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To cite this article: Yong-Hee Lee, Sung-Ju Lee, Ji-Won Park & Hyun-Joong Kim (2016) Synthesis and properties of flexible polyester with urethane polyol for automotive pre-coated metals, Journal of Adhesion Science and Technology, 30:14, 1537-1554, DOI: [10.1080/01694243.2016.1150673](https://doi.org/10.1080/01694243.2016.1150673)

To link to this article: <https://doi.org/10.1080/01694243.2016.1150673>



Published online: 18 Feb 2016.



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## Synthesis and properties of flexible polyester with urethane polyol for automotive pre-coated metals

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### ABSTRACT

Four types of flexible polyester are synthesized between urethane polyol of polycarbonatediol (PCDL)-isocyanate and carboxylic-terminated polyester pre-polymer. Urethane polyol of PCDL-isocyanate is synthesized between isocyanates such as IPDI and H<sub>12</sub>MDI and PCDL which has long alkyl chain. Carboxylic-terminated polyester pre-polymers are synthesized using 1,4-CHDA, Ph-An, NPG, 1,6-HD, and 1,4-CHD. The synthesized flexible polyester is measured using GPC and <sup>1</sup>H NMR. From the <sup>1</sup>H NMR spectra, urethane polyol of PCDL-isocyanate has been introduced to the polymer chain of synthesized resin. Those resins are formulated and characterized using DMA and tensile strength, and to control formability and anti-corrosion property. Results showed that storage modulus decreased, and the glass transition temperature shifted to a lower temperature with increasing contents of the urethane polyol of PCDL-isocyanate. So, it provides lower stiffness and higher flexibility to the polyester coatings. CU-IPDI-2 had higher elongation, good formability, and a good anti-corrosion property; thus, it could be used as a primer for automotive coatings.

### ARTICLE HISTORY

Received 17 November 2015  
Revised 1 February 2016  
Accepted 2 February 2016

### KEYWORDS

Polyester; polycarbonatediol; isocyanate; formability; anti-corrosion

## 1. Introduction

Many stringent environmental legislations have been made around the world. These legislations also affect manufacturing sectors that employ coating process. Pre-painted or coil-coated metals (PCM) provide an opportunity to eliminate coating processes. The PCMs are manufactured to be subsequently processed and assembled in factories based on the principle “finish first-fabricate later.” PCMs also offer many other advantages such as increased productivity, effective use of space in the factories, and reduced volatile organic compounds (VOCs).[1,2] These PCMs are pre-manufactured in a continuous process coils of flat steel sheets are de-coiled, cleaned, pre-treated, coated, and re-coiled.[3,4]

In the automotive industry, it is necessary to reduce the manufacturing time and costs; therefore, consolidate processes are employed. In a consolidated process, the operation is

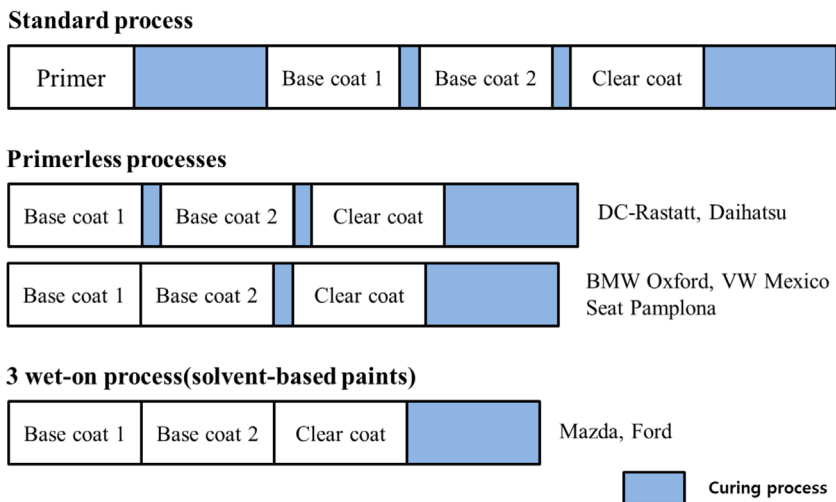


Figure 1. Suggested new process in automotive industry.[5]

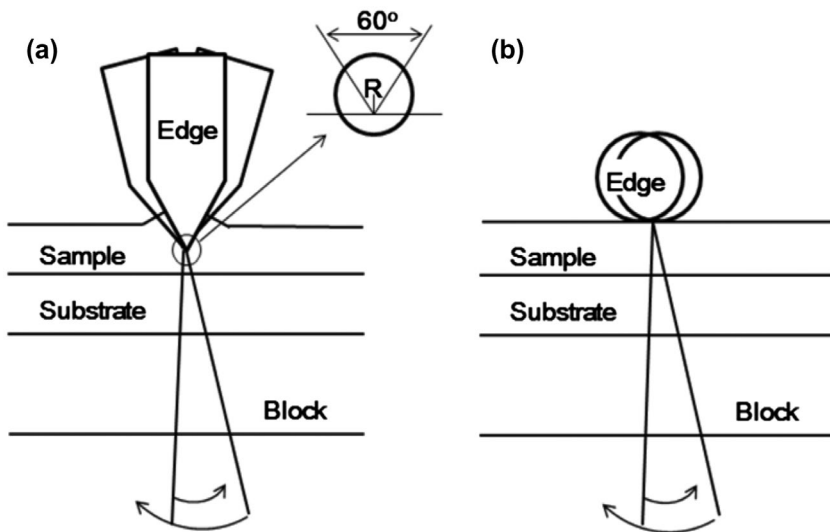


Figure 2. Rigid-body-type pendulum in RPT instrument; (a) knife edge-type for curing process, (b) cylindrical edge type for physical property.

concluded in a shorter process times, the primer application is dispensed with, and coats are applied wet-on-wet, without lengthy drying. As shown in Figure 1, the pre-primed process in the consolidated systems is an environmentally friendly process because it replaces wet coating processes such as pre-treatment and electrophoretic coating.[5] Indeed, PCM is a new attempt to reduce the manufacturing time and it has been used for various shapes such as door panels and trim parts.

The most important property of PCM is formability. If the film on the coated PCM parts is damaged, the products are rendered useless.[6] The characteristic of coated films for good formability is dependent on the maximum strain and tensile strength of PCMs in the

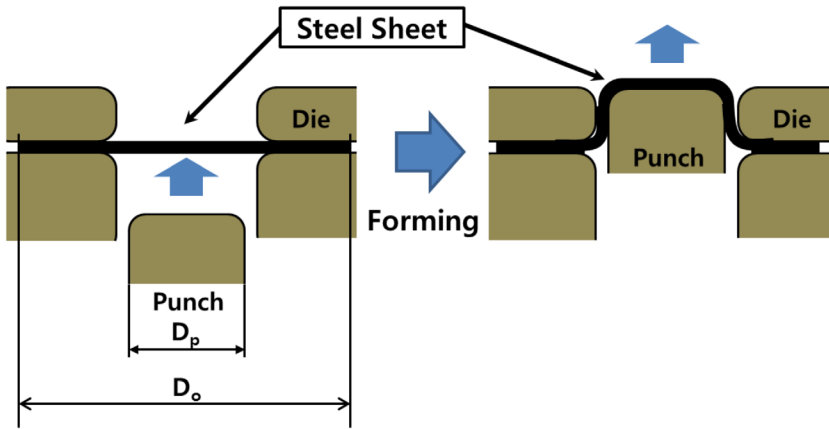


Figure 3. Procedure of the deep drawing.[6]

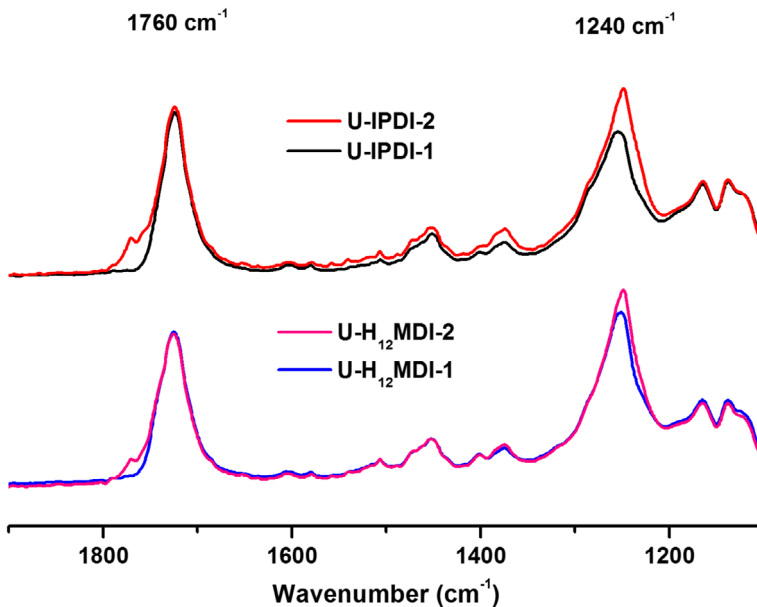
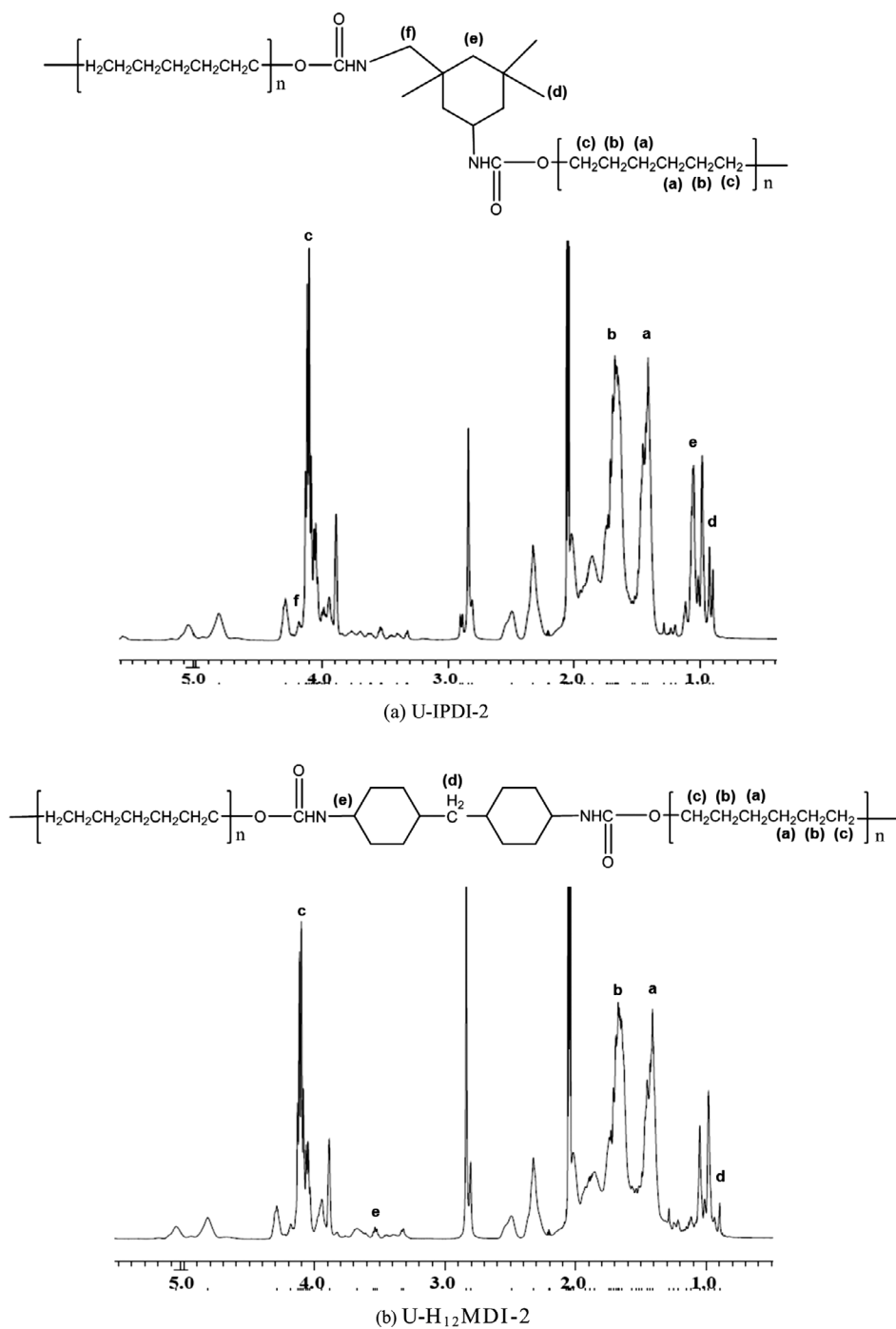


Figure 4. IR spectra of flexible polyester resin with urethane polyols (1240, 1760 cm<sup>-1</sup>: carbonate group).

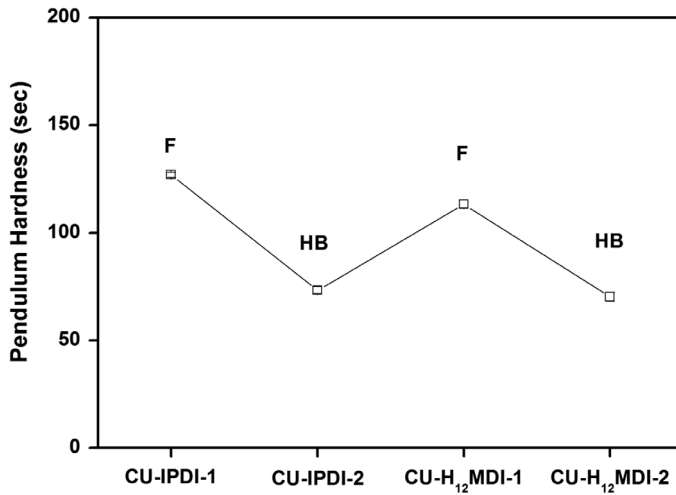
deep drawing.[7] These mechanical properties, in turn, depend on the types of used resins. Polyester has been used for automotive coatings not only as a primer and basecoat but also in interior or exterior parts. These resins have higher durability and physical properties such as chipping resistance and optical property compared to acrylic resins.[8]

In this study, four types of flexible polyester with the urethane polyol of PCDL-isocyanate were synthesized and polyester coatings were formulated as a primer to control formability and anti-corrosion property. These resins were synthesized between urethane polyol of PCDL-isocyanate and -COOH-terminated polyester pre-polymer. The urethane polyol of PCDL-isocyanate was synthesized between isocyanates such as IPDI, H<sub>12</sub>MDI, and PCDL.

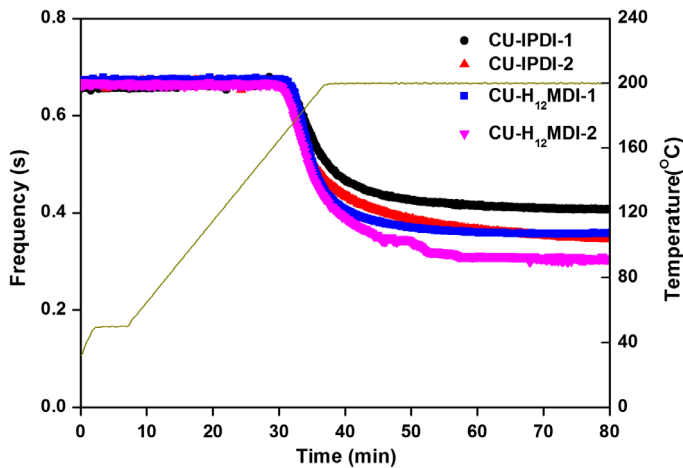


**Figure 5.** <sup>1</sup>H NMR spectrum of flexible polyester resin with urethane polyols.

The -COOH-terminated polyester pre-polymers were synthesized using 1,4-CHDA, Ph-An, NPG, 1,6-HD, and 1,4-CHD. Also, flexible polyester coatings, viscoelastic behavior, curing behavior, and tensile strength were investigated. Physical properties of deep drawing and



**Figure 6.** Surface hardness of flexible polyester coatings; pendulum hardness and pencil hardness.



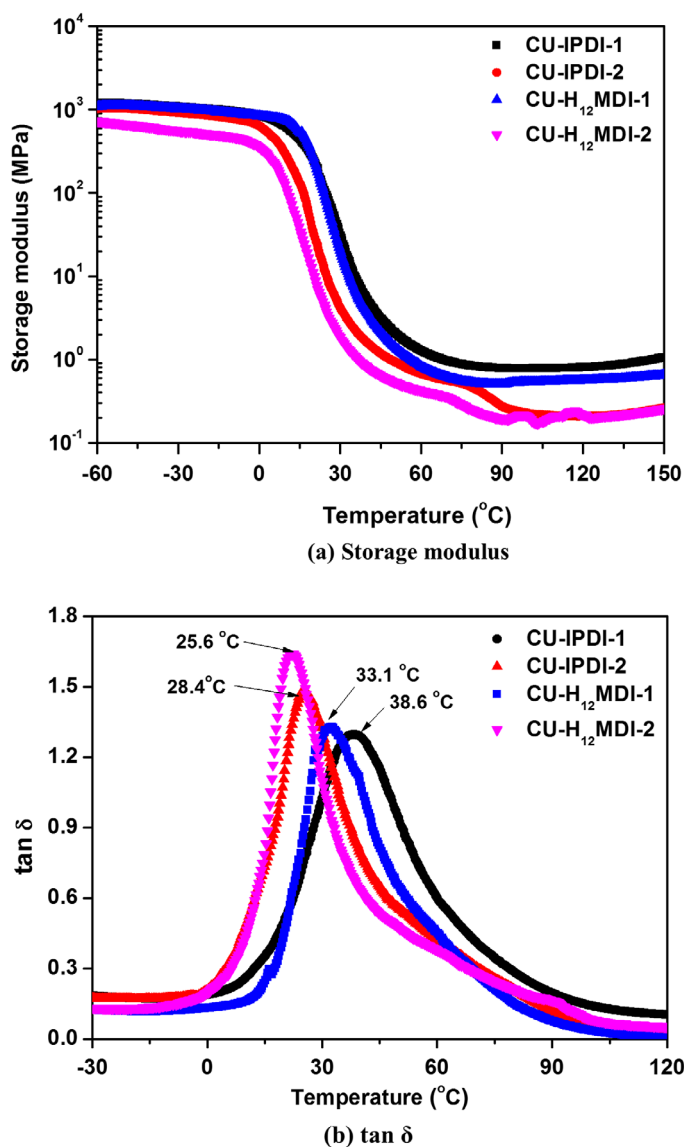
**Figure 7.** Curing behavior of flexible polyester coatings on the steel substrate using a RPT instrument.

corrosion resistance were also measured to verify suitability of the pre-coated metal system for automotive coatings.

## 2. Experimental

### 2.1. Materials

A polycarbonate diol (PCDL,  $M_n = 500$ , Asahi Kasei Chemicals Corp.) was prepared to control the flexibility of the main chain. Isophorone di-isocyanate (IPDI, Covestro) and bis-(4-isocyanatocyclohexyl) methane ( $H_{12}$ MDI, Covestro) were dried using a 4-Å molecular sieve prior to use. The polybasic acids were adipic acid (AA, Samchun Pure Chemical), 1,4-cyclohexanedicarboxylic acid (1,4-CHDA, Tokyo Chemical), phthalic anhydride (Ph-An, Samchun Pure Chemical); and the polybasic alcohols were



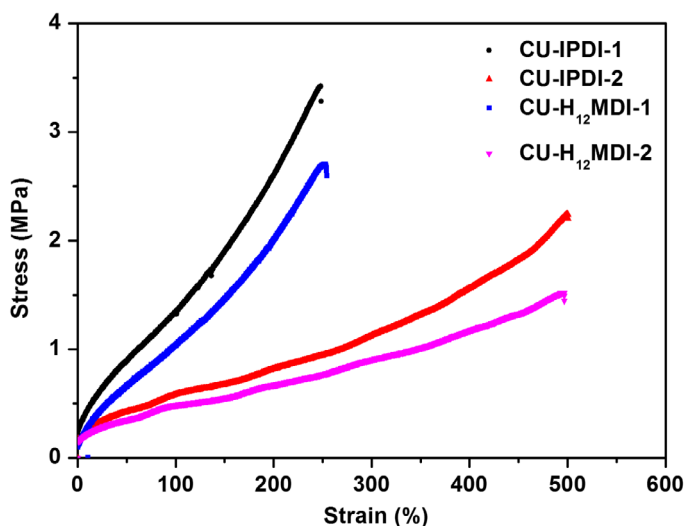
**Figure 8.** Viscoelastic properties of flexible polyester coatings with urethane polyols.

2,2-dimethyl-1,3-propanediol (NPG, Kanto Chemical Co., Inc.), 1,6-hexandiol (1,6-HD, Samchun Pure Chemical), and 1,4-cyclohexanediol (1,4-CHD, Tokyo Chemical Industry Co., Ltd.). Those materials were used without further purification.

Flexible polyester coatings were formulated with synthesized polyester and curing agents. Hexamethoxymethylmelamine (HMMM, Cytec Industries Inc., USA) was used as the curing agent, and Nacure (NACURE 1953, King Industries, Inc., USA) was used as a curing catalyst.

## 2.2. Synthesis of flexible polyester with urethane polyol

The synthesis process of flexible polyester with the urethane polyol consisted of three steps. The first step is the synthesis of two different urethane polyols of PCDL-isocyanate, and the



**Figure 9.** Stress–strain curve of flexible polyester coatings with urethane polyols.

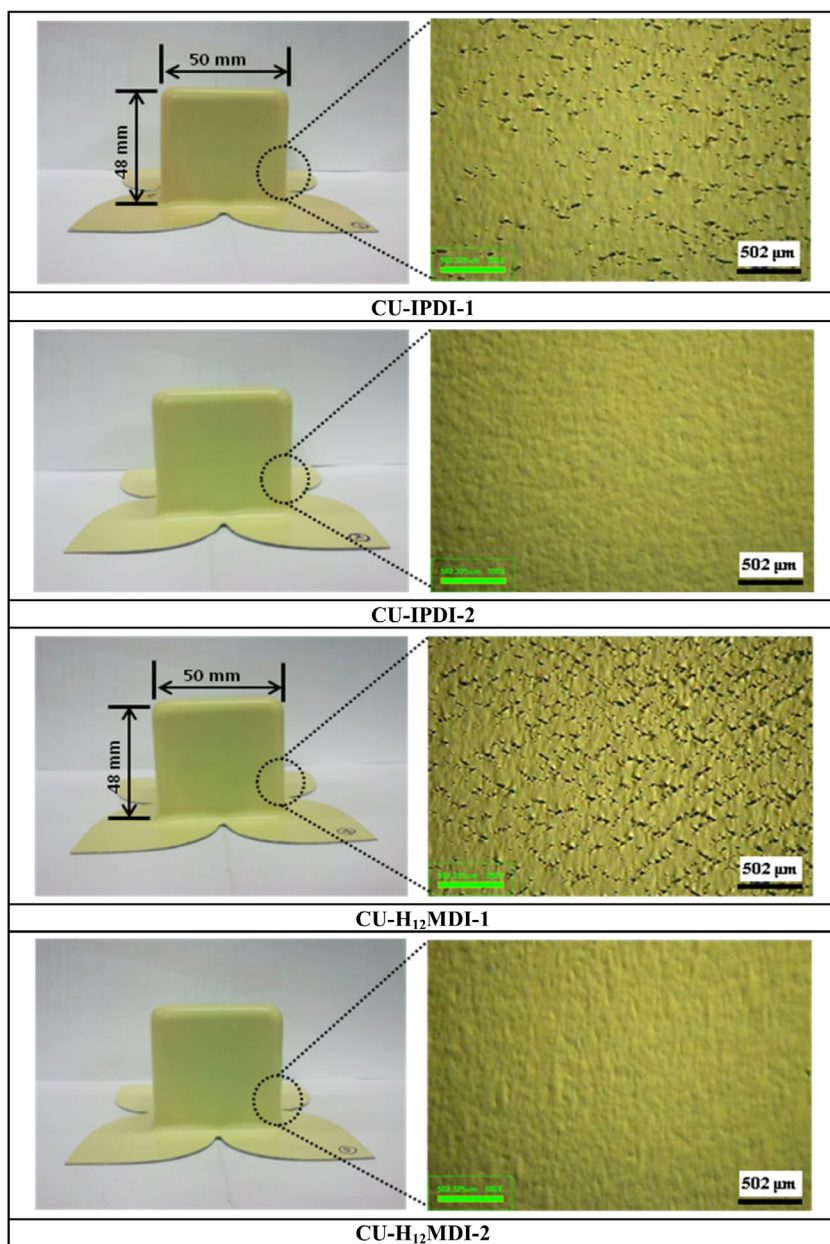
second step is synthesis of –COOH-terminated polyester pre-polymer. In the third step, the resin is synthesized between the urethane polyol of PCDL-isocyanate and –COOH-terminated polyester pre-polymer according to Scheme 1. The synthesis formulation is as listed in Table 1.

First step: Two different urethane polyols of PCDL-isocyanate were synthesized between IPDI or H<sub>12</sub>MDI and PCDL. The reaction time was determined by observing the changes of the FT-IR peak at 2265 cm<sup>-1</sup> (NCO peak) which decreased with the progression of the urethane reaction. A 500-mL round-bottom flask was equipped with a four-necked flask having a mechanical stirrer, thermometer, and condenser, and N<sub>2</sub> inlet was used as the reactor. A heating mantle was used to control the reaction temperature at each reaction step. At first, PCDL and DBTDL as a catalyst (approximately 300 ppm) were charged and the temperature was increased to 80 °C. Then, IPDI or H<sub>12</sub>MDI were added dropwise over 2 h and maintained for further 3 h.

Second step: Carboxylic-terminated polyester pre-polymer was synthesized from AA, 1,4-CHDA, Ph-An, NPG, 1,6-HD, and 1,4-CHD by the following procedure which consisted of two synthesis processes. One was the fusion process and the other was the solvent process. A 500-mL round-bottom flask equipped with a four-necked flask having a mechanical stirrer, thermometer, condenser, and water trap was used. The condenser and water trap were used to remove condensed water during the polycondensation reaction. In the fusion process, all raw materials were charged into a dried reactor and the reaction temperature was set to 130 °C with stirring for 2 h under N<sub>2</sub> purge. Subsequently, reaction temperature was increased from 130 to 180 °C at the rate of 0.5 °C/min. During the fusion process, all raw materials were melted and the condensed water was collected. And then the fusion process was converted into solvent process using xylene which was carried out as condensed water during the solvent process.

Third step: The urethane polyol of PCDL-isocyanate and –COOH-terminated polyester pre-polymers were charged into a 500-mL round-bottom flask equipped with a four-necked flask having a water trap. Subsequently, the reaction temperature was set to 130 °C with stirring for 1 h under N<sub>2</sub> purge. The reaction temperature was increased from 130 to 150 °C



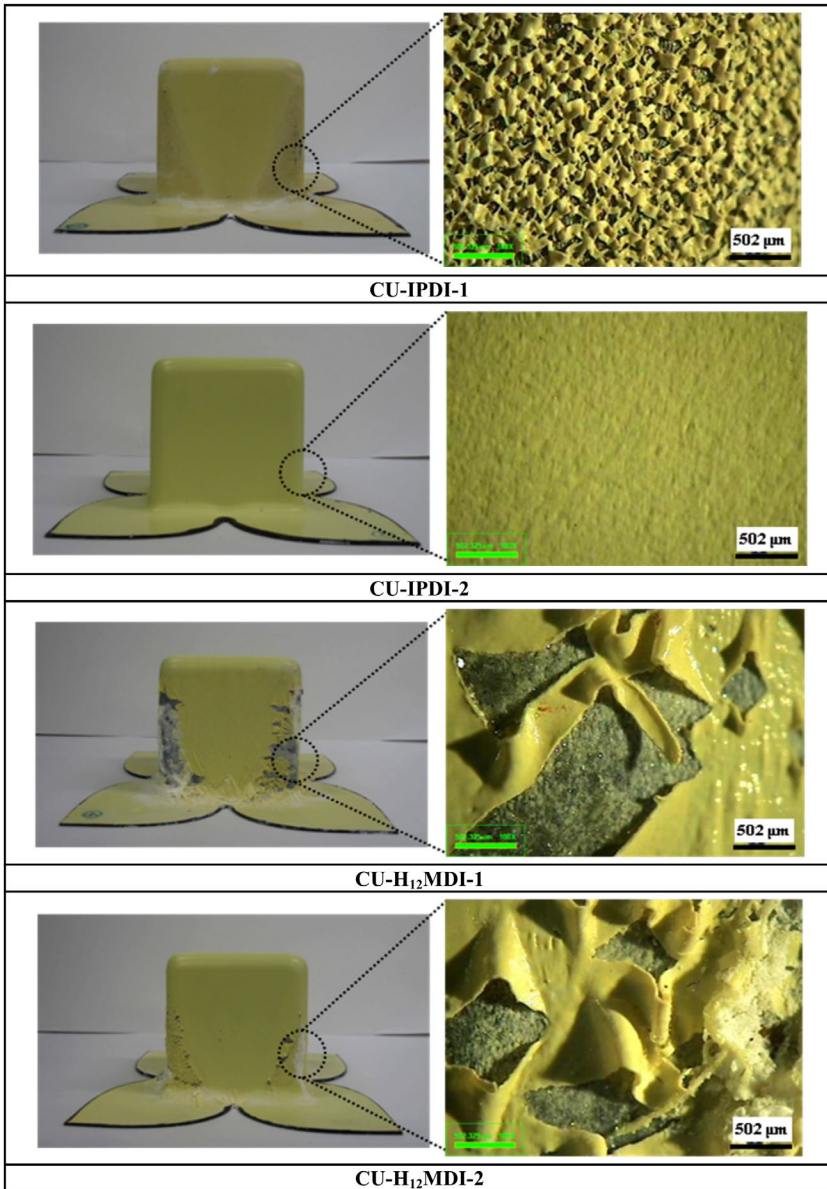


**Figure 10.** Formability of flexible polyester coatings with urethane polyols.

at the rate of 0.5 °C/min. During the solvent process, acid value titration was measured by 0.1 N KOH solution and reaction temperature was maintained for several hours until the acid value was under 3 mg of KOH/g resin.[8]

### 2.3. Preparation of flexible polyester coatings

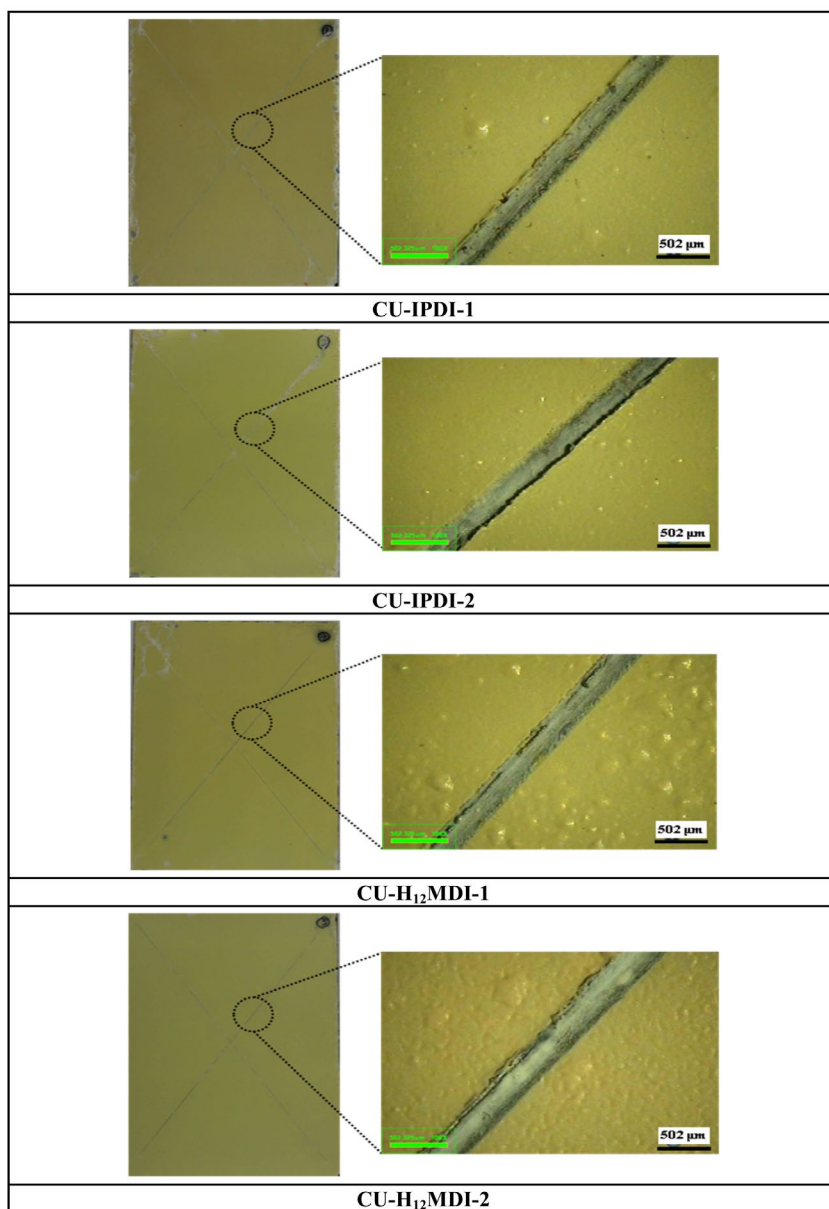
Synthesized flexible polyester was mixed with the cross-linker, HMMM, additives, and solvents. Four different formulations were prepared as listed in Table 2.



**Figure 11.** Corrosion resistance of flexible polyester coatings with urethane polyols by salt spray test for 1000 h after drawing test.

**Free film:** Polyester coatings were casted on to aluminum pan and dried to evaporate solvent in the oven at 60 °C for 12 h and then baked at 150 °C for 1 h. The thickness of the films was ranged from 200 to 250 μm. It used to measure tensile strength and dynamic mechanical analysis.

**PCM:** Galvanized steel sheets (thickness of 0.8 mm) were coated with alkali solution and baked at the peak metal temperature (PMT) of 220 °C for 15 s for pre-treatment. The cured pre-treated films were 5 μm in thickness. The flexible polyester coatings as a primer were coated on the cured pre-treated film and then baked at the PMT of 245 °C for 35 s. The thickness of those cured film of primers was 20 μm.



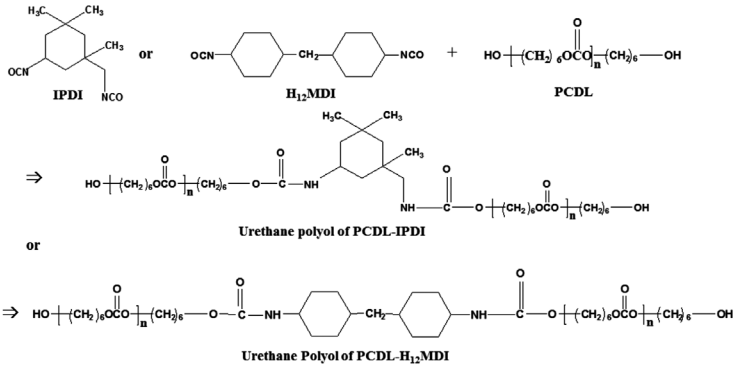
**Figure 12.** Corrosion resistance of flexible polyester coatings with urethane polyols via salt spray for 1000 h.

## 2.4. Methods

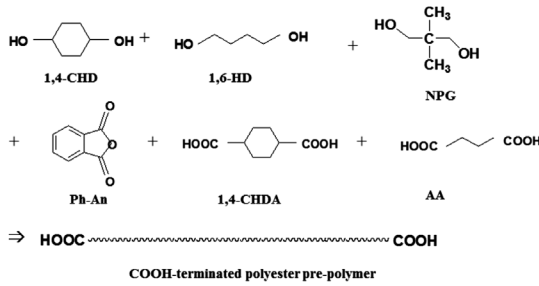
### 2.4.1. Characterization of the flexible polyester resin

Infrared spectra were obtained using a JASCO FT/IR-6100 (Jasco Corp., 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 and 1700–300  $\text{cm}^{-1}$ . The spectra were collected using ATR mode in the wave number range of 4000–650  $\text{cm}^{-1}$  and the resolution of the spectra recorded was 4  $\text{cm}^{-1}$ . From the spectra, the disappearance of characteristic peaks of NCO groups (2270  $\text{cm}^{-1}$ ) was monitored to control

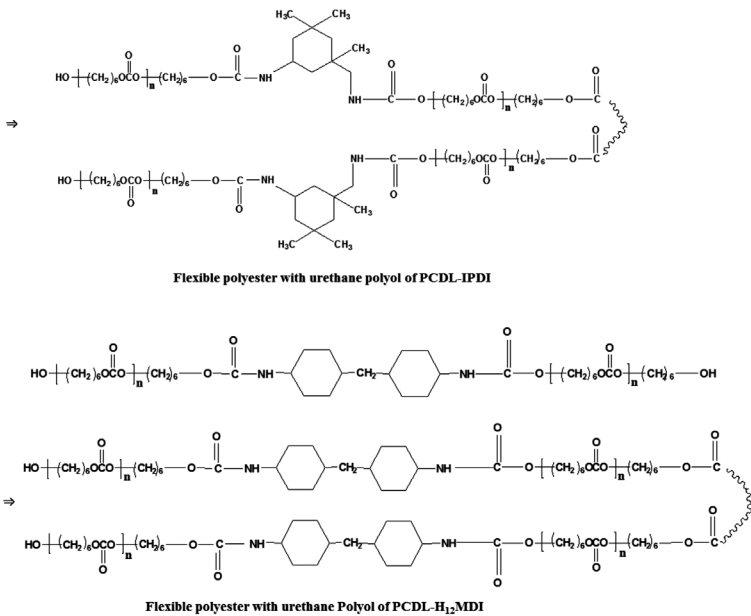
**1<sup>st</sup> Step**



**2<sup>nd</sup> Step**



**3<sup>rd</sup> Step**



**Scheme 1.** Synthesis scheme of flexible polyester resin with urethane polyols.

synthesis of the urethane polyol of PCDL-isocyanate. The molecular weight and polydispersity of the synthesized flexible polyester were measured using YL9100 GPC SYSTEM (Young Lin Instrument Co., Ltd., 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. [9] To

**Table 1.** Formulations used for synthesis of flexible polyester resin (units in mole).

Sample	PCDL <sup>a</sup>	IPDI <sup>b</sup>	H <sub>12</sub> MDI <sup>c</sup>	AA <sup>d</sup>	1,4-CHDA <sup>e</sup>	Ph-An <sup>f</sup>	NPG <sup>g</sup>	1,6-HD <sup>h</sup>	1,4-CHD <sup>i</sup>
U-IPDI-1	2	1		7.3	17.3	14.6	11.3	9.9	16.9
U-IPDI-2	4	2	–	7.3	17.3	14.6	11.3	7.9	16.9
U-H <sub>12</sub> MDI-1	2		1	7.3	17.3	14.6	11.3	9.9	16.9
U-H <sub>12</sub> MDI-2	4	–	2	7.3	17.3	14.6	11.3	7.9	16.9

<sup>a</sup>polycarbonate diol ( $M_n = 500$ ),<sup>b</sup>isophorone diisocyanate,<sup>c</sup>bis-(4-isocyanatocyclo-hexyl)methane,<sup>d</sup>AA (adipic acid),<sup>e</sup>1,4-CHDA (1,4-cyclohexanedicarboxylic acid),<sup>f</sup>Ph-An (phthalic anhydride),<sup>g</sup>NPG (2,2-dimethyl-1,3-propanediol),<sup>h</sup>1,6-HD (1,6-hexandiol),<sup>i</sup>1,4-CHD (1,4-cyclohexanediol).**Table 2.** Coating formulations of flexible polyester coatings as a primer for automotive coating. (Unit: wt %).

Contents	CU-IPDI-1	CU-IPDI-2	CU-H <sub>12</sub> MDI-1	CU-H <sub>12</sub> MDI-2
*U-IPDI-1	50.0	–		–
*U-IPDI-2	–	51.0		–
*U-H <sub>12</sub> MDI-1	–	–	50.0	–
*U-H <sub>12</sub> MDI-2	–	–		51.0
Aromatic solvent	10.0	10.0	10.0	10.0
TiO <sub>2</sub>	6.0	6.0	6.0	6.0
**Anticlor yellow tint paste	12.0	12.0	12.0	12.0
CaCO <sub>3</sub>	3.0	3.0	3.0	3.0
HMMM	4.6	4.0	4.6	4.0
Additives	1.0	1.0	1.0	1.0
Solvent	13.4	12.4	13.4	12.4

\*Solid content of polyester resins: 60.7%.

\*\*Anticlor yellow tint paste: a commercial corrosion protective pigments.

characterize the flexible polyester resin, <sup>1</sup>H NMR spectra were obtained using a 400 MHz NMR spectrometer (Jeol JNM-LA400, JEOL Ltd., Japan).

#### 2.4.2. Rigid-body pendulum physical property testing

The curing behavior of the flexible polyester coatings was measured using rigid-body pendulum physical property testing instrument (RPT, A&D Co., Ltd. Japan). Figure 2 shows two types of rigid-body pendulum. One is a knife edge-type pendulum which is used to measure the curing behavior and another is a cylindrical edge-type which is used to analyze physical properties of the cured coatings such as  $T_g$ . It consists of heating oven, steel substrate, and a main controller. The curing behavior was measured by detecting movement of a knife-type pendulum on the coated steel as a function of temperature. The oscillation pattern of the pendulum is related to the change in surface properties such as chemical or physical networking. Polyester coatings were coated on the steel substrate (50 mm × 20 mm × 0.3 mm) using a 40- $\mu$ m coating tool to examine curing behavior. The heating condition was set at 50 °C for 3 min to stabilize the uncured coatings. And then, the temperature was increased from 50 to 200 °C at 5 °C /min, and maintained at 200 for 30 min.[10]

#### 2.4.3. Dynamic mechanical analysis (DMA)

The glass transition temperature and viscoelastic properties of the polyester/melamine films were analyzed using a dynamic mechanical analysis instrument (Q800, TA Instruments).

The cross-link density ( $v_c$ ) was derived from the minimum storage modulus ( $E'_{\min}$ ) and temperature at minimum storage modulus ( $T_{E'_{\min}}$ ) (the rubbery plateau region). The cross-link density was calculated using the following equation [11]:

$$v_c = \frac{E'_{\min}}{3RT_{E'_{\min}}}$$

Rectangular specimens, 12 mm in length, 6.45 mm in width, and 200  $\mu\text{m}$  in thickness were prepared. The specimens were tested in tension mode at a frequency of 1 Hz and strain of 0.3%. The temperature ranged from -60 to 160  $^{\circ}\text{C}$  at a scanning rate of 2  $^{\circ}\text{C}/\text{min}$ .

#### 2.4.4. Physical properties

Surface hardness of polyester coatings was measured by a pendulum hardness tester (Ref. 707PK, Sheen Instruments Ltd.) according to the König method (ANS/ISO 1522) at  $23 \pm 1^{\circ}\text{C}$  and  $50 \pm 2\%$ . The surface scratch resistance was measured using a No. 553 pencil hardness tester (Yasuda Seiki Seisakusho Ltd.). It was following to ASTM D3363-05.[12,13] The adhesion of flexible polyester coatings was measured using a cross-cut method according to the ASTM D3359-09. The distance between cuts is 1 mm with a cutting guide. The evaluation adhesion result is for 0B to 5B. 0B means that flaking of the cross-cut area has over than 65% and 5B is no flaking. The degree of 1 - 4B is determined between 0B and 5B.[14,15]

#### 2.4.5. Tensile strength

Tensile strength was measured using a Universal Testing Machine (Zwick Corp.) at the ambient temperature with a crosshead speed of 30 mm/min. The polyester/melamine films were prepared as rectangular specimens, 40 mm in length (span length), 6.35 mm in width, and 250  $\mu\text{m}$  in thickness. The tensile strength was calculated by dividing the maximum load in Newton (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 (%).[16]

#### 2.4.6. Deep drawing

Rectangular deep drawing tests were performed to examine formability of the pre-coated metal (PCM) as shown in Figure 3. The shape of PCM before drawing had a rectangular shape and it was (120  $\times$  120) mm in dimension. The size of the punch (50  $\times$  50) mm, the shoulder radius of the punch, the corner radius of the punch, and the shoulder radius of the die were 5 mm. Specific conditions of the deep drawing are shown Table 3. This test was performed at 23  $^{\circ}\text{C}$  and the speed of the punch was 30 mm/min. After deep drawing, damages to the cured films of the drawn PCM were observed via optical microscope.[6]

#### 2.4.7. Salt spray test

The anti-corrosion property of PCM and deep drawn PCM was measured using salt spray test. The PCM was prepared on galvanized steel substrates and a cross-scratch line was made on the coating surface with a sharp instrument. The salt spray test condition was according to ASTM B-117 in a 5% NaCl solution at 35  $^{\circ}\text{C}$ . After 1000 h, changes of surface morphology, especially around the cross-line on the coating was measured based on ASTM D 610-08 and the surface was examined via optical microscope.[17] Specimens that had

**Table 3.** Conditions for the deep drawing of PCM.

Shape of punch	Rectangular
Corner radius of punch (mm)	6
Should radius of punch (mm)	6
Should radius of die (mm)	6
Size of punch (mm)	40 × 40
Size of PCM (mm)	120 × 120
Drawing height (mm)	50
Lubricant	PP sheet

**Table 4.** Characterization of flexible polyester resin.

Property	U-IPDI-1	U-IPDI-2	U-H <sub>12</sub> MDI-1	U-H <sub>12</sub> MDI-2
Number average M.W. ( $M_n$ )	3520	4050	3690	4020
Weight average M.W. ( $M_w$ )	4520	6360	4870	6560
Polydispersity index ( $M_w/M_n$ )	1.51	1.57	1.32	1.63
$n_{OH}$ (mg KOH/g)	17.2	14.7	17.1	14.6
$M_n/n_{OH}$ (g/mg KOH)	204.6	275.5	215.7	275.3
Cross-link density ( $10^{-3}$ mol/cm <sup>3</sup> )	0.24	0.07	0.24	0.08

$n_{OH}$  – Hydroxyl value.

earlier been tested for deep drawing were also subjected to the same salt spray testing and surface morphology examination.

### 3. Results & Discussion

#### 3.1. Characterization of flexible polyester resin

Flexible polyester resins are synthesized based on different ratios between the soft segment of the urethane polyol of PCDL-isocyanate and the hard segment of the –COOH-terminated polyester pre-polymer. The carbonate group in the flexible polyester is determined using FT-IR. As shown in Figure 4, the carbonated group which is from polycarbonatediol is detected at 1240 and 1760 cm<sup>-1</sup> and the intensity of these bands has been increased with the content of urethane polyol of PCDL-isocyanate.[18] Table 4 lists the molecular weight and polydispersity of the flexible polyester. The ratio between the number average molecular weight and hydroxyl value ( $M_n/n_{OH}$ ) indicates the length of the repeating unit in the cross-link network of the synthesized polyester resin.[19] The  $M_n/n_{OH}$  value is observed to decrease with increasing contents of the urethane polyol of PCDL-isocyanate. The <sup>1</sup>H NMR spectra of U-IPDI-2 and U-H<sub>12</sub>MDI-2 peak have been assigned as shown Figure 5. Typical resonances of U-IPDI-2 are at 1.3–1.7 ( $\delta$  H<sup>a</sup>,  $\delta$  H<sup>b</sup>) and 4.02–4.14 ( $\delta$  H<sup>c</sup>) due to the polycarbonatediol.[20] Additionally, peaks are 0.75–0.90 ( $\delta$  H<sup>d</sup>), 1.02–1.12 ( $\delta$  H<sup>e</sup>), and 4.13–4.2 ( $\delta$  H<sup>f</sup>) due to the IPDI.[21,22] U-H<sub>12</sub>MDI-2 has a similar to U-IPDI-2. 0.90 ( $\delta$  H<sup>d</sup>) and 3.5 ( $\delta$  H<sup>e</sup>) due to the H<sub>12</sub>MDI.[23,24] From the <sup>1</sup>H NMR spectra, the urethane polyol of PCDL-isocyanate has been introduced to the polymer chain of synthesized resin.

#### 3.2. Characterization of flexible polyester coatings

##### 3.2.1. Physical properties

Figure 6 shows the surface hardness of flexible polyester coatings with different contents of the urethane polyol of PCDL-isocyanate. CU-IPDI-1 has maximum hardness around

**Table 5.** Physical properties of flexible polyester coatings.

	Pendulum hardness	Pencil hardness	Cross-hatch adhesion
CU-IPDI-1	126.9	F	5B
CU-IPDI-2	73.3	HB	5B
CU-H <sub>12</sub> MDI-1	113.2	F	5B
CU-H <sub>12</sub> MDI-2	70.2	HB	5B

127 s and F and CU-IPDI-2 has 83 s and HB. Surface hardness has been decreased with the increase in urethane polyol of PCDL-isocyanate because of a long chain of polycarbonatediol. As listed in Table 5, the adhesion between the polyester coatings and steel substrate is 5B which is no flaking after tape peeling test. For this reason, all coatings have a good adhesion on the galvanized steel sheet.

### 3.2.2. Curing behavior

Curing behavior is an important property in an automotive PCM. Automotive PCM has a short curing zone compared to conventional automotive coatings process. The RPT detects the curing behavior of the coatings on the steel substrate as a function of temperature. The initial curing of each polyester coating begins at approximately 180 °C as shown in Figure 7. The change in the frequency of each coating is similar. But, the final frequency is in the following orders: CU-IPDI-1 > CU-H<sub>12</sub>MDI-1 > CU-IPDI-2 > CU-H<sub>12</sub>MDI-2. The final frequency is generally related to the stiffness of coatings, thus the result suggests that CU-IPDI-1 is stiffer than other samples. There is a correlation between the trends observed in stiffness with the results of hardness in Table 5. Although different properties are measured, the effect of the chemical structure affects both of them similarly.

### 3.2.3. Viscoelastic behavior

Dynamic mechanical analysis (DMA) is a convenient and useful method to study thermal and mechanical viscoelastic properties of heat-cured polymeric materials. The DMTA data allow observations of changes in loss and storage modulus, glass transition temperature ( $T_g$ ), and cross-link density.[25] Figure 8(a) shows storage modulus as a function of temperature for two types of resins from the urethane polyol of PCDL-isocyanate. The storage modulus of CU-IPDI-2 at a higher content of urethane polyol is considerably lower compared to CU-IPDI-1. The lower modulus of CU-IPDI-2 corresponds to the higher ratio between the number average molecular weight and hydroxyl value ( $M_n/n_{OH}$ ), which is the length of the repeating unit between cross-links.[11] A longer length between cross-links corresponds to a lower cross-link density, thus explaining the lower modulus of the resin when the content of the urethane polyol of PCDL-isocyanate is increased as listed in Table 4. Also, the  $T_g$  of CU-IPDI-2 shifted to a lower temperature as shown in Figure 8(b) due to the higher content of the urethane polyol of PCDL-isocyanate.[8] It could be implied that the urethane polyol of PCDL-isocyanate would favorably provide low stiffness and give high softness to the polyester coatings.

CU-H<sub>12</sub>MDI series have a behavior similar to CU-IPDI series. Comparing between CU-IPDI-1 and CU-H<sub>12</sub>MDI-1, CU-IPDI-1 exhibits higher storage modulus, because IPDI has better hydrogen bonding than H<sub>12</sub>MDI and it has increased intermolecular interaction.

### 3.2.4. Flexibility

Flexibility is the most important property for cutting, pressing, and stamping processes in the pre-coated system. Tensile strength tests are carried out to study basic mechanical



properties – modulus, tensile strength, elongation at break, and toughness of polymeric materials.[26] Figure 9 presents effects of the contents of urethane polyol on tensile behaviors of the flexible polyester. The tensile strength of CU-IPDI-1 is 3.4 MPa, that of CU-IPDI-2 was 2.2 MPa, and with their respective elongation at break are 235% and 495%. Also, the tensile strength of CU-H<sub>12</sub>MDI-1 is 2.6 MPa and that of CU-H<sub>12</sub>MDI-2 is 1.4 MPa, with their elongation at break are 254 and 496%, respectively. These values represent a high flexibility and high breaking strain, which are a consequence of the high stretchable property imparted by the soft segments of urethane polyol. Therefore, it could be implied that the urethane polyol of PCDL-isocyanate would favorably provide low stiffness and give high softness to the polyester coatings.

### 3.2.5. Formability

The deep drawing test is a common test method for formability in pre-coated metals. During deep drawing, the corner areas experience a major tensile strain developed in the vertical direction and minor compressive strain developed in the horizontal direction.[6] So, the corner areas are easily damaged during the deep drawing tests.

As shown in Figure 10, flexible polyester coatings are formed at a rectangular cup with 30 mm/min. After 48-mm drawing, drawn specimens have been observed at 100 times magnified under the optical microscope, and the scale bar is 502 μm. CU-IPDI-1 and CU-H<sub>12</sub>MDI-1 had little cracks and tears at the corner, but CU-IPDI-2 and CU-H<sub>12</sub>MDI-2 have no cracks and tears. CU-IPDI-1 has small-sized cracks, but CU-H<sub>12</sub>MDI-1 has lots of cracks and delamination. Ueda *et al.* reported that films with low  $T_g$  and low cross-linking density have good formability.[8] Agreeing with their finding, CU-IPDI-2 shows good formability in deep drawing because it has a low  $T_g$  and low cross-linking density compared to CU-IPDI-1. CU-H<sub>12</sub>MDI-2 is similar to CU-IPDI-2 and it also exhibits good formability. This formability test result is a good evidence for the long chain effect in the improvement of formability. Therefore, it could be implied that the urethane polyol of PCDL-isocyanate would favorably provide low stiffness and give high flexibility to the polyester coatings

### 3.2.6. Anti-corrosion property

Anti-corrosion property is one of the important physical properties of pre-coated metals and automotive coatings. After deep drawing, specimens were subjected to a salt spray test for 1000 h. As shown in Figure 11, CU-H<sub>12</sub>MDI-1 is heavily damaged at the corner, but CU-IPDI-1 was little damaged. The damages at the corner are caused by the major tensile strain and minor compressive strain. From the result of deep drawing, both CU-IPDI-2 and CU-H<sub>12</sub>MDI-2 exhibit good forming property, but in the anti-corrosion test CU-H<sub>12</sub>MDI-2 shows heavy damages. This observation suggests that CU-H<sub>12</sub>MDI-2 is not a strong film, and is not tough enough to overcome salt spray damage. On the other hand, CU-IPDI-2 has no damages, implying that the PCDL-based urethane polyol with IPDI has a strong film to overcome harsh condition. It means that IPDI can form strong hydrogen bonding, which increases intermolecular interaction.[27]

As shown in Figure 12, CU-IPDI-1, CU-IPDI-2, CU-H<sub>12</sub>MDI-1, and CU-H<sub>12</sub>MDI-2 coatings appeared clear surface after 1000 h. Rust ratings of each coating are counted on ASTM D 610 and presented in Table 6. These specimens show no rusts in the non X-cut area, and there is little blistering around the X-cut. CU-H<sub>12</sub>MDI series have more blistering than CU-IPDI series. From the two types of anti-corrosion test, it can be concluded that CU-IPDI-2 is suitable to be used for pre-coated metal and automotive coatings as a primer.

**Table 6.** Scale and description of rust ratings after salt spray test.

Contents	Rust grade	Percent of surface rusted	Visual examples		
			Spot(s)	General (G)	Pinpoint (P)
CU-IPDI-1	10	less than or equal to 0.01 percent	None	None	None
CU-IPDI-2	10	less than or equal to 0.01 percent	None	None	None
CU-H <sub>12</sub> MDI-1	10	less than or equal to 0.01 percent	None	None	None
CU-H <sub>12</sub> MDI-2	10	less than or equal to 0.01 percent	None	None	None

Rust Distribution Types:

S: Spot Rusting – the bulk of the rusting is concentrated in a few localized areas.

G: General Rusting – various sizes of rust spots are randomly distributed across the surface.

P: Pinpoint Rusting – the rust is distributed across the surface as very small individual specks of rust.

## 4. Conclusion

Four types of flexible polyester resins with the urethane polyol of PCDL-isocyanate are synthesized and formulated to control formability for pre-coated metal systems. These resins are designed to show the flexibility of long chain effect of urethane polyol. 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 content of the urethane polyol of PCDL-isocyanate was increased in the flexible polyester synthesized with IPDI, the stiffness of the product (CU-IPDI-2) was decreased considerably and  $T_g$  of each coatings was shifted to a lower temperature. The same long chain effect (lower stiffness and  $T_g$  in CU-H<sub>12</sub>MDI-2) was noted for the PCDL-based urethane polyol synthesized with H<sub>12</sub>MDI. In terms of flexibility and formability, CU-IPDI-2 and CU-H<sub>12</sub>MDI-2 had higher elongation and better formability for cutting, pressing, and stamping in pre-coated metal system. Therefore, the urethane polyol of PCDL-isocyanate is a major factor to improve flexibility and formability of the polyester coatings for the PCM. CU-IPDI-2 has good formability in deep drawing and a good anti-corrosion property, and thus it would be an appropriate primer for automotive coatings.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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