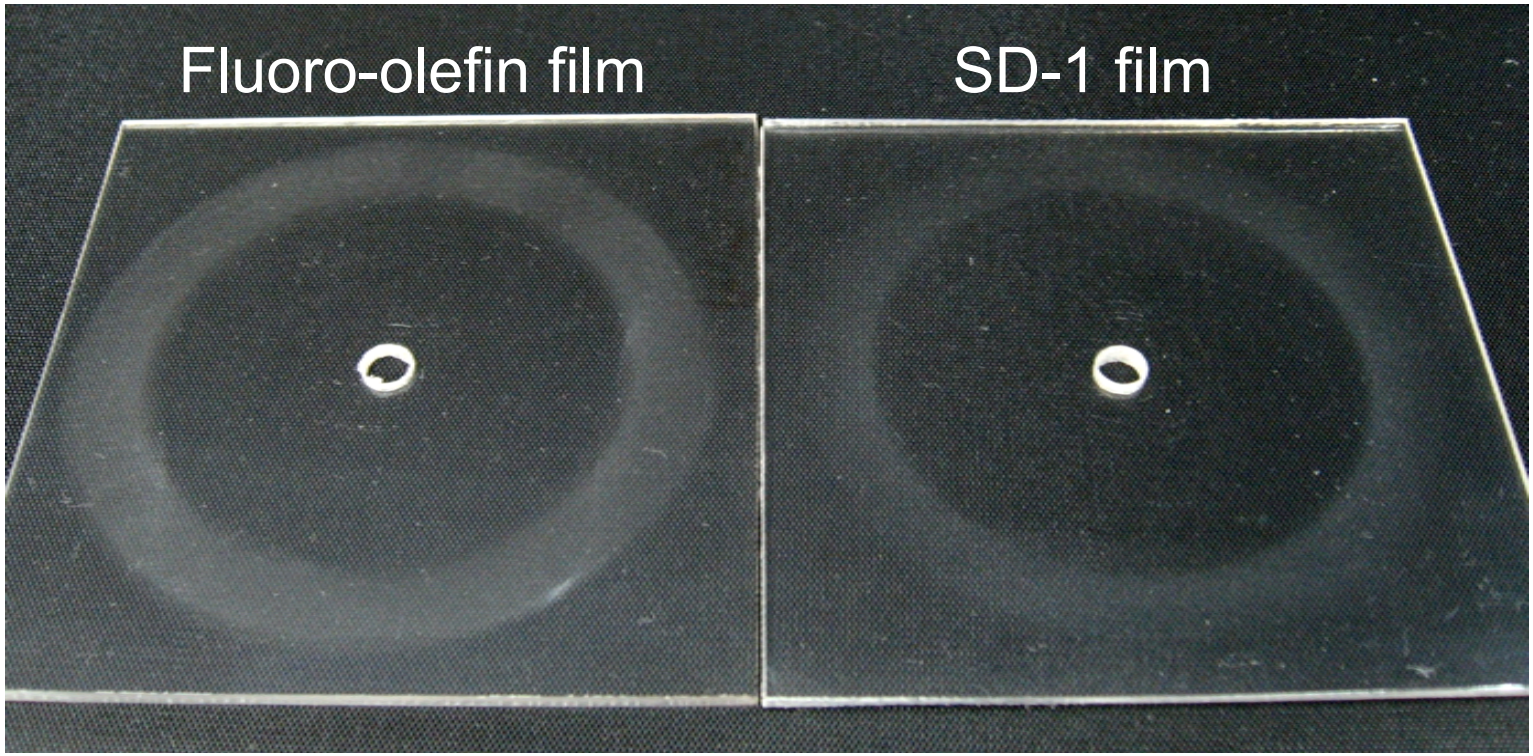
Sample No.	Taber abrasion test (ASTM D1044)	
	500g / 100 cycles ⊿H [%]	500g /500 cycles ⊿H [%]
SD-1	9.9	55.0
SD-2	7.4	38.6
SD-3	6.3	33.2
Fluoro-olefin coat	24.3	68.7
2K Acrylic-urethane coat	46.1	70.4
UV-Oligomer coat	1.5	5.8

Abrasive wheel : CS-10F Type4

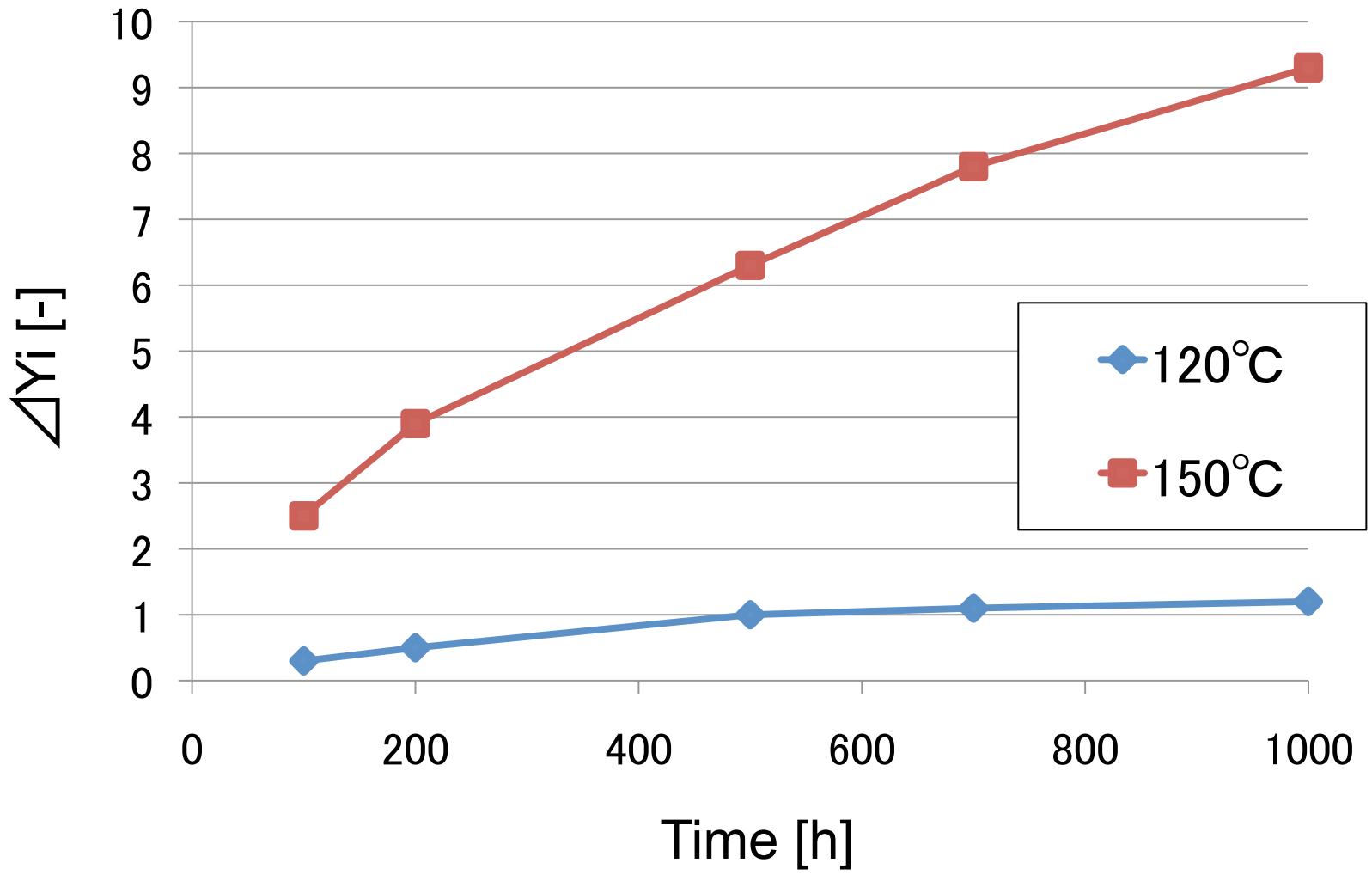
Substrate : Polycarbonate

Abrasion resistance of the clear coat film

Substrate : Polycarbonate
Method : Taber abrasion test (ASTM D1044)
(500g/100cycles)



Thermal stability of the SD-1 coating



Conclusion

◆ We established a novel synthesis method specially designed by combining polysiloxane and acrylic polymer. By using this method, we obtained several types of UV curable inorganic-organic hybrid resins with various amounts of polysiloxane.

◆ We found out that UV curable inorganic-organic hybrid resins have advantages of self-cleaning effect and abrasion resistance over commonly-used other durable coatings.

Thank you for your kind attention.

Color & Comfort by Chemistry

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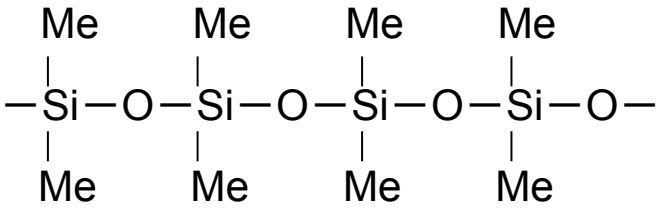
Polysiloxane Types and their Character

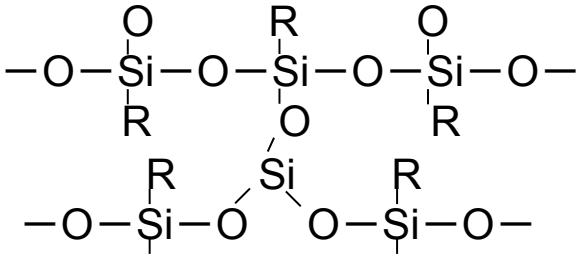
① Bifunctional polysiloxane



Dimethylpolysiloxane

Character : linear, liquid
Application : oil, slip agent, antifoamer

② Trifunctional polysiloxane



R : Me-, Ph-

Monoorganopolysiloxane

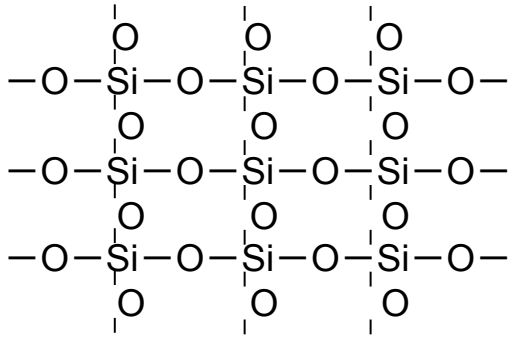
Character : branched
Application : coating material, hard resin

【the hydrolysis and the condensation of alkoxysilanes】

$RSi(OMe)_3 + 3H_2O \rightarrow RSi(OH)_3 + 3MeOH$

$2RSi(OH)_3 \rightarrow R\text{-}Si\text{-}O\text{-}Si\text{-}R + H_2O$

③ Tetrafunctional polysiloxane



Silica (SiO_2)

Character : 3-dimensional network, solid
Application : glass, colloidal silica

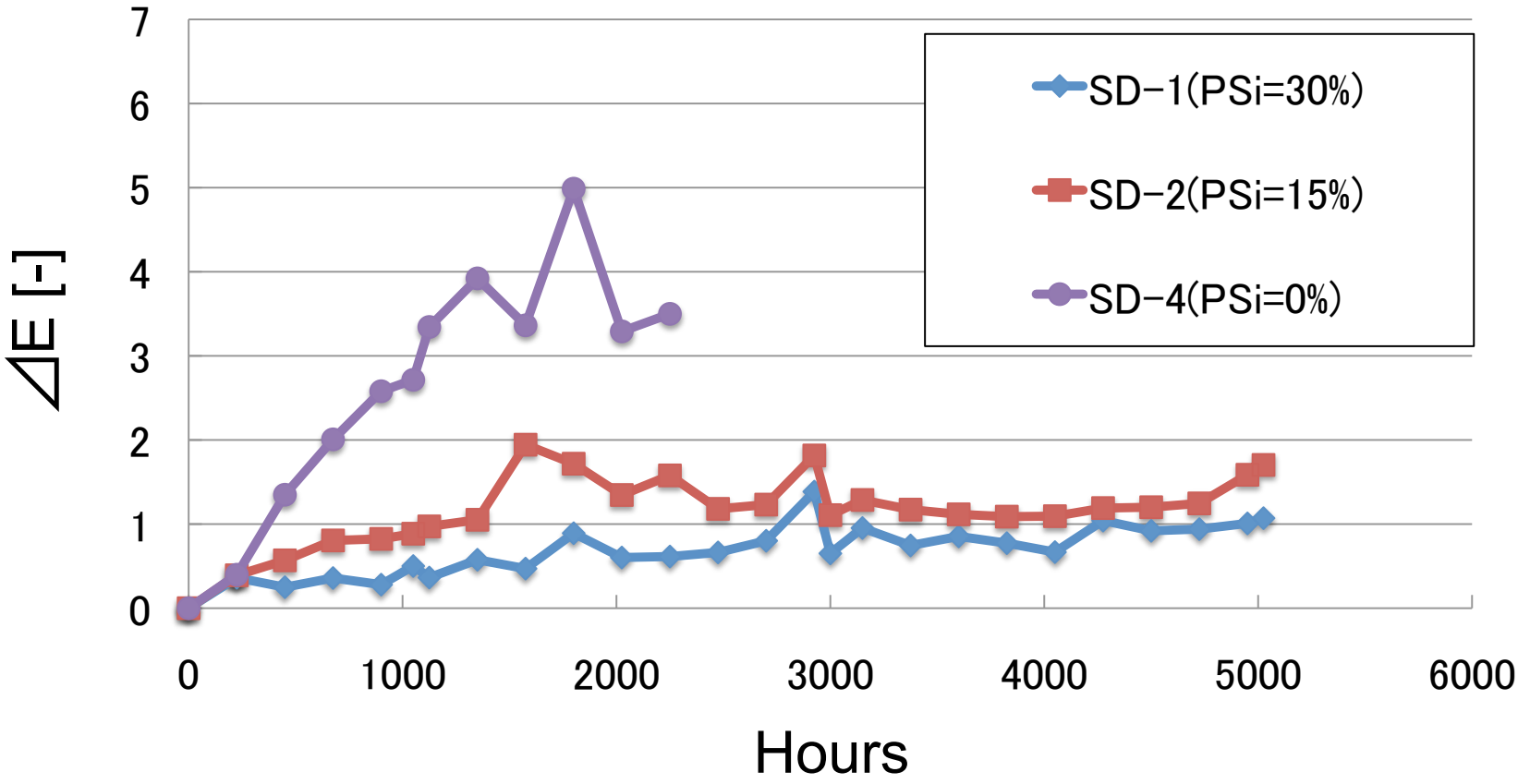
Characteristics of Synthesized Resins

Resin No.	Polysiloxane Cont. [%]	Acrylic polymer Cont. [%]	Solid Cont. [%]	Appearance	Viscosity [Gardner]	Stability 40℃/30days
R-1	25	75	55	Clear	D-K	Excellent
R-2	50	50	55	Clear	A-G	Excellent
R-3	75	25	70	Clear	A-G	Good
R-4	90	10	80	Clear	A-G	Poor

Properties of SD-1 Coating

Performance	Results
Gloss 60°	>95%
Transmittance	>91%
Refractive index	1.497
Storage elastic modulus (Tg+50℃)	170MPa (60μm)
Tg	95℃
Pencil hardness (on glass substrate)	H
Durability	
Chemical resistance/Appearance	
Sulfuric acid (15% Aq.)	Excellent
Sodium hydroxide (25% Aq.)	Excellent
Heat resistance/Appearance	
120℃ 1000h	Excellent
150℃ 1000h	good
Weather resistance/Appearance	
Outdoor exposure in Okinawa for 3 years	Excellent
Accelerated S.W.O.M exposure for 5000 hours	Excellent

Effect of polysiloxane content on preventing yellowing of the film (SWOM)



In the case of PSi contents > 15wt%,
color change (⊿E) doesn't exceed 2 within 5000 hours

Effects of light-dose on color change.

SD-1 UV light-dose	Color change(⊿E)	
	SWOM for 5000 hrs	Exposed in Okkinawa for two years
1000 mJ / cm^2	0.80	0.2
500 mJ / cm^2	1.24	0.48
250 mJ / cm^2	1.68	0.77

It is necessary to set an optimum UV light-dose

not to prevent the film from turning yellow!