Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Synthesis and characterization of silicone-modified polyester as a clearcoat for automotive pre-coated metals

Yong-Hee Lee^a, Hyun-Joong Kim^{a,b,*}, Steven Schwartz^c, Miriam Rafailovich^d, Jonathan Sokolov^d

^a Laboratory of Adhesion and Bio-Composites, Program in Environmental Materials Science Seoul Natioal University, Seoul 151-921, Republic of Korea

^b Research Institute for Agriculture and Life Sciences, Seoul National University, Seoul 151-921, Republic of Korea

^c Department of Physics, Queens College, Flushing, NY 11367-1597, USA

^d Chemical & Molecular Engineering, Department of Materials Science & Engineering, State University of New York at Stony Brook, NY 11794-2275, USA

ARTICLE INFO

Article history: Received 22 November 2012 Received in revised form 17 August 2013 Accepted 12 September 2013 Available online 15 October 2013

Keywords: Polyester Pre-coated metals Formability Deep drawing Clearcoat Semi-removable

ABSTRACT

Four types of silicone-modified polyester resins were synthesized for cleanable characteristics with silicone intermediate, which has a long chain, to extend the polymer chains of the resins. These resins were formulated to make polyester/melamine heat-cured coatings to control the formability. The characteristics, viscoelastic behavior and flexibility of the resins were measured by DMA and tensile test. The contact angle measurement can be measured by the water repellence of the coating surface, which is a standard method to evaluate cleanable characteristics. The surface free energy was calculated by the contact angle measurement, and the surface analysis of each cured coating was evaluated using an XPS. Silicone-modified polyester coatings were coated on the cold rolled steel sheets to verify their formability, using a deep drawing test. Results showed that the storage modulus decreased, and the glass transition temperature shifted to a lower temperature with increasing contents of silicone intermediate. So, silicone intermediate provides lower stiffness and higher softness to polyester coating. To analyze the formability, we calculated F_{11} (the forming coefficient based on strain energy) and F_{e} (the forming coefficient based on strain). When F_U and F_{ε} are both larger than 1, the polyester coatings have good formability. CSiPE-3 and CSiPE-5 had good formability. Also, CSiPE-5, which had the highest amount of silicone intermediate, had 93.5° of water contact angle, and had 26.5 mN/m of surface free energy and had 5.5 N/25 mm of the peel strength. So, it is implied that silicone intermediate can give a low surface energy and peel strength to polyester coatings. From those tests, the polyester/melamine coating of CSiPE-5 that had 0.5 mol of silicone intermediate had good formability and low peel strength, which are semi-removable characteristics. So, it would be an appropriate coating as a clearcoat for automotive pre-coated metals. © 2013 Elsevier B.V. All rights reserved.

1. Introduction

Pre-painted or coil-coated metals (PCM) have been used in many applications, such as household electric appliances, building materials and others. In this system, the wet coating process can be eliminated by using a roll coating process, making it possible to circumvent the problem of air pollution arising from evaporation. In addition, a pre-coated metal system offers other advantages, such as improved productivity and energy saving; thus the use of PCM has been spreading [1,2]. One of the most important properties of PCM is its formability. If the film on coated PCM parts is

E-mail address: hjokim@snu.ac.kr (H.-J. Kim).

damaged, the products are rendered useless [3]. Polyester resins crosslinked with melamine resins or isocyanates are widely used for improvement resistance to abrasion and scratching.

The interest in developing organic–inorganic hybrid coatings has been increasing, because of the unique properties obtained from combining inorganic and organic components into a single coating system. One approach is a sol–gel process, involving the hydrolysis and condensation reaction of metal alkoxides [4,5]. Sol–gel provides an easy, cost-effective and efficient way to incorporate inorganic components into an organic binder. The other is using nanoparticles dispersed in organic binder [6,7]. The incorporation of inorganic nanofillers in an organic coating is often reported. Organic–inorganic hybrid materials improve properties such as toughness, impact strength, tensile strength, and thermal stability [8].

In this study, we designed an organic-inorganic hybrid resin with a silicone intermediate. We synthesized a silicone-modified







^{*} Corresponding author at: Laboratory of Adhesion and Bio-Composites, Program in Environmental Materials Science, Seoul National University, Seoul 151-921, Republic of Korea. Tel.: +82 2 880 4784; fax: +82 2 873 2318.

^{0300-9440/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.porgcoat.2013.09.004



Raw materials used for synthesis of silicone-modified polyester resin.



polyester resin from polyester resin and silicone intermediate, by methylol reaction between –OH and –CH₃. Silicone intermediate is an inorganic material, and branched polyester resin is organic material. Silicone modified polyester coatings are able to be used as an automotive clearcoat. The surface free energy of polyester coatings was calculated by the contact angle measurement. Also, the peel test was measured for the surface properties, and was used to determine any correlation with cleanable ability. The elongation, tensile strength and viscoelastic properties of synthesized resins of free-coated film were measured. The formability of PCMs was evaluated using a cylindrical drawing test. The stress and strain of the coatings were calculated from the deep drawing results. Finally, the relationship between the contents of silicone intermediate and the formability of the polyester coatings was discussed.

2. Experimental

2.1. Materials

Table 1 presents the chemical structures and basic information of the raw materials used for the synthesis. A silicone intermediate (DC 3037, M_n = 1000, Dow Corning, USA) was prepared to control the flexibility of the main chain. 1,4-cyclohexanedicarboxylic acid (1,4-CHDA, Tokyo Chemical Industry, Japan), adipic acid (AA, Samchun Pure Chemical, Republic of Korea), trimethylol propane (TMP, Tokyo Chemical Industry, Japan), 1,6-hexandiol (1,6-HD, Samchun Pure Chemical, Republic of Korea), and 2,2-dimethyl-1,3-propendiol mono(hydroxypivalate) (HPHP, Tokyo Chemical Industry, Japan) were used without further purification. Butylstannoic acid (FASCAT 4100, Arkema Inc., USA) was used as a catalyst to catalyze polymerization, and to prevent a transesterification reaction during the polymerization [8]. Hexamethoxy-methylmelamine (HMMM, Cytec Industries Inc., USA) was used as the curing agent, and Nacure blocked acid catalyst (NACURE 1953, King Industries, Inc., USA) was used.

2.2. Synthesis of silicone-modified polyester resin

The synthesized scheme of silicone-modified polyester resin is shown in Scheme 1 and the formulations are listed in Table 2. Polyester was synthesized from polybasic alcohols and polybasic acids with the following procedure, which consisted of two synthetic processes. One was the fusion process, and the other was the solvent process. The synthesis took place in a 500 mL round bottom flask equipped with a four-necked flask, having a mechanical stirrer, thermometer, condenser and water trap. The condenser and water trap were meant to remove condensed water during the poly-condensation reaction.

The synthesis of polyester has two steps. The first step is to the synthesized base polyester resin remaining –OH group. 1,4-CHDA, AA, TMP, 1,6-HD, HPHP were charged into a dried reactor, and the reaction temperature was set to 150 °C with stirring for 2 h under N₂ purge. Subsequently, the reaction temperature was increased from 150 to 210 °C, at the rate of 0.5 °C/min. During the fusion process, all raw materials were melted, and the condensed water was collected. After finishing the fusion process, it was converted into solvent process, by adding xylene. The solvent process was carried out to collect condensed water, and to make a low acid value. The reaction temperature was measured by 0.1 *N* KOH. The reaction temperature was maintained for several hours, until the acid value was under 20 mg KOH/g resin [9].

The second step is a methylol reaction between the–OH group of polyester resin, and the $-CH_3$ of silicone intermediate, with catalyst. Silicone intermediated was charged into a synthesized

Table 2

186

Formulations used for synthesis of silicone-modified polyester resin (unit: mole).

Sample	CHDA ^a	AA ^b	TMP ^c	1,6-HD ^d	HPHPe	SI-IM ^f
SiPE-0	13	2	3	5	8	0
SiPE-1	13	2	3	5	8	0.1
SiPE-3	13	2	3	5	8	0.3
SiPE-5	13	2	3	5	8	0.5

^a 1,4-CHDA (1,4-cyclohexanedicarboxylic acid).

^b AA (adipic acid).

^c TMP (trimethylolpropane).

d 1,6-HD (1,6-hexandiol).

^e HPHP (neopentyl gylcol mono(hydroxypivalate)).

^f SI-IM (silicone intermediate, $M_n = 1000$).

polyester resin at a reactor, and the reaction temperature was set to 80°C with stirring for 2 h under N₂ purge. Subsequently, the reaction temperature was increased from 80 to 160 °C, at the rate of 0.2 °C/min. During the methylol reaction, the by-product of methanol was collected by a condenser. The reaction temperature was maintained for several hours to collect the methanol. The solid content of synthesized silicone-modified polyester was 70%.

2.3. Preparation of silicone-modified polyester coatings

Synthesized silicone-modified polyester resin was mixed with the cross-linker, HMMM, additives, and solvents. Four different coating formulations were prepared, as listed in Table 3.

Table 3
Formulations of silicone-modified polyester coatings as a clearcoat (unit: wt%).

Contents	CSiPE-0	CSiPE-1	CSiPE-3	CSiPE-5
SiPE-0 (70%)	46.0	-		_
SiPE-1 (70%)	-	46.8		-
SiPE-3 (50%)	-	-	67.6	-
SiPE-5 (50%)	-	-		69.5
Solvent ^a	15.0	15.0	0.0	0.0
TiO ₂	25.0	25.0	25.0	25.0
HMMM	5.9	5.3	4.2	3.1
Additives	1.0	1.0	1.0	1.0
Nacure 1953	0.6	0.5	0.4	0.3
Solvent ^a	6.5	6.4	2.1	1.1

^a Solvent: solvesso #100.



Scheme 1. Synthesis process of silicone-modified polyester resin.

Table 4

Characterization of the silicone-modified polyester resin.

Property	SiPE-0	SiPE-1	SiPE-3	SiPE-5
Number average M.W. (M_n)	4570	4650	4820	5000
Polydispersity index (M_w/M_n)	2.9	3.4	3.3	3.2
n _{OH} (mg KOH/g) ^a	61.4	54.3	40.8	30.4
M_n/n_{OH} (g/mg KOH)	74	86	118	164
Crosslink density (10 ⁻³ mol/cm ³)	1.38	1.02	0.69	0.47

 ${}^{a}n_{OH}$, theoretical hydroxyl number of polyester resins.

Free film. The coating formulations were cast on to an aluminum pan, and dried to evaporate solvent in the oven at 60 °C for 12 h, and then baked at 150 °C (oven temperature) for 1 h. The thickness of the baked films ranged from 150 to 200 μ m. The resulting films became the samples for tensile strength and dynamic mechanical analysis.

PCM. Cold rolled steel sheets (thickness of 0.8 mm) were coated with primer, and baked at 180 °C for 10 min. The cured primer films were 15 μ m in thickness. Primer is polyester-based nanocomposites coating which has 3 wt% of organoclay and has good deep drawing and anti-corrosion properties [10]. Then, basecoat was coated and baked at 180 °C for 20 min. The cured basecoat films were 25 μ m in thickness. Basecoat is cyclic structured polyester coating which has 20 mol of 1,4-cyclohexanedicarboxylic acid and has good deep drawing and chipping resistance properties [11]. The silicone-modified polyester coatings as a clearcoat were coated on the cured primer and basecoat film, and then baked at 180 °C for 20 min. The thickness of the cured film was 25 μ m. The total film thickness was 65 μ m.

2.4. Characterization

2.4.1. Fourier transform infrared spectroscopy (FT-IR)

Infrared spectra were obtained using a JASCO FT/IR-6100 (Jasco, Japan) spectrometer, which is equipped with a Miracle accessory, and attenuated total reflectance (ATR) setup. The ATR crystal was made of diamond, and its refractive index was 2.4 at $8500-2500 \text{ cm}^{-1}$ and $1700-300 \text{ cm}^{-1}$. The spectra were collected using the ATR mode in the wavenumber range of $4000-650 \text{ cm}^{-1}$, and the resolution of the spectra recorded was 4 cm^{-1} .

2.4.2. Gel permeation chromatography (GPC)

The molecular weight and polydispersity of the synthesized silicone-modified polyester resins were measured using a YL9100 GPC SYSTEM (Young Lin, Republic of Korea) apparatus, consisting of a pump and a RI detector. Tetrahydrofuran (THF) was used as the eluent, and the flow rate was 1 mL/min. The molecular weight and polydispersity index of the synthesized resins are listed in Table 4 [12].

2.4.3. Viscoelastic properties by dynamic mechanical analysis (DMA)

The glass transition temperature and viscoelastic properties of the polyester/melamine heat-cured films were analyzed using a dynamic mechanical analysis instrument (Q800, TA Instruments). The crosslink density (v_c) was derived from the minimum storage modulus (E'_{min}) and temperature at minimum storage modulus ($T_{E'_{min}}$) in the rubbery plateau region. The crosslink density was calculated using the following equation [13]:

$$\upsilon_{\rm c} = \frac{E'_{\rm min}}{3RT_{E'_{\rm min}}}$$

Rectangular specimens of 20 mm in length and 6.45 mm in width were prepared. The specimens were tested in tension mode at a

frequency of 1 Hz and strain of 0.3%, at temperature levels from -60 °C to 160 °C, at a scanning rate of 2 °C/min.

The creep strain of the free-coated films was determined using a dynamic mechanical analysis instrument (Q800, TA Instruments). Rectangular specimens of 20 mm in length, 6.45 mm in width and 200 μ m in thickness were prepared. The time-dependence of creep strain of the free-coated films was obtained at a stress level of 5.1×10^6 Pa. Those tests were performed at 25 °C, and with a loading time of 90 s. The 90 s of testing time was designed to correspond to the deep drawing testing time.

2.4.4. Analyzing of formability [14]

The strain behavior of the coating film in a deep drawing is very complicated because both tensile and compressive strains are developed. To analyze formability, we have been considered strain energy and strain using tensile and creep test.

Compressive stress on PCM (σ_p) and forming ratio (R_f) can be calculated using Eqs. (1) and (2)

$$\sigma_{\rm p} = \frac{\text{blank force (N)}}{\text{total area before drawing test (mm^2)}} \tag{1}$$

$$R_{\rm f} = \left(\frac{\text{total area after drawing test } (mm^2)}{\text{total area before drawing test } (mm^2)} - 1\right) \times 100$$
(2)

The calculated value of the compressive stress was 5.1 MPa, and that of the forming ratio was 23.4%.

Strain energy at R_f in tensile strength test (U_T) can be calculated using Eq. (3). The value of U_T means that the pure strain energy of coating film to forming at R_f in the stress–strain curve during the drawing.

$$U_{\rm T} = \int_0^{R_{\rm f}} \text{Strain-dependent stress curve } d\varepsilon \tag{3}$$

Strain energy for 90 s in creep test (U_C) can be calculated using Eq. (4). The value of U_C means that the pure strain energy of coating film to forming at 5.1 MPa for 90 s.

$$U_{\rm C} = \int_0^{90} \text{Strain-dependent stress curve } d\varepsilon \tag{4}$$

From those equations, forming coefficient based on strain energy (F_U) can be calculated using Eq. (5) and forming coefficient based on strain (F_{ε}) can be can be calculated using Eq. (6)

$$F_{\rm U} = \frac{U_{\rm C}}{U_{\rm T}} \tag{5}$$

$$F_{\varepsilon} = \frac{\varepsilon_{\rm C}}{R_{\rm f}} \tag{6}$$

where ε_c is the strain during the creep test.

2.4.5. Tensile strength

Tensile strength was measured using a Universal Testing Machine (Zwick Corp.) at a crosshead speed of 20 mm/min, which was designed to correspond to the deep drawing testing speed at



Fig. 1. Procedure of the deep drawing [2].

ambient temperature. The tensile specimens prepared from freecoated films were 40 mm in length (span length), 6.45 mm in width and 200 μ m in thickness. The tensile strength was calculated by dividing the maximum load in Newtons (N), by the average original cross-sectional areas in the gage length of the specimen in square meters. The percent elongation (strain%) was calculated by dividing the change in gage length by the original specimen gage length, expressed as a percentage (%) [15].

2.4.6. Deep drawing

A cylindrical deep drawing test was performed to examine the formability of the heat-cured coatings, as shown in Fig. 1. The shape of the PCM before deep drawing was a disk, of diameter 105 mm. The shape of the punch was a circle of diameter 40 mm, and the shoulder radius of the punch and the corner radius of the punch were 5 mm. Specific conditions of the deep drawing are shown in Table 5. The speed of punch was 20 mm/min, and the drawing testing time was 90 s. The blank force was 4.9×10^4 N, and this test was performed at 25 °C.

2.4.7. Surface free energy

The surface free energy of the heat-cured films was evaluated from the static contact angles measured using a contact angle analyzer (SEO 300A, Surface & Electro-Optics Corp.). The temperature and relative humidity were 23 ± 2 °C. The equilibrium contact angle is defined as the angle between the solid surface and a tangent drawn on the drop-surface, passing through the atmosphere–liquid–solid triple-point [16].

The surface free energy from contact angles was calculated based on Young's equation. In this study, the three liquids method

Table 5

Conditions of the deep drawing of PCM [2].

Shape of punch	Cylindrical
Corner radius of punch (mm)	5
Shoulder radius of punch (mm)	5
Size of punch (mm)	40
Size of PCM (mm)	105
Drawing height (mm)	30
Drawing of speed (mm/min)	20

was employed. This method was suggested by Good and van Oss, and has been widely used to examine the surface free energy of polymeric coating films. The test liquids used in this study were distilled water, formamide and diiodomethane. From these contact angles of the liquids, the surface free energy can be calculated using the following equations:

$$\begin{aligned} \gamma_{LV}(1+\cos\theta_1) &= 2\sqrt{\gamma_S^{LW}\gamma_{LV1}^{LW}} + \sqrt{\gamma_S^+\gamma_{LV1}^-} + \sqrt{\gamma_S^-\gamma_{LV1}^+} \\ \gamma_{LV}(1+\cos\theta_2) &= 2\sqrt{\gamma_S^{LW}\gamma_{LV2}^{LW}} + \sqrt{\gamma_S^+\gamma_{LV2}^-} + \sqrt{\gamma_S^-\gamma_{LV2}^+} \\ \gamma_{LV}(1+\cos\theta_3) &= 2\sqrt{\gamma_S^{LW}\gamma_{LV3}^{LW}} + \sqrt{\gamma_S^+\gamma_{LV3}^-} + \sqrt{\gamma_S^-\gamma_{LV3}^+} \\ \gamma &= \gamma_S^{LW} + \gamma_S^{AB} = \gamma_S^{LW} + 2\sqrt{\gamma_S^+\gamma_s^-} \end{aligned}$$

where *LW* is the Lifshitz-van der Waals force and *AB* is the acid-basic interaction, and γ is the surface free energy, acid-base interaction (γ^{AB}). γ^+ and γ^- are the Lewis acid parameter and the Lewis base parameter of the surface free energy, respectively [17–19].

2.4.8. X-ray photoelectron spectroscopy (XPS)

Chemical analysis was performed on the surface of cured coatings with an X-ray photoelectron spectroscopy (Sigma Probe, Thermo Scientific, USA), equipped with spherical sector analyzer. The XPS spectra of the region correspond to 0–700 eV. The signals of oxygen, carbon and silicone were observed at 530, 283 and 100 eV, respectively [20].

2.4.9. Measurement of cleanable characteristics using the 180° peel test

The cleanable characteristic of polymers is measured by using a contact angle measurement, from which can be calculated the surface free energy. According to these measurements, the surface free energy is decreased with fluorine or silicone derivatives. The peel test is a normal method to measure the adhesion of pressure sensitive adhesives (PSAs) when the coated film is removed from



Fig. 2. Measurement of the cleanable characteristic using the 180° peel test [18].

substrates. This method can be applied to determine the cleanable characteristic of silicone-modified coatings. The cleanable characteristic of silicone-modified coatings measured the adhesion between the coating surface and the PSAs. With decreasing surface free energy, the adhesion between different surfaces is decreased. The measurement of cleanable characteristic is illustrated in Fig. 2 [21].

SCOTCH No. 810 tape, which is a product of 3M, was prepared to evaluate the cleanable characteristic of coatings. Polyester coatings were coated on a stainless steel substrate, and cured at $150 \,^{\circ}$ C for 30 min. After curing, a width of 18 mm PSA tape was attached to a coating surface, and a 2 kg rubber roller was passed over it twice. The peel strength was measured using a Stable Micro Systems TA-XT2i Texture Analyzer (UK). The testing condition was at a speed of 300 mm/min at 20 °C, based on ASTM D 3330. The peel strength was recalculated from g/18 mm to g/25 mm [21,22].

2.4.10. Comparison properties between before and after shaping

Shaped of the coated metal sheet and non-shaped the coated metal sheet were tested physical properties such as gloss, hardness, MEK rub test and anti-corrosion. 20° angle of gloss was measured by Gloss meter (BYK-Gardner, Germany) and hardness was measured by pencil hardness. MEK rub test was tested by rubbing the surface of a baked film with cheesecloth soaked with MEK for 100 times.

The anti-corrosion property was measured using salt spray test. All specimens had cross-scratch line. The salt spray test condition was according to ASTM B-117 in a 5 wt% NaCl solution at 35 °C. After 500 h, changes of surface morphology, especially around the crossline on the coating and surface defects were examined via VIEEWTM digital image analyzer (VIEEWTM, Atlas Electric Devices Co., USA) [23,24]. Recoat was measured by cross-cut test and changes of surface morphology were examined via VIEEWTM. VIEEWTM is capable of capturing digital images of samples under various lighting schemes optimized to highlight and enhance surface defects to digitally process images. Sample images were analyzed for surface texture and smooth by grayscale.

3. Results and discussion

3.1. Characterization of silicone-modified polyester resin

Silicone-modified polyester resins were synthesized based on different contents of silicone intermediate. The Si–O and Si–O–Si groups in the synthesized polyester resin were determined using FT-IR. As shown in Fig. 3, the Si–O and Si–O–Si group that was from silicone intermediate was detected at 800 and 1083 cm⁻¹, respectively, and the intensity of these bands increased with increasing content of silicone intermediate [25].



Fig. 3. IR spectra of silicon-modified polyester resin (Si—O—Si: 800 cm⁻¹, Si—O: 1083 cm⁻¹).

Table 4 lists the molecular weight and polydispersity of the synthesized silicone-modified polyester resin. The theoretical hydroxyl number of polyester resin (n_{OH}) decreased with increasing content of silicone intermediate, because (n_{OH}) is dependent on the molecular weight of synthesized resin. Also, the ratio between the number average molecular weight and hydroxyl number (M_n/n_{OH}) indicates the length of the repeating unit in the crosslink network of the synthesized polyester resin [13]. The value of M_n/n_{OH} was observed to increase with increasing content of silicone intermediate, thus indicating decreasing crosslinking density.

3.2. Viscoelastic behavior

Dynamic mechanical analysis (DMA) is a convenient method to study thermal and mechanical viscoelastic properties of polymeric materials. The DMA data allow observations of changes in loss and storage modulus, glass transition temperature (T_g), and crosslink density [26].

Fig. 4(a) shows the storage modulus as a function of temperature for synthesized polyester resins with different contents of silicone intermediate. The storage modulus of polyester coatings decreased with increasing contents of silicone intermediate, i.e. CSiPE-0>CSiPE-1>CSiPE-3>CSiPE-5. Silicone intermediate has a long chain; it is generally recognized that the mobility and flexibility of polymer chain increases with the length of the linear chain segment [3]. In addition, the storage modulus decreased with the increase of the ratio between the number average molecular weight and hydroxyl number (M_n/n_{OH}) [27]. As listed in Table 4, a longer length between crosslinks corresponds to a lower crosslink density, thus explaining the lower modulus of the resin. Also, the T_{g} shifted to a lower temperature with increasing contents of silicone intermediate, as shown in Fig. 4(b) [27]. From the dynamic mechanical analysis, silicone intermediate would provide a lower stiffness and higher softness to polyester coatings.

3.3. Flexibility

Flexibility is the most important property for the cutting, pressing and stamping processes in the pre-coated system. Tensile strength tests were carried out to study basic mechanical properties – modulus, tensile strength, elongation at break, and toughness of polymeric materials [28]. Fig. 5 presents the effects of the contents of silicone intermediate on the tensile behaviors of the synthesized





Fig. 4. Viscoelastic properties of silicone-modified polyester coatings: (a) storage modulus, (b) tan δ .

resins. The tensile strength decreased with increasing content of silicone intermediate (CSiPE-0 > CSiPE-1 > CSiPE-3 > CSiPE-5). In contrast, the maximum strain increased when the content of silicone intermediate was higher (CSiPE-0 < CSiPE-1 < CSiPE-3 < CSiPE-5).

The maximum stress of CSiPE-0 and CSiPE-1 was 32.2 MPa and 24.8 MPa, and the value of the strain was 91% and 109%, respectively. However, in terms of elongation, the opposite trend to that of the stress appeared. The elongation of coatings increased sharply with increasing content of silicone intermediate. In the case of CSiPE-3 and CSiPE-5, the strain value was over 150%, and the stress was 11.6 MPa and 6.1 MPa. These values represent a high flexibility and high breaking strain, which were a consequence of the high

Table 6

Calculated values from tensile test and creep test [14].



 $U_{\rm T}$, strain energy at 23.4% in tensile test; $U_{\rm C}$, strain energy of coating film in creep test; $F_{\rm U}$ ($U_{\rm C}/U_{\rm T}$), forming coefficient based on strain energy; $\varepsilon_{\rm C}$, strain at 5.1 MPa during the creep test; F_{ε} ($\varepsilon_{\rm C}/R_{\rm f}$), forming coefficient based on strain.



Fig. 5. Stress-strain curve of silicone-modified polyester coatings.

stretchability imparted by the linear chains. Silicone intermediate would provide a linear chain that could give better mobility and flexibility to the polymer network. Therefore it could be implied that silicone intermediate can give flexibility, and would provide lower stiffness and higher softness to polyester coatings [3].

3.4. Formability

The deep drawing test is a common method for determining the formability in pre-coated metals. During the deep drawing test, which took 90 s to complete, the calculated stress was 5.1 MPa, and the strain was 23.4% on the PCM.

Fig. 6 shows the formability resulting from the deep drawing. CSiPE-0 and CSiPE-1 had cracks and delamination, even though they exhibited higher tensile strength values from the flexibility test. CSiPE-0 and CSiPE-1 were not flexible enough to be stretched out during the deep drawing. CSiPE-3 and CSiPE-5 exhibited good formability, because those specimens had sufficient tensile strength and elongation values based on the flexibility test, and also had sufficient flexibility, based on the creep test.

 $F_{\rm U}$, forming coefficient based on strain energy, was calculated form Eq. (5). $F_{\rm U} = U_{\rm C}/U_{\rm T}$ and, $U_{\rm C}$ and $U_{\rm T}$ were calculated from Eqs. (3) and (4). $U_{\rm C}$ of CSiPE-0 is 81.42 and $U_{\rm T}$ of CSiPE-0 is 246.8. $F_{\rm U}$ of CSiPE-0 is 0.33 and CSiPE-1, CSiPE-3 and CSiPE-5 were 0.51, 1.54 and 5.79, respectively. $F_{\rm e}$, a forming coefficient based on strain, was calculated form Eq. (6). $F_{\rm e} = \varepsilon_{\rm C}/R_{\rm f}$ and, $\varepsilon_{\rm c}$, the developed strain for 90 s was measured by Creep strain. As shown in Fig. 7 (Table 6) the developed strains of CSiPE-0, CSiPE-1, CSiPE-3 and CSiPE-5 were 16.0%, 20.1%, 43.2% and 88.3%, respectively. $F_{\rm e}$ of CSiPE-0 is 0.68 and CSiPE-1, CSiPE-3 and CSiPE-5 were 0.86, 1.85 and 3.77, respectively. $F_{\rm U}$ should be larger than 1, and $F_{\rm e}$ should be larger than 1 to have good formability [14]. So, CSiPE-0 and CSiPE-1 were not flexible enough to stretch out during the deep drawing test. However, the $F_{\rm U}$ of CSiPE-3 and CSiPE-5 were larger than 1, and those of $F_{\rm e}$ were also



Fig. 6. Formability of silicone-modified polyester coatings on the cold roll steel.



Fig. 7. Strain of silicone-modified polyester coatings by the creep test.

larger than 1. So, those specimens can be stretched without being damaged during the deep drawing. The calculated values are listed in Table 7. From the deep drawing test, silicone intermediate would provide lower stiffness and higher softness to polyester coatings, and could provide good formability.

3.5. X-ray photoelectron analysis

To analyze the amount of silicone component, XPS was used to detect O, C and Si atom on a cured coating surface. Photoemission peaks from O_{1s} , C_{1s} and Si_{2p} core levels can clearly be observed, with bonding energies of 530, 283, and 100 eV, respectively [20]. As shown in Fig. 8, a silicone atom peak was not shown in the photoemission curve of CSiPE-0. The silicone atom to carbon ration increased with increasing content of silicone intermediate. The Si_{2p} peak increased with increasing content of silicone intermediate. CSiPE-1, CSiPE-3, and CSiPE-5 have 1.0, 3.0 and 5.0 wt% of silicone intermediated contents, while at the surface of the silicone group, the concentration was 8.5, 13.6 and 16.6 wt%, respectively. Those results implied that the silicone group can migrate to the surface of cured polyester coatings.

3.6. Surface free energy

Fig. 9 shows the surface energy calculated by the Lewis acid–base three liquids method. These results are summarized in Table 7. The contact angle of the film surface increased with increasing silicone content, which was incorporated to increase film hydrophobicity. The water contact angle and surface free energy of CSiPE-0 were 77.6° and 46.2 mN/m, respectively. CSiPE-5, which had the highest amount of silicone intermediate, had 93.5° of water contact angle, and had 26.5 mN/m of surface free energy.

Table 7
Contact angle and surface free energy of silicone-modified polyester coatings

Samples	Contact angle (°)			Surface free energy (mN/m)		
	Water	Formamide	Diiodomethane	γ_{s}	$\gamma_{\rm s}^{\rm d}$	γ_{s}^{p}
CSiPE-0	77.6	46.4	29.8	46.2	43.1	3.4
CSiPE-1	82.7	55.6	45.1	38.0	34.7	3.2
CSiPE-3	89.5	62.8	51.9	34.1	31.9	2.1
CSiPE-5	93.5	72.3	67.5	26.5	24.3	2.0



Fig. 8. XPS curves of silicone-modified polyester coatings.



Fig. 9. Surface free energy and contact angle of silicone-modified polyester coatings.

Table 9

Classification of pressure-sensitive adhesive vs. peel adhesion [30].



Fig. 10. Peel strength of silicone-modified polyester coatings.

Si—O and Si—O—Si groups can easily tailor to the outermost surface, and they can produce hydrophobicity on the cured film [29].

3.7. Cleanable characteristics of clearcoat

The peel test results for the evaluation of cleanable characteristic with the silicone group are shown in Fig. 10. The maximum strength of CSiPE-0 was 8.5 N/25 mm, and that of CSiPE-5 was 5.5 N/25 mm. CSiPE-5 has the highest content of silicone; the value had a similar

Table 8

Classification of pressure-sensitive adhesive vs. peel adhesion [30].

Kind of PSA	Adhesion of PSA (N/25 mm) (180° peel test)
Excellent permanent Permanent	>14 10-14
Semi-removable	6-8
Removable	2-4
Excellent removable	<1



peel adhesion to that of semi-removable PSAs (pressure sensitive adhesives), as listed in Table 8 [30]. With the increasing silicone intermediate contents, peel strength was gradually decreased. In the result of the peel test, the peel strength was steady decreased, with silicone intermediate content ranging from 0 to 5 wt%. From those results, increasing contents of silicone intermediate to the silicone-modified polyester resin increased the contact angle of water, and decreased the peel strength of the cured silicone-modified polyester coatings.

3.8. Physical properties of before and after shaping of the coated metal sheet

Tested results were listed in Table 9. Hardness and MEK rub were same after shaping compared to before shaping of the coated metal sheet. Goss (20°) and anti-corrosion property was little bit decreased, because heat-cured film was stretched out during the deep drawing. Heat-cured film can be damaged by compressive strength during the deep. But it could overcome the stress and it had very little damage. Also, corrosion area of after shaping was 1.15%. It means that silicone-modified polyester coating had good anti-corrosion property.

Recoat was good. Peeling area of clearcoat was 0.6% and that of recoat of clearcoat was 1.15%. It means that clearcoat had good recoat property.

4. Conclusions

Four types of silicone-modified polyester resins with different contents of silicone intermediate were synthesized, and formulated to control formability for pre-coated metal systems. Those resins were designed to show the flexibility of the long chain of the silicone intermediate. The viscoelastic behavior, flexibility and formability were measured, to determine the long chain effect on the flexibility of the pre-coated metal system.

When the contents of the long chain of silicone intermediate were increased in the resins synthesized, the stiffness of the product decreased considerably, and the T_g of each cured coating shifted to the lower temperature. Therefore, silicone intermediate is a major factor in improving flexibility and formability of the polyester coatings. To analyze the formability, we calculated F_U (the forming coefficient based on strain energy) and F_{ε} (the forming coefficient based on strain). F_U of CSiPE-0 is 0.33 and CSiPE-1, CSiPE-3 and CSiPE-5 were 0.51, 1.54 and 5.79, respectively. F_{ε} of CSiPE-0 is 0.68 and CSiPE-1, CSiPE-3 and CSiPE-5 were 0.86, 1.85 and 3.77, respectively. When F_U and F_{ε} are both larger than 1, the polyester coatings have good formability. So, CSiPE-3 and CSiPE-5 have good formability.

Silicone intermediate can give low surface energy and cleanable characteristics to polyester coatings. The peel strength of CSiPE-5 was 5.5 N/25 mm, which was that of semi-removable PSAs. CSiPE-5 which had 0.5 mol of silicone intermediate had good formability in the deep drawing, and also had low peel strength. Also, physical properties of before and after shaping of the coated metal sheet were almost same. It has good physical properties.

So, CSiPE-5 would be an appropriate coating as a clearcoat for automotive pre-coated metals.

References

- [1] K. Ueda, H. Kanai, T. Suzuki, T. Amari, Prog. Org. Coat. 43 (2001) 233-242.
- [2] K. Ueda, H. Kanai, T. Amari, Prog. Org. Coat. 43 (2002) 267-272.
- [3] J.-I. Moon, Y.-H. Lee, H.-J. Kim, Prog. Org. Coat. 73 (2012) 123-128.
- [4] S. Frings, H.A. Meinema, C.F. Van Nostrum, R. Van der Linde, Prog. Org. Coat. 33 (1998) 126–130.
- [5] Y. Chen, S. Zhou, G. Chen, L. Wu, Prog. Org. Coat. 54 (2005) 120–126.
- [6] X. Chen, L. Wu, S. Zhou, B. You, Polym. Int. 52 (2003) 993–998.
- [7] S.X. Zhou, L.M. Wu, J. Sun, W.D. Shen, J. Appl. Polym. Sci. 88 (2003) 189–193.
- [8] D.K. Chattopadhyay, D.C. Webster, Prog. Org. Coat. 66 (2009) 73–85.
- [9] T. Hamada, H. Kanai, T. Koike, M. Fuda, Prog. Org. Coat. 30 (1997) 271–278.
- [10] Y-H. Lee, H-J. Kim, J-H. Park, Prog. Org. Coat. 76 (2013) 1329-1336.
- [11] Y-H. Lee, H-J. Kim, Prog. Org. Coat. POC-D-12-00392R1.
- [12] G. Hayward, C.J. Standen, M.J. Husbands, A Manual of Resins for Surface Coatings, SITA Technology, London, 1987.
- [13] M.B. Stroisznigg, G.M. Wallner, B. Straub, L. Jandel, R.W. Lang, Prog. Org. Coat. 65 (2009) 328–332.
- [14] J.-I. Moon, Y.-H. Lee, H.-J. Kim, S. Schwartz, M. Rafailovich, J. Sokolov, Polym. Test. 31 (2012) 433–438.
- [15] Standard Test Method for Tensile Properties of Plastics, ASTM D638-10.
- [16] M. Gindl, G. Sinn, W. Gindl, A. Reiterer, S. Tschegg, Colloids Surf. A 181 (2001) 279–287.
- [17] Y.K. Lee, H.-J. Kim, M. Rafailovich, J. Sokolov, Int. J. Adhes. Adhes. 22 (2002) 375–384.
- [18] J.W. Wang, L.P. Wang, J. Fluorine Chem. 127 (2006) 287-290.
- [19] M.J. Geerken, R.G.H. Lammertink, M. Wessling, Colloids Surf. A 292 (2007) 224–235.
- [20] H. Miao, L. Cheng, W. Shi, Prog. Org. Coat. 65 (2009) 71-76.
- [21] D. Satas, Handbook of Pressure Sensitive Adhesive Technology and Application, Satas & Associates. Warwick. RI. USA, 2002.
- [22] Y.J. Park, D.H. Lim, H.-J. Kim, J. Adhes. Sci. Technol. 22 (2008) 1401–1423.
- [23] J.H. Choi, H-.J. Kim, J. Ind. Eng. Chem. 12 (2006) 412–417.
- [24] R.L. Howard, S.B. Lyon, J.D. Scantlebury, Prog. Org. Coat. 37 (1999) 91–98.
- [25] R. Tian, O. Seitz, M. Li, W.W. Hu, Y. Chabal, Langmuir 26 (2010) 4563–4566.
- [26] A. Asif, W.F. Shi, X.F. Shen, K.M. Nie, Polymer 46 (2005) 11066–11078.
- [27] Q. Hou, D.W. Grijpma, J. Feijen, Acta Biomater. 5 (2009) 1543–1551.
- [28] F. Levine, J. La Scala, W. Kosik, Prog. Org. Coat. 69 (2010) 63–72.
- [29] P. Fabbi, M. Messori, M. Montecchi, S. Nannarone, L. Pasauali, F. Pilati, C. Tonelli, M. Toselli, Polymer 47 (2006) 1055–1062.
- [30] Z. Czech, Int. J. Adhes. Adhes. 26 (2006) 414-418.