Preparation and Characterization Of Weather Resistant Silicone/Acrylic Resin Coatings

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Preparation and characterization of weather resistant silicone/acrylic resin coatings were conducted. In order to prepare these coatings, a silicone/acrylic resin (KLD) was first prepared by an addition polymerization reaction of monomers, including n-butyl acrylate, methyl methacrylate, n-butyl methacrylate, and 3-methacryloxypropyltrimethoxysilane (MPTS). In the preparation of the silicone/acrylic resin, T_g of the acrylic copolymer was fixed at 40°C and the contents of MPTS were varied to be 10, 20, and 30 wt%. The weather resistant silicone/acrylic resin coatings were then prepared by blending the synthesized silicone/acrylic resin and TiO_2. The viscosity of the synthesized resin decreased with the content of MPTS, whereas the thermal stability at high temperature increased. The prepared coatings exhibited excellent adhesion to various substrates, and various physical properties of the coatings were satisfactory. The weatherability of the coatings was tested three ways: outdoor exposure test, Weather-Ometer (WOM), and QUV accelerated weatherability tester (QUV). The gloss retention, yellowness index difference, color difference, and lightness index difference were improved at high MPTS concentration. The coatings containing 30 wt% MPTS have especially good weather properties.

INTRODUCTION

It is inevitable for a coated film to undergo deterioration with exposure. Weatherability is a property that resists deterioration caused by several environmental factors, such as radiation, temperature, moisture, substrate, and chemicals.[1,2] Since the film of a weatherable coating is densely crosslinked and exhibits high hardness, it stands well against the factors causing deterioration of the film. Therefore, there is a growing need for weatherable coatings in various architectural industries.

Since weatherable coatings require special film properties, it has been difficult to meet the needs with common synthetic resins. Since the 1980s, coatings containing fluorine resin which are copolymerized by fluoroethylene and alkyl vinyl ether have been used as weatherable coatings.[3] However, coatings containing fluorine resin have some disadvantages, such as being expensive, environmentally pollutive, poor in hardness, and bad in workability. Recently, coatings containing silicone/acrylic resins have gained recognition as weatherable coatings. Since the coatings containing silicone/acrylic resins are a composite of organic and inorganic polymeric materials, it is easy to control the film hardness and to apply them to various substrates. There are two types of coatings containing silicone/acrylic resins: temperature-cured and moisture-cured at room temperature. Of these two, the type of hardening by moisture at room temperature will be spotlighted because of its good workability and weatherability.

There have been some reports on the coatings containing silicone/acrylic resins. Rao and Babu[4] synthesized a copolymer of vinyltriacetoxysilane and bromomethacrylate and investigated its thermal behavior. Yasuyuki[5] reported phase separation of a silicone/acrylic rubber prepared by grafting silicone emulsion and acryl emulsion. Witucki[6] prepared a silicone/acryl emulsion by cold blending an alkoxy silane and acryl emulsion through the following two-step processes. The first step was hydrolysis of an alkoxy functional group, and the second step was the formation of silicone polymer. He reported that the existence of 10% silicone increases gloss retention and decreases chalk phenomenon and color difference. There

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Table 1—Polymerization Conditions and Physical Properties for Silicone/Acrylic Resins

Resin	Materials: BA[a] g(mol)	MMA[b] g(mol)	BMA[c] g(mol)	MPTS[d] g(mol)	T_g(°C) Calc.	by DSC	Color (G.H.)	Viscosity (Stoke)	Si Content (%) Calc.	by AA	Non-Volatile (%)	Conversion (%)
SA-4000	12.1 (0.09)	69.4 (0.69)	98.5 (0.69)	—	40	39	1	12.0	—	—	49.8	90.1
KMB-40	11.5 (0.09)	65.9 (0.66)	93.6 (0.66)	9.0 (0.04)	40	38	1	16.4	0.52	0.50	49.8	89.6
KLD-41	10.7 (0.09)	61.0 (0.61)	86.5 (0.61)	21.9 (0.09)	40	37	1	6.1	1.25	1.24	49.9	89.8
KLD-42	8.2 (0.07)	51.3 (0.52)	72.9 (0.52)	47.6 (0.19)	40	32	1~2	4.5	2.72	2.69	49.6	89.2
KLD-43	7.2 (0.06)	41.1 (0.41)	58.4 (0.41)	73.3 (0.30)	40	38	1~2	2.4	4.20	4.18	48.9	87.7

(a) BA : *n*-Butyl acrylate
(b) MMA : Methyl methacrylate
(c) BMA : *n*-Butyl methacrylate
(d) MPTS : 3-Methacryloxypropyltrimethoxysilane

have been some patents similar to this work. Kanegafuchi Kagaku Kogyo Co. holds two patents[7,8] on weather resistant coatings, in which curing catalysts are used. DuPont Co. also holds a patent[9] on weather resistant coatings that consist of hydroxyl group-containing acrylic polymer/hydroxyl or alkoxy group-containing siloxane. The coatings are not the moisture-curing type, but the two-component reactive type. PPG Co.[10] also patented weather resistant coatings that use a cure-accelerating catalyst. However, there have been few papers reporting on the synthesis of the silicone/acrylic resin that is cured by moisture at room temperature and its application to weather resistant coatings.

In this study a silicone/acrylic resin, a quaternary copolymer, was prepared by the copolymerization of *n*-butyl acrylate, methyl methacrylate, *n*-butyl methacrylate, and 3-methacryloxypropyltrimethoxysilane. The T_g of the resin had been predetermined to be 40°C and two types of silicone/acrylic resins were prepared separately: mill-base silicone/acrylic resin and let-down silicone/acrylic resin. A white coating was then prepared by blending the mill-base silicone/acrylic resin and let-down silicone/acrylic resin in a ratio of 3:7, which is a typical blending ratio for architectural coatings. To examine the weather resistance of the prepared coatings, various weatherability tests were carried out.

Table 2—Preparation of White Coatings for Architectural Coatings

Types	Materials	Weight (wt%)
Mill-base	Mill-base silicone/acrylic resin	21.6
	TiO_2(rutile)	24.0
Let-down	Let-down silicone/acrylic resin	50.4
	Levelling agent	0.1
	UV absorber	0.2
	UV stabilizer	0.1
	Xylene	3.6
Mill-base/Let-down		3/7

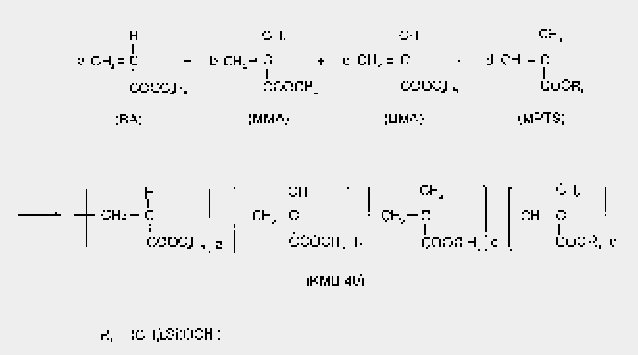
EXPERIMENTAL

Materials

The monomers used were 3-methacryloxypropyltrimethoxysilane (MPTS, Sigma Chemical Co.) as a reactive silicone monomer and three kinds of acrylic monomers, including *n*-butyl acrylate (BA, Tokyo Kasei Kogyo

Table 3—Physical Properties and Their Testing Methods

Physical Property	Instrument and Method
Viscosity (KU)	Krebs-Stormer viscometer Pacific Scientific Co., serial 80328 KS M 5000-2122
Specific gravity	KS M 5000-2131
Fineness of grind	Braive Instruments Co., type 2020 KS M 5000-2141
Drying time	Set-to-touch, Dry-hard, Dry-through method KS M 5000-2512
Hardness	Yasuda Seiki Seisakusho, serial 4664 JIS K 5400 (8.4.1)
Flexibility	Mandrel: Pacific Scientific Co., Conical KS M 5000-3331
Impact resistance	Dupont impact tester type 552 Ureshima Seisakusho JIS K 5400 (8.3.2)
60° Specular gloss	Glossmeter Pacific Scientific Co., Glossgard II KS M 5000-3312
Crosshatch adhesion	ISO 2409
Abrasion resistance	Abrasion tester Toyo Seiki Seisakusho, Taber FS 141C-6192.1
Contrast ratio	KS M 5000-3111
Salt exposure test	ASTM B-117
Storage stability	KS M 5000-2031



Scheme 1

Co.), methyl methacrylate (MMA, Aldrich Chemical Co.), and *n*-butyl methacrylate (BMA, Tokyo Kasei Kogyo Co.). They were all reagent grade. 2,2′-azobisisobutyronitrile (AIBN, Junsei Chemical Co.) was used as an initiator, and methyltrimethoxysilane (MTS, Sigma Chemical Co.) and trimethyl orthoformate (TMO, Junsei Chemical Co.) were used as moisture scavengers. TiO_2 (Dupont Co.) was used as a white pigment; Tinuvin-384 (benzotriazole derivative, Ciba-Geigy Co.) as a UV absorber; Tinuvin-292 (HALS, Ciba-Geigy Co.) as a UV stabilizer; di-*n*-butyltindilaurate (DBTDL, Songwon Co.) as a curing catalyst; and Dow Corning-11 (silicone glycol copolymer, Dow Chemical Co.) as a flowing agent.

Synthesis of Silicone/Acrylic Resin

Mill-Base Silicone/Acrylic Resin: In order to synthesize a mill-base silicone/acrylic resin, 70 g of xylene and 60 g of toluene were introduced into a 500 mL four-necked flask and the materials listed in *Table* 1 (for KMB-40) were added to the flask under a nitrogen atmosphere. Then, another solution of 1.26 g of AIBN initiator and 2.7 g of MTS moisture scavenger was dropped into the flask at 82°C for 120 min, and the mixture was allowed to age at 82°C for 120 min. A solution of 0.18 g of AIBN that had been dissolved in 1.8 g of xylene was then added to the mixture four times as follows: (a) right after aging, (b) after 30 min, (c) after 60 min, and (d) during heating to 90°C for 30 min. Then, the mixture was aged at 105°C for 30 min. Next, the end of the reaction was determined by measuring solid contents of the mixture. With the addition of 6.3 g of MTS and 50 g of xylene to the mixture, finally, the product containing 50% of solid content was obtained. Unreacted materials were removed by use of excess normal hexane, and the precipitate was dried at 50°C under a vacuum of 5 mmHg, producing a transparent viscous copolymer, KMB-40.

Let-Down Silicone/Acrylic Resin: To synthesize a let-down silicone/acrylic resin, 130 g of xylene, materials listed in *Table* 1 (for KLD-41), 1.26 g of AIBN, and 1.16 g of TMO were introduced into a 500 mL four-necked flask. The reaction and aging conditions were the same as the above section (mill-base silicone/acrylic resin). At the end of the reaction, 2.7 g of TMO and 50 g of xylene were added to the reaction mixture, producing a product containing 50% solid content. The purifying condition was the same as the above section and the precipitate was dried at 50°C under a vacuum of 5 mmHg, producing a transparent viscous copolymer, KLD-41. Furthermore, copolymers (KLD-42 and KLD-43), which contain 20 and 30 wt% of MPTS, respectively, were prepared by the same procedure as for KLD-41.

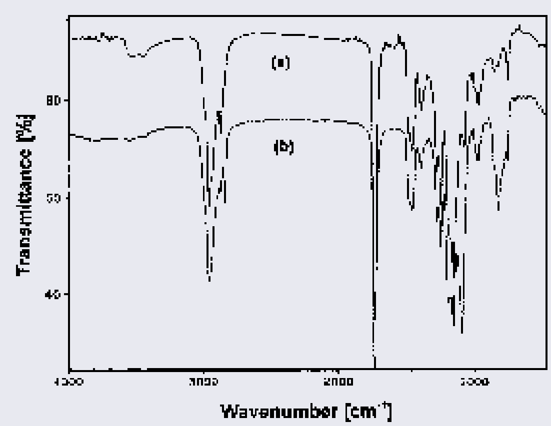


Figure 1—FTIR spectra of (a) KMB-40 and (b) KLD-43.

Instrumental Analysis

For spectroscopic analysis, FTIR (FTS-40, Bio-Rad) and ^{1}H-NMR (Unity-300, Varian) were used. The molecular weight and molecular weight distribution of the products

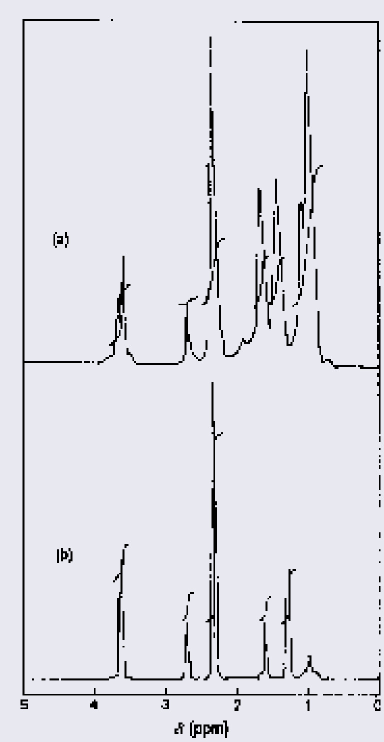


Figure 2—^{1}H-NMR spectra of (a) KMB-40 and (b) KLD-43.

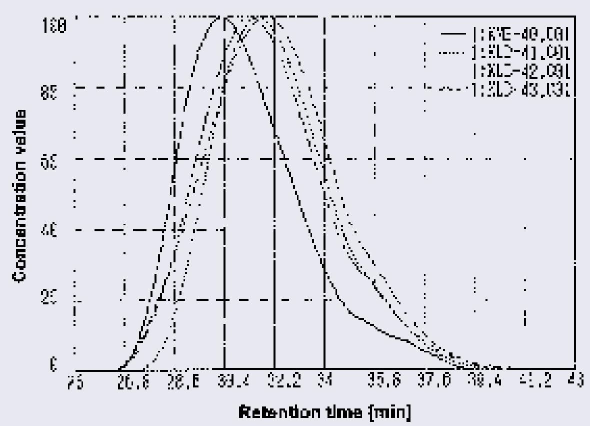


Figure 3—Molecular weight distribution curves for KMB-40, KLD-41, KLD-42, and KLD-43 determined by GPC.

were measured using GPC (R-410, Waters). Thermal analysis was carried out using TGA (TGA-50H, Shimazu) and DSC (DSC 4000, Thermold). Silicon content was measured according to ASTM D 3733 with a Perkin-Elmer 5200 atomic absorption spectroscope. The surface and side structures of the films of the prepared coatings were observed using SEM (XL-30, Philips).

Measurement of Kinematic Viscosity, Color, and Solid Content

The kinematic viscosity was measured according to KS M 5000-2121[11] (corresponding to ASTM D 1545-1989), and the color of the synthesized resin, according to KS M 5000-4012[12] (corresponding to ASTM D 1544-1989). The solid content of the synthesized resin was measured according to KS M 5000-2113[13] (corresponding to ASTM D 1644-1988).

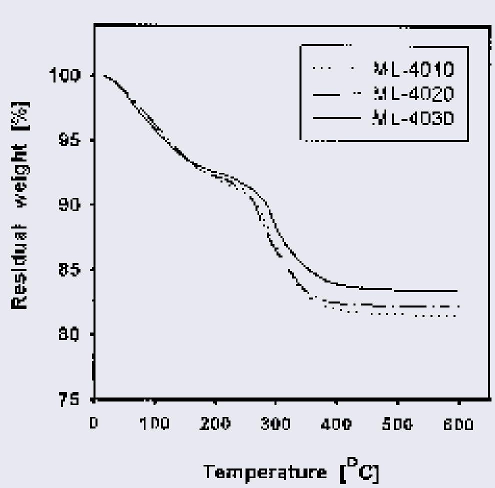


Figure 4—TGA thermograms of silicone/acrylic resins. ML-4010: KMB-40/KLD-41=3/7, ML-4020: KMB-40/KLD-42=3/7, ML-4030: KMB-40/KLD-43=3/7

Formulation of Coatings

The coatings were formulated with TiO_2, by blending the mill-base silicone/acrylic resin and let-down silicone/acrylic resin at a ratio of 3:7 wt%. The details of the formulation are listed in *Table* 2. Coatings containing 0, 10, 20, 30 wt% of MPTS were designated as SA-4000, SA-4010, SA-4020, and SA-4030, respectively. The SA-4000 was used for comparison.

Measurement of Physical Properties

To measure physical properties of the films coated on various substrates, seven specimens were prepared. For a cold-rolled carbon steel plate substrate, specimens were prepared according to KS M 5000-1111[14] (corresponding to ASTM D 609-1990); for a tin plate, prepared according to KS M 5000-1112[15] (corresponding to ASTM A 624-1998); for a glass plate, prepared according to KS M 5000-1121[16] (corresponding to ASTM D 3891-1990); and for aluminum, PET, brass, and tile plates, prepared according to KS M 5000-1112[15] (corresponding to ASTM A 624-1998). All the specimens were prepared by a Bird film applicator to be a thickness of 0.076 mm of the wet film, and dried at 23±1°C and 50±4% of relative humidity for seven days. Physical properties of the specimens were measured in accordance with the methods listed in *Table* 3.

Weatherability Test

The outdoor exposure test was carried out according to KS M 5000-3241[17] (corresponding to ASTM D 1014-1998). The accelerated weatherability test was carried out according to KS M 5000-3231[18] (corresponding to ASTM G 26-1990) by two instruments: Weather-Ometer (WOM, Atlas Electric Devices Co., Ci65A) and QUV accelerated weatherability tester (QUV, Q-Panel Co.). Gloss retention, yellowness index difference, lightness index difference, and color difference were tested at exposure times of 500, 1000, 2000, 3000, and 4000 hr.

RESULTS AND DISCUSSION

When synthesizing silicone/acrylic resins to prepare architectural coatings, T_g was fixed at 40°C according to the Fox equation,[19] and the molar ratio of MMA to BMA was 1:1 to control film properties.[20] In the synthesis of the resins, acidic and basic monomers were not used because they act as curing catalysts.[21] Furthermore, the contents of MPTS that provides silicone component were regulated to be 10, 20, and 30 wt% of the solid component of the resin. More than 30% of the MPTS content makes films hard and poor in abrasion resistance, and makes the coatings expensive.

Since the silicone/acrylic resin is cured by moisture at room temperature, moisture scavenger MTS (having good moisture absorbability in pigment) and TMO (good moisture absorbability in air) were used at a weight ratio of 1:1.

Analysis of Mill-Base Resins

The reaction scheme of the mill-base silicone/acrylic resin is shown in *Scheme* 1, and the compositions of the

Table 4—Physical Properties of Silicone/Acrylic Resin Coatings

Physical Property		SA-4000	SA-4010	SA-4020	SA-4030
Viscosity(KU)		98	90	106	70
Fineness of grind		7^+	7^+	7^+	7^+
Contrast ratio		0.948	0.951	0.944	0.942
Pencil hardness (7 days)		2H	H	H	F~H
60° Specular gloss		85.5	85.7	82.0	85.2
Drying time (min)	Set-to-touch	3	3	2	3
	Dry-hard	27	57	33	55
	Dry-through	38	67	43	70
Storage stability (60°C×10 days)		good	good	good	good
Abrasion resistance (mg loss/1000 cycle)		0.72	0.35	1.07	0.60
Flexibility(1/8")		fair	good	good	good
Heat Resistance (150°C×1hr)	Gloss retention(%)	87	92	94	96
	Color difference(ΔE)	0.78	0.39	0.26	0.64
Impact resistance (500 g/30, 50 cm)	Direct 30cm	Good	Good	Good	Good
	Direct 50cm	Fair	Good	Good	Good
	Reverse 30cm	Poor	Good	Poor	Poor
	Reverse 50cm	Poor	Poor	Poor	Poor
Crosshatch Adhesion (%)	Steel plate	100	100	100	100
	Tin plate	100	100	100	100
	Aluminum	55	100	100	100
	PET	0	100	100	100
	Brass	20	100	100	100
	Tile	0	100	100	100

reactants and physical properties of the products are listed in *Table* 1. The reaction conditions were fixed as listed in *Table* 1. The optimum reaction conditions have already been determined.[22]

KMB-40 could be verified by FTIR spectrum as shown in *Figure* 1a. The stretching vibration peaks of Si–O–CH_3, C–O, and C=O were observed at 845, 1150, and 1740 cm^{-1}, respectively. KMB-40 could also be verified by ^{1}H–NMR spectrum as shown in *Figure* 2a. The chemical shifts were as follows: CH_3–C, at 1.0 ppm; C–CH_2–C, at 1.4 ppm; C–H, at 1.6 ppm; C–CH_2–CO–, at 2.4 ppm; CH–CO–, at 2.7 ppm; and CH_3–O–/Si–O–CH_3, at 3.6 ppm.

The molecular weight and its distribution of KMB-40 were determined by GPC as shown in *Figure* 3. The average molecular weights were M_n = 26200, M_w = 58600, and M_z = 97000, and the polydispersity was 2.24, which indicates a narrow distribution.

Analysis of Let-Down Resins

The compositions of reactants and physical properties of let-down silicone/acrylic resins (KLD) are listed in *Table* 1. As listed in *Table* 1, no significant differences in conversions were observed, but viscosity decreased with increased content of MPTS. This may be due to the high solubility of MPTS in hydrocarbons.

The FTIR spectrum of KLD-43, similar to *Figure* 1a, is shown in *Figure* 1b. The higher content of MPTS in KLD-43 led to increased intensities of Si–O–CH_3 and Si–O peaks at 820 and 1090 cm^{-1}, respectively. KLD-43 could be

Table 5—Results of Salt Exposure Tests

Test	Scribed Areas								Unscribed Areas							
	Rusting				Blistering				Rusting				Blistering			
Time (hr)	100	200	300	400	100	200	300	400	100	200	300	400	100	200	300	400
Name of sample																
SA-4000	10	9F	8M	8MD	10	8F	8MD	6D	10	10	10	9F	10	10	10	8F
SA-4010	10	10	10	9F[a]	10	10	8F	8MD	10	10	10	10	10	10	10	10
SA-4020	10	10	9M[b]	8MD[c]	10	10	8F	8D[d]	10	10	10	10	10	10	10	10
SA-4030	10	10	10	9F	10	10	8F	8M	10	10	10	10	10	10	10	10

(a) F : few
(b) M : medium
(c) MD : medium dense
(d) D : dense

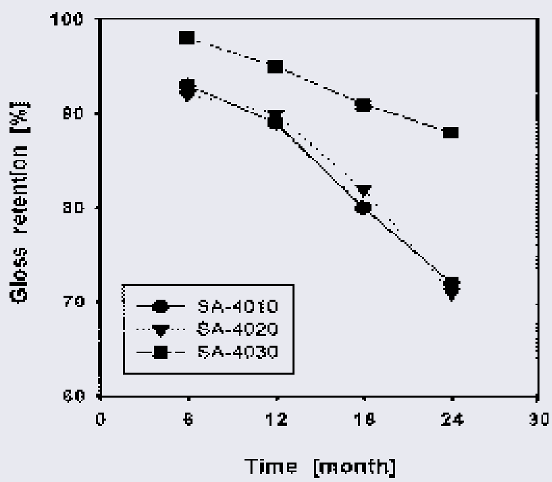


Figure 5—Effects of outdoor exposure time on the gloss retention of silicone/acrylic resin coatings.

verified by ^{1}H-NMR spectrum, shown in *Figure* 2b. Chemical shifts were as follows: CH_3–C, at 1.0 ppm; C–CH, at 1.6 ppm; C–CH_2–CO–, at 2.0 ppm; CH–CO–, at 2.7 ppm; and CH_3–O–/Si–O–CH_3, at 3.6 ppm.

GPC results of KLDs are represented in *Figure* 3. The average molecular weights of KLD-41 were M_n = 17900, M_w = 35900, and M_z = 59600, and the polydispersity was 2.01. The average molecular weights of KLD-42 were M_n = 18800, M_w = 44500, and M_z = 83300, and the polydispersity was 2.37. The average molecular weights of KLD-43 were M_n = 17200, M_w = 41300, and M_z = 84400, and the polydispersity was 2.40. The average molecular weights of the three kinds of KLDs were similar, however the polydispersity of the KLDs slightly increased with the contents of MPTS. This result may stem from the production of more polydispersed copolymers with increasing the contents of MPTS.

Thermal Stability of Silicone/Acrylic Resins

Paul reported that the thermal stability of MMA-ethyl acrylate copolymers increased with the content of ethyl acrylate.[23] Finzel[24] examined the weight loss of several coatings by WOM accelerated test method, and reported that the weight loss of a coating containing alkyd resin was 38.7%, while the weight loss of a coating containing 30% of silicone/acrylic resin was 20.3%. Furthermore, the weight loss of the coating containing polyester was 38.7%, but the weight losses of the coatings containing 30 and 50% silicone/acrylic resins were 21.4 and 15.8%, respectively. This indicates that the increase in the content of silicone increases the thermal stability of coatings.

Figure 4 shows TGA results of a blend of KMB-40 and KLDs in a weight ratio of 3:7. The thermal stability of the blend increased with the content of MPTS, in which the order of stability was: ML-4030 > ML-4020 > ML-4010. This result is consistent with Finzel's results, in which the thermal stability of coatings increased with increasing silicone content. The weight losses of ML-4000, which did not contain silicone components, were 9, 17, and 40% at 250°C, 300°C, and 350°C, respectively, which indicates the poor thermal stability of ML-4000.

Physical Properties of the Films of Silicone/Acrylic Resin Coatings

The curing mechanism of the silicone/acrylic resin is known as follows: first, silanol is produced by the reaction of methoxy silyl group of the silicone/acrylic resin chain with moisture in the air, then the silanol reacts with another silanol or methoxy silyl group of the resin chain, causing cure in films by crosslinking. It took 25 days to cure completely at 23±1°C and 50±4% of relative humidity.

The physical properties of the films of the prepared silicone/acrylic resin coating are tabulated in *Table* 4. The viscosities of all the coatings were in a suitable range for application. The fineness of grind[25] was satisfactory in spite of quick dispersion of 60 min with a shaker. The

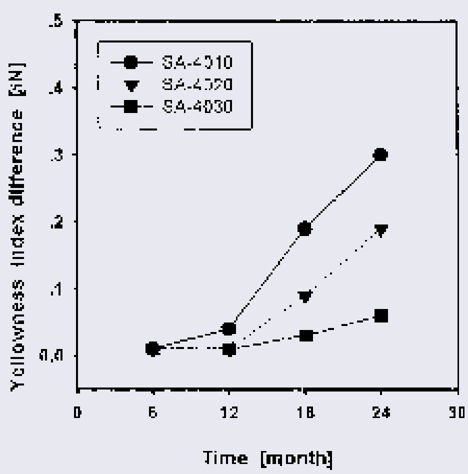


Figure 6—Effects of outdoor exposure time on the yellowness index difference of silicone/acrylic resin coatings.

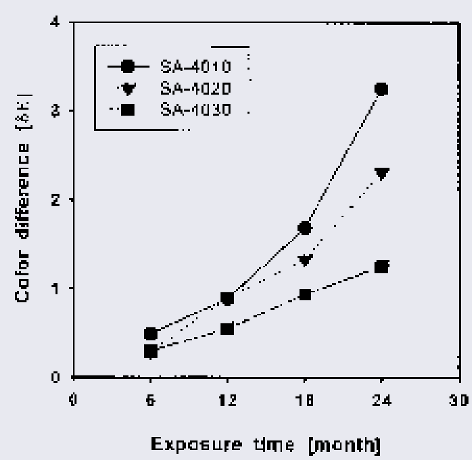


Figure 7—Effects of outdoor exposure time on the color difference of silicone/acrylic resin coatings.

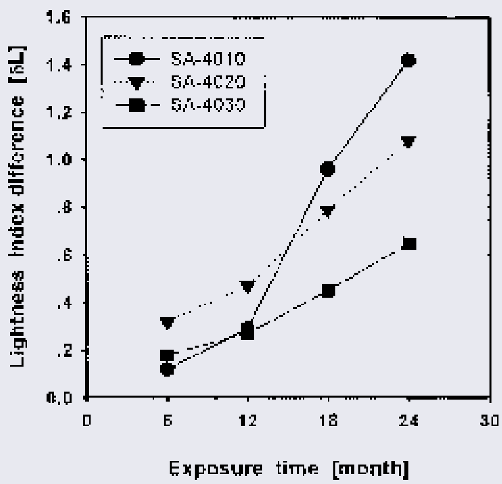


Figure 8—Effects of outdoor exposure time on the lightness index difference of silicone/acrylic resin coatings.

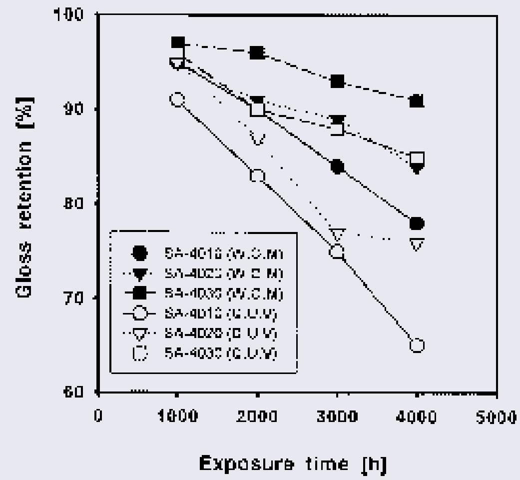


Figure 9—Effects of exposure time on the gloss retention of silicone/acrylic resin coatings in the accelerated weatherability test.

contrast ratios, which strongly depend on the content of white pigment, were satisfactory values of 0.935~0.052 at 40% of the white pigment. The pencil hardness of the films was H~2H, indicating the coatings were suitable for architectural coatings. The gloss of the films was slightly low when comparing with standard values. Without any curing catalyst, drying time was less than 60 min, which indicates that the coatings are fast drying ones.[26] The weight losses caused by abrasion were 0.71~1.00 mg, which indicates that the abrasion resistance is not affected by the content of MPTS. Flexibility was good for all the coatings, and heat resistance increased with the content of MPTS. Impact resistance was good for all the direct sides but mostly poor for reversed sides. Crosshatch adhesions on various substrates were all excellent, which indicates a possibility of the coatings to apply on various substrates. On the other hand, for SA-4000, which did not contain silicone components, pencil hardness and drying time were good, and flexibility, heat resistance, and adhesion were poor, and the other physical properties were similar to the other coatings.

Salt Exposure Test

For salt exposure tests, the coatings were applied to cold rolled carbon steel sheets in a thickness of 0.076 mm and dried at 23±1°C for seven days. X-shaped scribe areas were then prepared on the samples according to ASTM D 1654-2. Degree of rusting and blistering[27] at both the scribed area and the unscribed area were determined according to ASTM D 610 and ASTM D 714, respectively. The degree of rusting was subdivided into 11 grades; for example, when the rusting was less than 0.01%, the grade was 10, and when the rusting was 100%, the grade was 0. The degree of rusting and blistering were tested after 100, 200, 300, and 400 hr of exposure and are listed in *Table* 5. SA-4000 exhibited slightly lower values in rusting and blistering when comparing with the others as shown in *Table* 5. All the coatings proved to be highly resistant to salt. It was found that the resistance to salt increased with the content of MPTS.

Outdoor Exposure Test

The outdoor exposure test was carried out with an exposure angle of 30° at the rooftop for two years (from March 1998 to February 2000). The gloss retention, yellowness index difference, color difference, and lightness index difference of the samples were tested after outdoor exposures of 6, 12, 16, and 24 months.

The gloss retention as a function of exposure time is shown in *Figure* 5. The gloss retention increased with increasing MPTS content. For SA-4030 (containing 30 wt% of MPTS), the gloss retention remained at 88% even after 24 months of exposure.

Figure 6 shows the yellowness index difference as a function of exposure time. The yellowness index differences were all less than 0.3. After 12 months of exposure, the yellowness index differences increased rapidly. The yellowness index difference was quite dependent upon

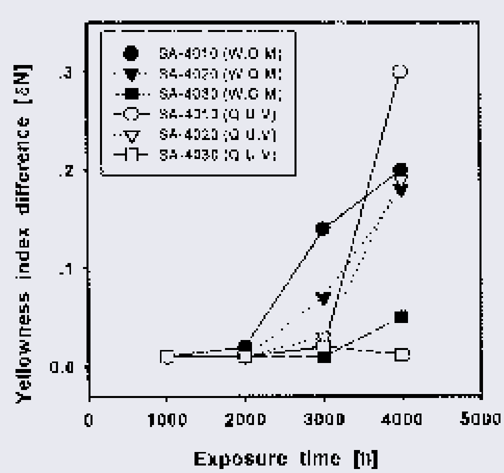


Figure 10—Effects of exposure time on the yellowness index difference of silicone/acrylic resin coatings in the accelerated weatherability test.

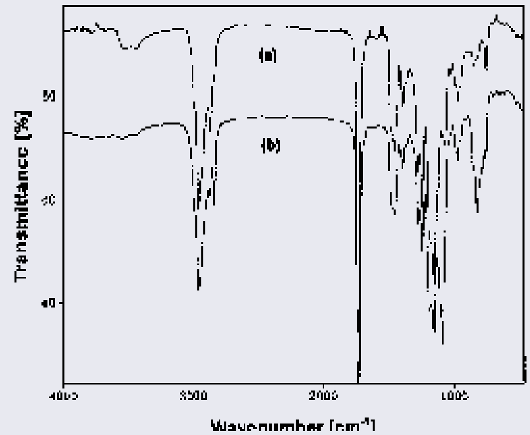


Figure 11—Effects of exposure time on the color difference of silicone/acrylic resin coatings in the accelerated weatherability test.

the content of MPTS; the yellowness index difference of SA-4030 (containing 30 wt% of MPTS) was only 0.06 after 24 months of exposure, indicating that yellowness had hardly taken place.

Figure 7 shows color difference as a function of exposure time. The color difference was also quite dependent upon the content of MPTS. After 24 months of exposure, the color difference of SA-4010 (containing 10 wt% MPTS) was 3.3, in which the color difference was discernable with the naked eye; the color difference of SA-4020 was 2.4; and the color difference of SA-4030 was 1.2, in which the color difference was indiscernible with the naked eye.

Figure 8 shows lightness index differences as a function of exposure time. The lightness index differences were all less than 1.5 after 24 months of exposure. The lightness index difference was also dependent upon the content of MPTS. For SA-4030, the lightness index difference was less than 0.7, indicating no chalk phenomenon had taken place.

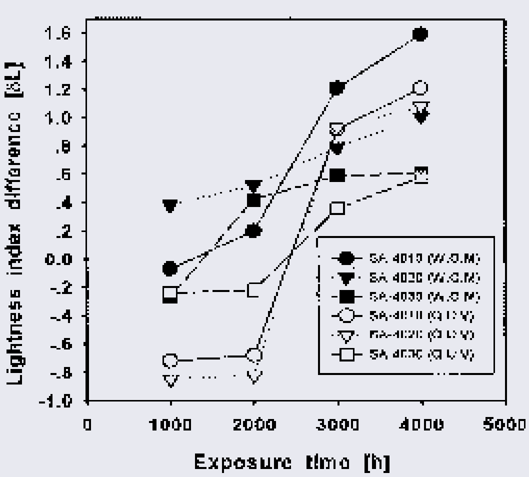


Figure 12—Effects of exposure time on the lightness index difference of silicone/acrylic resin coatings in the accelerated weatherability test.

On the other hand, the results of outdoor exposure tests of SA-4000 for six to 24 months were as follows: gloss retention, yellowness index difference, color difference, and lightness index difference were 85-38%, 1.2-3.2, 3.2-7.9, and 1.3-0.6, respectively. When comparing these values with the values of the coatings that contain MPTS as shown in *Figures* 5-8, it was found that the weatherability of the coatings was improved with increasing MPTS content. This improvement in the weatherability of the coatings containing MPTS may be stemmed from the high binding energy of siloxane bond.

Accelerated Weatherability Test

The accelerated weatherability test was carried out using WOM and QUV for 1000, 2000, 3000, and 4000 hr. *Figure* 9 represents gloss retention of coatings as a function of exposure time. The gloss retention increased with the content of MPTS. The gloss retentions of SA-4030, showing the best result, were 91% (by WOM) and 86% (by QUV) after 4000 hr of exposure. When comparing these values with the weatherability standard, SA-4030 proved to be a superweatherable coating.

The yellowness index difference, as a function of exposure time, is shown in *Figure* 10. After 4000 hr of exposure, the yellowness index difference was less than 0.3 for all the coatings tested. The yellowness index difference was dependent upon the content of MPTS; the yellowness index difference of SA-4030 was 0.1 after 4000 hr of exposure, indicating yellowness had hardly taken place.

Figure 11 shows the color difference as a function of exposure time. After 4000 hr of exposure, the color difference was less than 4.0 for all the coatings, showing a worse result than the result of 24 months of outdoor exposure test. When comparing the color differences in connection with the contents of MPTS, the color difference of SA-4010 was 3.3, in which a difference in color was perceptible with the naked eye; the color difference of SA-4020 was 2.0; and the color difference of SA-4030 was 1.3, in which a difference in color was almost not perceptible with the naked eye. It was proved that SA-4030 is a coating which has not changed its color after long-time exposure.

Figure 12 shows the lightness index differences as a function of exposure time. The lightness index difference was less than 1.6 for all the coatings after 4000 hr of exposure. The lightness index difference was dependent upon the content of MPTS that provides silicone component. The lightness index difference for SA-4030 was less than 1.0, showing no chalk phenomenon had taken place.

Through the several weatherability tests, it was found that the weatherability of the coatings was improved with increasing the content of MPTS that provides silicone component. It has been known that the coatings containing fluorine or silicone resin show an improved weatherability because of strong bonding energy of the fluorine or silicone resin.[28,29] This was also verified in this study.

On the other hand, the results of accelerated weatherability tests of SA-4000 using WOM and QUV for 1000-4000 hr were as follows: gloss retentions, 71-45% (WOM) and 48-32% (QUV); yellowness index differences, 0.9-2.4 (WOM) and 1.5-3.7 (QUV); color differences, 2.7-5.5 (WOM)

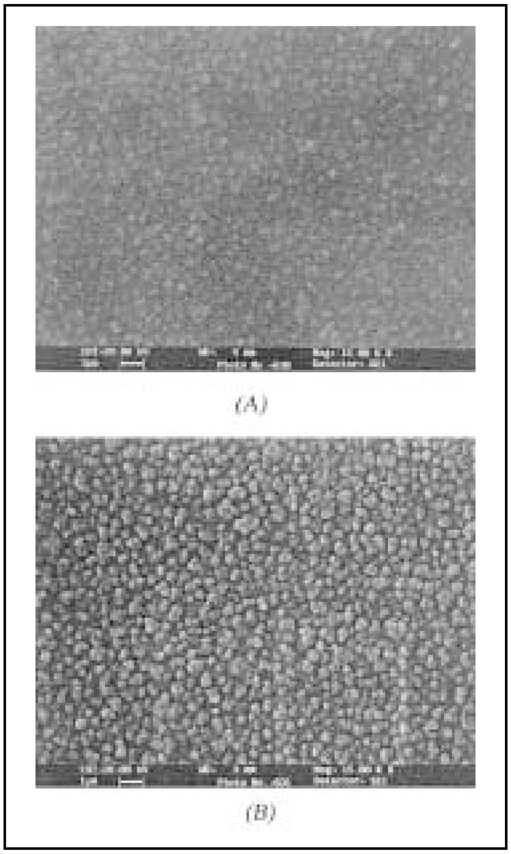


Figure 13—SEM photographs of the surface of silicone/acrylic resin coatings (SA-4030) : (A) unexposed, (B) 4000 hr QUV accelerated weatherability test (×15000).

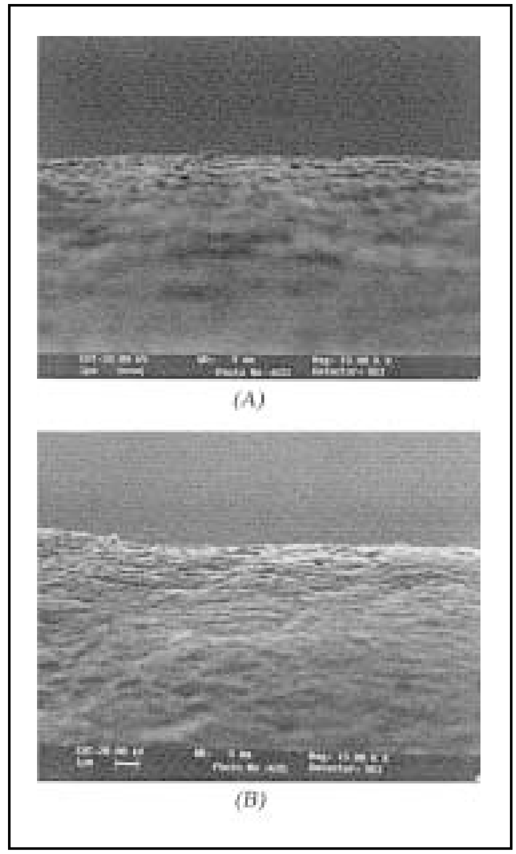


Figure 14—SEM photographs of the longitudinal structure of silicone/acrylic resin coating (SA-4030): (A) unexposed, (B) 4000 hr QUV accelerated weatherability test (×15000).

and 3.5-8.4 (QUV); and lightness index differences, 1.0-0.5 (WOM) and 1.5-0.4 (QUV). When comparing these values with the values of the coatings that contain MPTS as shown in *Figures* 9-11, it was also found that the weatherability of the coatings was improved with increasing MPTS content.

Film Morphology

The surface and longitudinal morphology of the films of SA-4030 that exhibited the best weatherability were investigated using SEM before and after 4000 hr of exposure and shown in *Figures* 13-14. As shown in *Figure* 13, the pigment distribution of the exposed film was clearly observed owing to the deterioration of the resin used. It was found that there were no fracture, no coagulation of TiO_2, no chalk phenomenon, and no phase separation observed.[30] As shown in *Figure* 14, there was no observable jaggedness caused by decrease in thickness, indicating no chalk phenomenon had taken place.

CONCLUSIONS

White coatings were prepared by blending TiO_2 and silicone/acrylic resin (KLD) synthesized by the copolymerization of *n*-butyl acrylate, methyl methacrylate, *n*-butyl methacrylate, and 3-methacryloxypyltrimethoxysilane (MPTS). The physical properties measurements and weatherability tests of the films of the prepared coatings were carried out.

The measured results of the synthesized silicone/acrylic resin were as follows: M_n, 17200~18800; M_w, 35900~44500; polydispersity, 2.01~2.40; viscosity, 2.4~6.1; and stoke and conversion, 87.7~89.8%. The prepared coatings exhibited excellent adhesion on various substrates, and most physical properties of the films were satisfactory. From the outdoor and accelerated exposure test, it was found that gloss retention, yellowness index difference, color difference, and lightness index difference were improved with the content of MPTS. Especially, SA-4030, containing 30 wt% MPTS and having T_g of 40°C, proved to be a weather resistant coating.

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