



# Effect of cycloaliphatic structure of polyester on the formability and stone-chip resistance for automotive pre-coated metals



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## ABSTRACT

Four types of cycloaliphatic structure of polyester were synthesized, using 1,4-cyclohexanedicarboxylic acid (1,4-CHDA). Those resins were formulated to make polyester/melamine coatings to control the formability, and to have good stone-chip resistance. The characteristics, viscoelastic behavior and flexibility of those resins were measured by DMA and tensile test. Cycloaliphatic structure of polyester coatings were coated on the cold roll steel sheets to verify formability, using a deep drawing test and stone-chip resistance was measured by the chipping resistance test at the  $-20^{\circ}\text{C}$ . Results showed that storage modulus decreased, and glass transition temperatures shifted to lower temperatures with increasing contents of cycloaliphatic structure. So, cycloaliphatic structure of 1,4-CHDA provides lower stiffness and higher softness to the polyester coating and has better elasticity than aromatic structure of IPA. To analyze the formability, we calculated  $F_U$  (the forming coefficient based on strain energy) and  $F_{\varepsilon}$  (the forming coefficient based on strain). When  $F_U$  and  $F_{\varepsilon}$  are both larger than 1, the polyester coatings have good formability. Also, BCHDA-20 had 0.44% of removed area by the chipping resistance test and it means that cyclic structure of 1,4-CHDA has better elasticity than aromatic structure, and can give better impact resistance

From those tests, BCHDA-20 which had 20 mol of 1,4-CHDA had good formability and also showed good stone-chip resistance. So, cycloaliphatic structure provides lower stiffness and higher softness to the polyester coating for automotive pre-coated metals.

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## 1. Introduction

Stringent environmental legislations have been made around the world. These legislations also affect manufacturing sectors that employ coating processes. Pre-painted or coil-coated metals (PCM) provide an opportunity to eliminate coating processes [1,2]. 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. One of the most important properties of PCM is formability. If the film on the coated PCM parts is damaged, the products are rendered useless [3]. During the drawing, a flat PCM is deeply drawn by a punch.

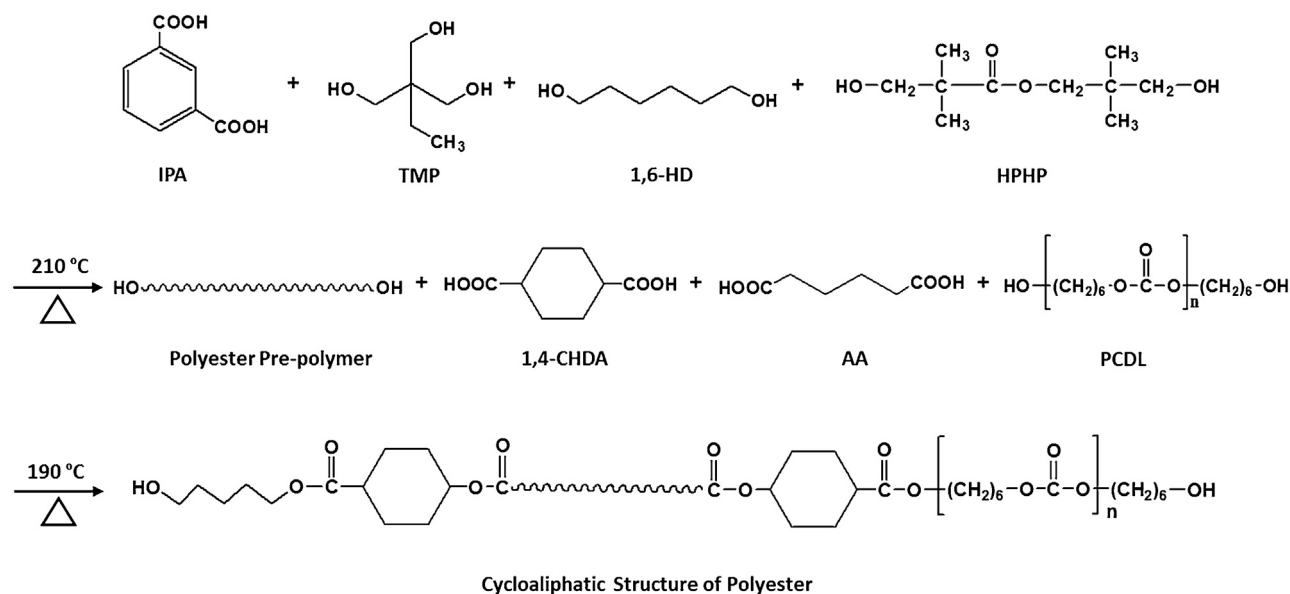
The strain behavior of coated film is complicated, because tensile and compressive strain are both developed during the drawing [4].

The stone-chip resistance of automotive coatings is considered to be one of the important characteristics during service [5]. Bendor has reported the stone-chip resistance and mechanical properties of polymer coating, and found that the glass transition temperature of the primer coating is the key factor in stone-chip resistance [6,7]. The chip resistance has been decreased by increasing the glass transition temperature, such as by increasing the baking temperature, and decreasing the oil length.

A cycloaliphatic structure, such as 1,3-cyclohexanedicarboxylic acid (1,3-CHDA), or 1,4-cyclohexanedicarboxylic acid (1,4-CHDA), gives physical properties that are intermediate between aromatic and linear aliphatic [8,9]. The  $T_g$  of cycloaliphatic polyester is lower than that of aromatic polyester, but is higher than that of linear aliphatic polyester. The flexibility of cycloaliphatic polyester is also intermediate between the aromatic and linear aliphatic polyesters due to the cyclic structure, which can absorb energy through the interconversion of chair and boat conformations. When cross-

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**Scheme 1.** Synthesis process of cycloaliphatic structure of polyester.

linked with melamine-formaldehyde, 1,4-CHDA based polyesters provided better humidity and impact resistance [10].

In this study, we designed an improvement of the elasticity of coatings using 1,4-CHDA, which can give lower  $T_g$  and higher flexibility to polyester coatings, compared to isophthalic acid, because 1,4-CHDA has a cycloaliphatic structure consisting of a  $\text{CH}_2\text{—CH}_2$  component, and it has better elasticity than the linear structure of adipic acid. Cycloaliphatic structure of polyester were synthesized with different contents of 1,4-CHDA. The elongation, tensile strength and viscoelastic properties of synthesized polyester of free film were measured. The formability of PCM was evaluated using a cylindrical drawing test and we calculated  $F_U$  (the forming coefficient based on strain energy) and  $F_\varepsilon$  (the forming coefficient based on strain). The stresses and strains of the coatings were analyzed by tensile test and DMA creep test. From those tests, the relationship between the contents of 1,4-CHDA and the formability of the polyester coatings was discussed. Stone-chip resistance was measured, to assess their potential as an automotive coatings.

## 2. Experimental

### 2.1. Materials

Cycloaliphatic structure of polyester was synthesized by polybasic acids and alcohols. The polybasic acids used were 1,4-cyclohexanedicarboxylic acid (1,4-CHDA, Tokyo Chemical Industry, Japan), adipic acid (AA, Samchun Pure Chemical, Republic of Korea), and isophthalic acid (IPA, Junsei Chemical Corp., Japan); and the polybasic alcohols that were used were trimethylol propane (TMP, Tokyo Chemical Industry, Japan), 1,6-hexandiol (1,6-HD, Samchun Pure Chemical, Republic of Korea), neopentyl glycol mono(hydroxypivalate) (HPPH, Tokyo Chemical Industry, Japan), and polycarbonatediol (PCDL,  $M_n = 500$ , Asahi Kasei Chemicals Corp., Japan), which were used without further purification. Butylstannic acid (FASCAT 4100, Arkema Inc., USA) was used as a catalyst to catalyze polymerization, and to prevent a transesterification reaction during the polymerization [11].

Polyester coatings were formulated with synthesized polyester and curing agents. Hexamethoxymethylmelamine (Cymel 303LF, Cytec Industries Inc., USA) was used as the curing agent, and Nacure

**Table 1**

Formulations used for the synthesis of cycloaliphatic structure of polyester (unit: mole).

Sample	1,4-CHDA <sup>a</sup>	IPA <sup>b</sup>	AA <sup>c</sup>	TMP <sup>d</sup>	PCDL <sup>e</sup>	1,6-HD <sup>f</sup>	HPPH <sup>g</sup>
CHDA-0	0	20	3	3	1	5	10
CHDA-5	5	15	3	3	1	5	10
CHDA-10	10	5	3	3	1	5	10
CHDA-20	20	0	3	3	1	5	10

<sup>a</sup> 1,4-CHDA (1,4-cyclohexanedicarboxylic acid).

<sup>b</sup> IPA (isophthalic acid).

<sup>c</sup> AA (adipic acid).

<sup>d</sup> TMP (trimethylolpropane).

<sup>e</sup> PCDL (polycarbonatediol).

<sup>f</sup> 1,6-HD (1,6-hexandiol).

<sup>g</sup> HPPH (neopentyl glycol mono (hydroxypivalate)).

(NACURE 1953, King Industries, Inc., USA) was used as a curing catalyst.

### 2.2. Synthesis of cycloaliphatic structure of polyester

Synthesis process is shown in Scheme 1 and the formulations of cycloaliphatic structure of polyester are listed in Table 1. It 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 separator. The condenser and separator were to remove the water produced during the poly-condensation reaction. Isophthalic acid (IPA) has two carboxyl groups, one of which reacts at around 190 °C, and the second one reacts at a temperature above 210 °C. It therefore requires a high reaction temperature. Polycarbonatediol could be decomposed around 210 °C. To avoid decomposition of polycarbonatediol, a modified synthesis process was carried out as follows.

Firstly, IPA, TMP, 1,6-HD, and HPPH were charged into a dried reactor, and the reaction temperature was set to 150 °C, with stirring for 2 h under  $\text{N}_2$  purge. Subsequently, the reaction temperature was increased from 150 °C to 210 °C, at the rate of 0.5 °C/min. The reaction temperature was set to 210 °C for 2 h. During the fusion

**Table 2**  
Formulations of cycloaliphatic structure of polyester coatings (unit: wt%).

Contents	BCHDA-0	BCHDA-5	BCHDA-10	BCHDA-20
CHDA-0	65.5	–	–	–
CHDA-5	–	65.5	–	–
CHDA-10	–	–	65.5	–
CHDA-20	–	–	–	65.5
<sup>a</sup> Solvent	15.0	15.0	15.0	15.0
Black pigment	7.5	7.5	7.5	7.5
HMMM	5.4	5.4	5.3	5.3
Additives	1.0	1.0	1.0	1.0
Nacure	0.6	0.6	0.6	0.6
<sup>a</sup> Solvent	5.0	5.0	5.1	5.1

<sup>a</sup> Solvent: solvesso #100.

process, all raw materials were liquefied, and the produced water was removed and collected by the separator.

After that 1,4-CHDA, AA, and PCDL were charged into the reactor containing liquefied reactants prepared from the preceding step, and the reaction temperature was set to 130 °C, with stirring for 2 h under N<sub>2</sub> purge. Subsequently, the reaction temperature was increased from 130 °C to 190 °C, at the rate of 0.3 °C/min. The reaction temperature was maintained to 190 °C for 2 h, and the produced water was removed and collected. During the fusion process, the acid value was measured by 0.1 N KOH solutions. When the acid value was under 40 mg KOH/g resin, the fusion process was finished.

The fusion process was then converted into solvent process, by adding 25 g of xylene. Xylene was reflux solvent for carrying out efficiently the produced water during the reaction. The solvent process was carried out to synthesize the polyester and to make a low acid value. The reaction temperature was set to 180 °C and was maintained for 4 h. During the solvent process, the acid value was measured by 0.1 N KOH solutions. When the acid value was under 3 mg KOH/g resin, the solvent process was finished [11].

After finishing the solvent process, the reactor was cooled down to 50 °C. Xylene was added to the reactor to control the solid content of synthesized polyester. The solid content of synthesized polyester was 75%.

### 2.3. Preparation of cycloaliphatic structure of polyester coatings

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

#### 2.3.1. Free film

The polyester coatings were cast onto 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 thicknesses of the baked films ranged from 150 to 200 μm. The resulting films became the samples for tensile strength and dynamic mechanical analysis.

#### 2.3.2. PCM

Cold roll steel sheets (thickness of 0.8 mm) were coated with primer, and baked at 180 °C for 20 min. The cured primer films were 15 μm in thickness. Then cycloaliphatic structure of polyester coatings were coated on the cured primer, and then baked at 180 °C for 20 min. The thickness of those cured films was 25 μm. The total film thickness was 40 μm.

### 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 that is equipped with a Miracle accessory, and attenuated total reflectance (ATR) setup. The ATR crystal was made

**Table 3**  
Conditions for 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
Speed of the punch (mm/min)	20

of diamond, and its refractive index was 2.4 at 8500–2500 cm<sup>-1</sup> and 1700–300 cm<sup>-1</sup>. The spectra were collected using ATR mode in the wavenumber range of 4000–650 cm<sup>-1</sup>, and the resolution of the spectra recorded was 4 cm<sup>-1</sup>.

#### 2.4.2. Gel permeation chromatography (GPC)

The molecular weight and polydispersity of the synthesized cycloaliphatic structure of polyester 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.

#### 2.4.3. Viscoelastic and creep properties by dynamic mechanical analysis (DMA)

The glass transition temperature and viscoelastic properties of the polyester/melamine coatings were analyzed using a dynamic mechanical analysis instrument (Q800, TA Instruments). The crosslink density ( $\nu_c$ ) 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 [12]:

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

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 strains of the free films were performed using a dynamic mechanical analysis instrument. Rectangular specimens of 20 mm in length, 6.45 mm in width and 200 μm in thickness were prepared. The time-dependences of creep compliance of the free films were obtained at a stress level of  $5.1 \times 10^6$  Pa. The tests were performed at 25 °C, and with a loading time of 90 s, which was designed to correspond to the deep drawing testing time.

#### 2.4.4. Deep drawing

A cylindrical deep drawing test was performed to examine formability of PCM, as shown in Fig. 1. The shape of PCM before deep drawing was a disk of 105 mm diameter. The shape of the punch was a circle of 40 mm diameter, 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 3. The speed of the punch was 20 mm/min, and the drawing time was 90 s.

#### 2.4.5. Analyzing of formability [4]

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 ( $\sigma_p$ ) and forming ratio ( $R_f$ ) can be calculated using Eqs. (1) and (2)

$$\sigma_p = \frac{\text{blank force (N)}}{\text{total area before drawing test (mm}^2\text{)}} \quad (1)$$

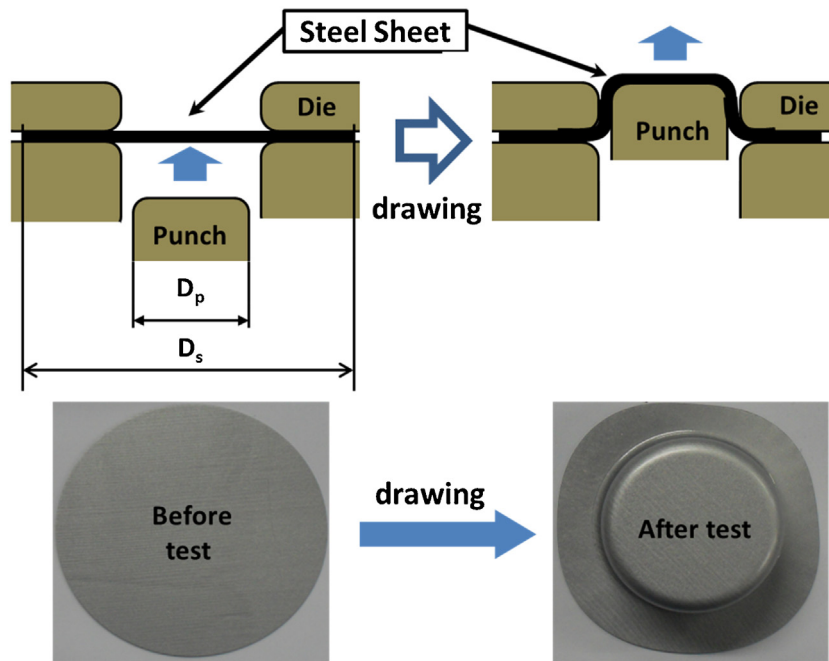


Fig. 1. Procedure of the deep drawing test [2].

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

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.

$$U_T = \int_0^{R_f} \text{Strain - dependent stress curve } d\varepsilon \quad (3)$$

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.

$$U_C = \int_0^{90} \text{Strain - dependent stress curve } d\varepsilon \quad (4)$$

From those equations, forming coefficient based on strain energy ( $F_U$ ) can be calculated using Eq. (5) and forming coefficient based on strain ( $F_\varepsilon$ ) can be calculated using Eq. (6)

$$F_U = \frac{U_C}{U_T} \quad (5)$$

$$F_\varepsilon = \frac{\varepsilon_C}{R_f} \quad (6)$$

where  $\varepsilon_C$  is the strain during the creep test.

#### 2.4.6. 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 an ambient temperature. The tensile specimens prepared from free films were 40 mm in length (span length), 6.45 mm in width and 200  $\mu\text{m}$  in thickness. The tensile strength value 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

Table 4  
Chip stone types of stone-chip resistance test.

Type	Standard	Range of particles (mm)	Remarks
Stone number #7	JIS A5001	2.5 ~ 5	Pass through sieve 13 mm and remaining sieve 2.5 mm

meters. The percent elongation (strain%) was calculated by dividing the change in gage length by the original specimen gage length, expressed as a percentage (%) [13].

#### 2.4.7. Stone-chip resistance

The Gravelometer is designed to evaluate the stone-chip resistance of surface coatings (paint, clear coats, metallic plating, etc.), caused by the impacts of gravel or other flying objects. The primary usage of this test is to simulate the effects of the impact of gravel or other debris on automotive parts.

A stone-chip resistance is proposed to evaluate surface damages by stones, sands and NaCl salts. Before the stone-chip resistance test, specimens were set at  $-20 \pm 3^\circ\text{C}$  for 3 h in the cold chamber. The tested pressure was  $4 \pm 0.2 \text{ kgf/cm}^2$ , and the chip stone is listed in Table 4. The specimens prepared from the galvanized steel coated films were 150 mm in length, 100 mm in width and 40  $\mu\text{m}$  in thickness [14].

#### 2.4.8. Video image enhanced evaluation of weathering (VIEEW)

After the stone-chip resistance test, the surface damages were evaluated by the VIEEW<sup>TM</sup>. VIEEW<sup>TM</sup> is capable of capturing digital images of samples under various lighting schemes that are optimized to highlight and enhance surface defects, to digitally process images. It is also capable of measuring and counting defects with a comprehensive statistical profile. The area under the scan was selected, and lights for the reflection were optimized using Atlas imaging software. Sample images were analyzed for surface texture and smoothness by grayscale. The value of the removed area of specimens was calculated by dividing the removed area by the tested area (%) [15].



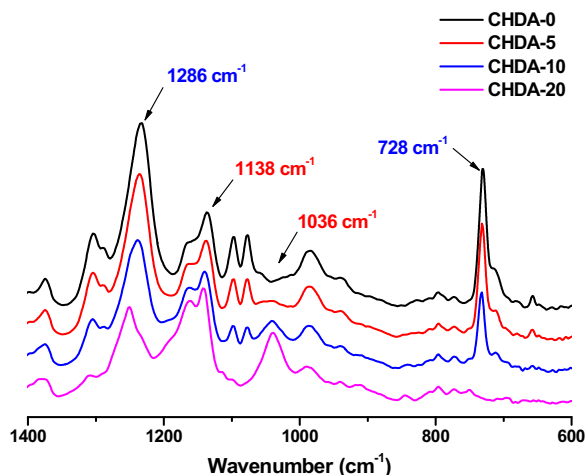


Fig. 2. IR spectra of cycloaliphatic structure of polyester (aromatic ring: 728, 1286  $\text{cm}^{-1}$ , cyclic ring: 1036, 1138  $\text{cm}^{-1}$ ).

Table 5  
Characterization of cycloaliphatic structure of polyester.

Property	CHDA-0	CHDA-5	CHDA-10	CHDA-20
Number average M.W. ( $M_n$ )	7220	7250	7280	7340
Polydispersity index ( $M_w/M_n$ )	2.9	3.1	3.3	2.8
$n_{\text{OH}}$ (mg KOH/g)	38.8	38.6	38.5	38.1
$M_n/n_{\text{OH}}$ (g/mg KOH)	186	187	189	192
Crosslink density ( $10^{-3}$ mol/ $\text{cm}^3$ )	0.47	0.35	0.25	0.16

<sup>a</sup>  $n_{\text{OH}}$ —Theoretical hydroxyl number of polyester resins.

### 3. Results and discussion

#### 3.1. Characterization of cycloaliphatic structure of polyester

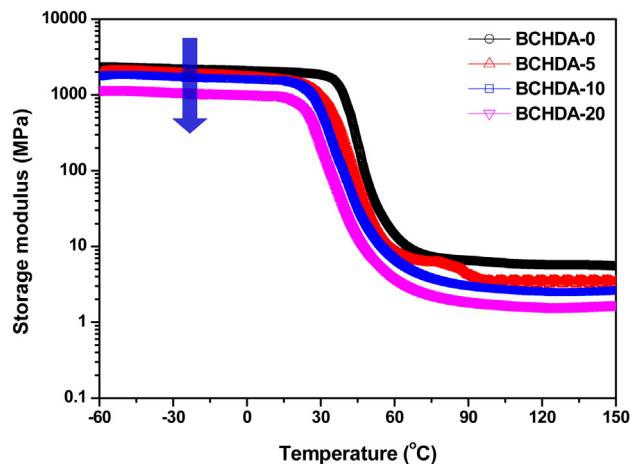
Cycloaliphatic structure of polyester were synthesized based on different contents of 1,4-CHDA. The aromatic ring and cyclic ring in the synthesized polyester were determined using FT-IR. As shown in Fig. 2, the aromatic ring of isophthalic acid was detected at 728 and 1286  $\text{cm}^{-1}$ , and the intensity of these bands decreased with increasing content of 1,4-CHDA. The cyclic ring of 1,4-CHDA was detected at 1036 and 1138  $\text{cm}^{-1}$ , and the intensity of these bands increased with increasing content of it [16,17].

Table 5 lists the molecular weight and polydispersity of the synthesized cycloaliphatic structure polyester. The theoretical hydroxyl number of polyester resin ( $n_{\text{OH}}$ ) was little decreased with increasing content of 1,4-CHDA, because ( $n_{\text{OH}}$ ) is dependent on the molecular weight of synthesized resin. Also, the ratio between the number average molecular weight and hydroxyl number ( $M_n/n_{\text{OH}}$ ) indicates the length of the repeating unit in the crosslink network of the synthesized polyester [18].

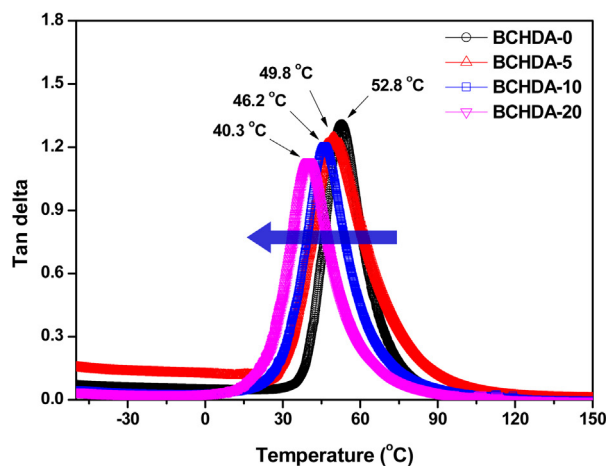
#### 3.2. Viscoelastic behavior

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 [19].

Fig. 3(a) shows the storage modulus as a function of temperature for cycloaliphatic structure of polyester. The storage modulus decreased with increasing contents of 1,4-CHDA, i.e. BCHDA-0 > BCHDA-5 > BCHDA-10 > BCHDA-20. These results can be explained by the cycloaliphatic structure of 1,4-CHDA. Compared to isophthalic acid (IPA), the cycloaliphatic structure of 1,4-CHDA is more flexible than the conjugate structure of aromatic struc-



(a) Storage modulus



(b)  $\tan \delta$

Fig. 3. Viscoelastic properties of cycloaliphatic structure of polyester coatings (a) storage modulus and (b)  $\tan \delta$ .

ture, because cycloaliphatic structure consists of only the  $\sigma$ -bond between  $\text{CH}_2$ — $\text{CH}_2$  components, and can be rotated and bent [20]. Also, the  $T_g$  shifted to a lower temperature with increasing content of 1,4-CHDA, as shown in Fig. 3(b) [21]. From the dynamic mechanical analysis, cycloaliphatic structure could provide flexibility to the polyester coatings [3].

#### 3.3. Flexibility

Flexibility is the most important property for the cutting, pressing and stamping processes in the pre-coated metals. Tensile strength tests were carried out to study the basic mechanical properties of modulus, tensile strength, elongation at break, and toughness of polymeric materials [22]. Fig. 4 presents the effects of the contents of 1,4-CHDA on tensile behaviors of the synthesized polyester. The tensile strength decreased with increased content of 1,4-CHDA (BCHDA-0 > BCHDA-5 > BCHDA-10 > BCHDA-20). In contrast, the maximum strain increased when the content of 1,4-CHDA increased (BCHDA-0 < BCHDA-5 < BCHDA-10 < BCHDA-20).

The maximum stress of BCHDA-0 and BCHDA-5 was 25.8 MPa and 23.1 MPa, and the value of strain was 76% and 100%, respectively. However, in terms of elongation, the opposite trend to that of the stress appeared. Elongation of polyester coatings generally increased with increasing content of cycloaliphatic structure.

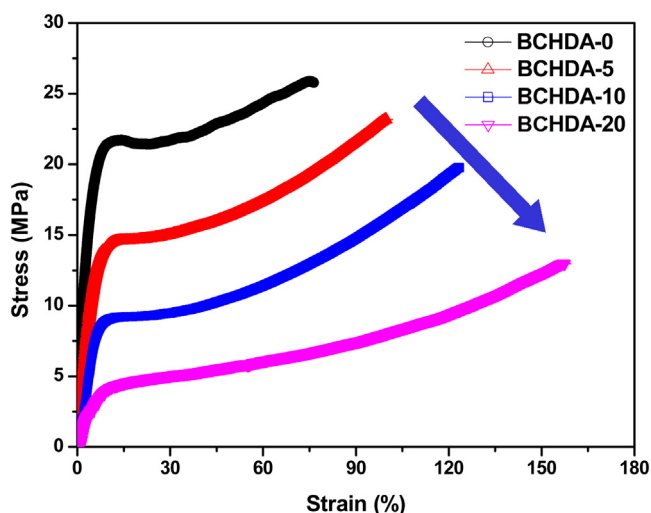


Fig. 4. Stress-strain curve of cycloaliphatic structure of polyester coatings.

In the case of BCHDA-10 and BCHDA-20, the maximum stress was 19.7 MPa and 12.9 MPa, and the value of strain was 123% and 157% respectively. These values could be explained by the cycloaliphatic structure between the ester linkages from the 1,4-CHDA. The cycloaliphatic structure was more flexible than the conjugate structure of IPA, because the cyclic structure consisted of only the  $\sigma$ -bond between  $\text{CH}_2$ - $\text{CH}_2$  groups [20]. Cycloaliphatic structure could give the flexibility of a polymer network. Therefore it could be implied that cycloaliphatic structure can give flexibility, and would provide lower stiffness to the polyester coatings [10].

### 3.4. Formability

The deep drawing test is a common method for determining 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 on the PCM was 23.4%.

Fig. 5 shows the formability resulting from the deep drawing. The BCHDA-0 specimen had cracks and delamination, even though it exhibited a higher tensile strength from the flexibility test. BCHDA-0 was not flexible enough to be stretched out during the deep drawing. The others 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.

$F_U$ , forming coefficient based on strain energy, was calculated from Eq. (5).  $F_U = U_C/U_T$  and  $U_C$  and  $U_T$  were calculated from Eqs. (3) and (4).  $U_C$  of BCHDA-0 is 145.7 and  $U_T$  of BCHDA-0 is 205.7.  $F_U$  of BCHDA-0 is 0.71 and BCHDA-5, BCHDA-10 and BCHDA-20 were 1.03, 1.44 and 2.42, respectively.  $F_\varepsilon$ , a forming coefficient based on strain, was calculated from Eq. (6).  $F_\varepsilon = \varepsilon_c/R_f$  and,  $\varepsilon_c$ , the developed strain for 90 s was measured by creep strain. As shown in Fig. 6. The developed strains of BCHDA-0, BCHDA-5, BCHDA-10 and BCHDA-20 were 18.5%, 23.6%, 29.6% and 43.2%, respectively.  $F_\varepsilon$  of BCHDA-0 is 0.79 and BCHDA-5, BCHDA-10 and BCHDA-20 were 1.08, 1.27 and 1.85, respectively.  $F_U$  should be larger than 1, and  $F_\varepsilon$  should be larger than 1 to have good formability [4]. So, BCHDA-0 was not flexible enough to stretch out during the deep drawing test. However, the  $F_U$  of BCHDA-5, BCHDA-10 and BCHDA-20 were larger than 1, and those of  $F_\varepsilon$  were also larger than 1. So, those specimens can be stretched without being damaged during the deep drawing. The calculated values are listed in Table 6. From the deep drawing test, cycloaliphatic structure of 1,4-CHDA of the  $\text{CH}_2$ - $\text{CH}_2$  group could

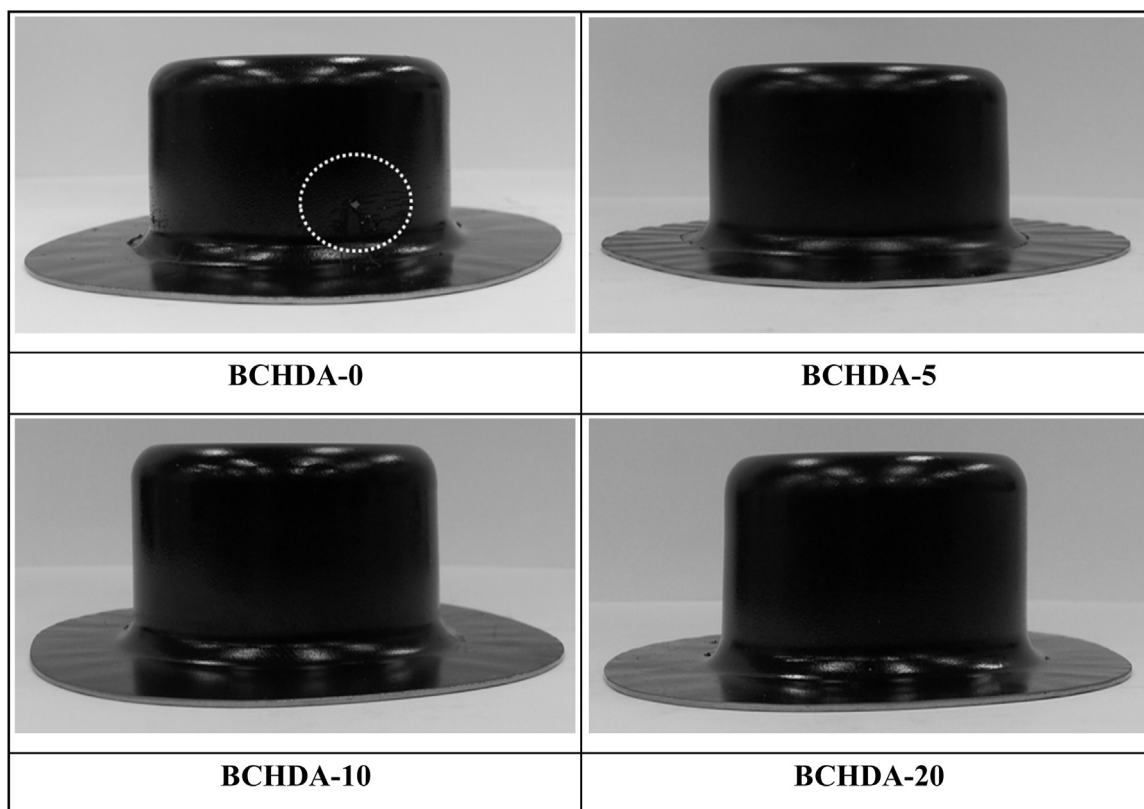


Fig. 5. Formability of cycloaliphatic structure of polyester coatings on the PCM.

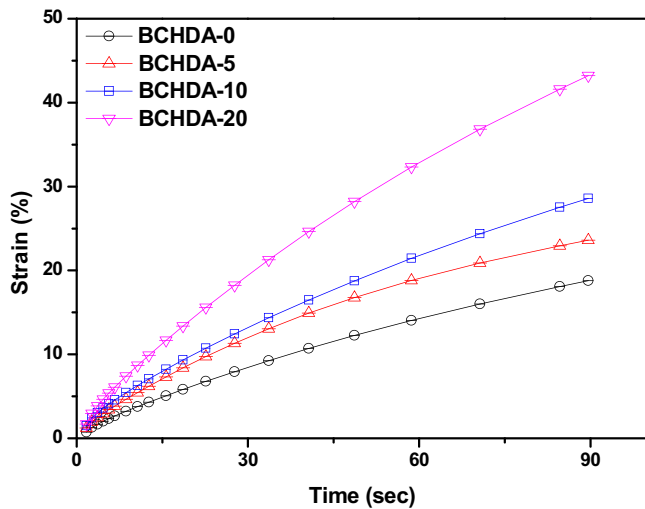


Fig. 6. Strain of cycloaliphatic structure of polyester coatings by the creep test.

Table 6

Calculated values from the tensile test and creep test [4].

Sample	$U_T$	$U_C$	$F_U (U_C/U_T)$	$\varepsilon_C$ (%)	$F_\varepsilon (\varepsilon_C/R_T)$
BCHDA-0	205.7	145.7	0.71	18.5	0.79
BCHDA-5	183.6	190.1	1.03	23.6	1.08
BCHDA-10	152.5	220.2	1.44	29.6	1.27
BCHDA-20	100.1	242.5	2.42	43.2	1.85

give the flexibility of polymer network, and could provide good formability.

### 3.5. Stone-Chip resistance

Fig. 7 shows the stone-chip resistance result as a function of the 1,4-CHDA content. With increasing 1,4-CHDA, synthesized polyester had increased cycloaliphatic structure in the polymer chain; and the cycloaliphatic structure affected a decrease in  $T_g$ , and increased flexibility. BCHDA-0 had 0 mol of 1,4-CHDA and 20 mol of IPA. It had the highest  $T_g$ , which meant that the polyester coatings would be very hard. A stone-chip resistance test was carried out at  $4 \pm 0.2 \text{ kgf/cm}^2$  of pressure. Specimens were set to  $-20^\circ\text{C}$  for 3 h in a cold chamber, before the chipping resistance test. So, the polyester coating of BCHDA-0 could be easily damaged and removed by the stone-chip under the low temperature. It had lots of removed areas, and large sized defects. However, by increasing the content of 1,4-CHDA, the removed areas were generally decreased. In the case of BCHDA-20, it had 20 mol of 1,4-CHDA. It had the highest amount of 1,4-CHDA, so it had the highest amount of cycloaliphatic structure, which could give flexibility to the polymer chain of polyester. So, BCHDA-20 had little removed area and small sized defects. This means that the cycloaliphatic structure was more flexible than the conjugate structure of aromatic structure.

Fig. 8 shows the removed area (%) of specimens, which is calculated from the removed area by the tested area using VIEEW<sup>TM</sup>. The removed area was dramatically decreased. The removed area of BCHDA-0 was 3.70%, but that of BCHDA-20 was 0.44%. From the stone-chip resistance test, the cycloaliphatic structure can give flexibility, and would provide lower stiffness than aromatic structure to the polyester coatings. Cycloaliphatic structure has better elasticity than aromatic structure, and can give better stone-chip resistance.

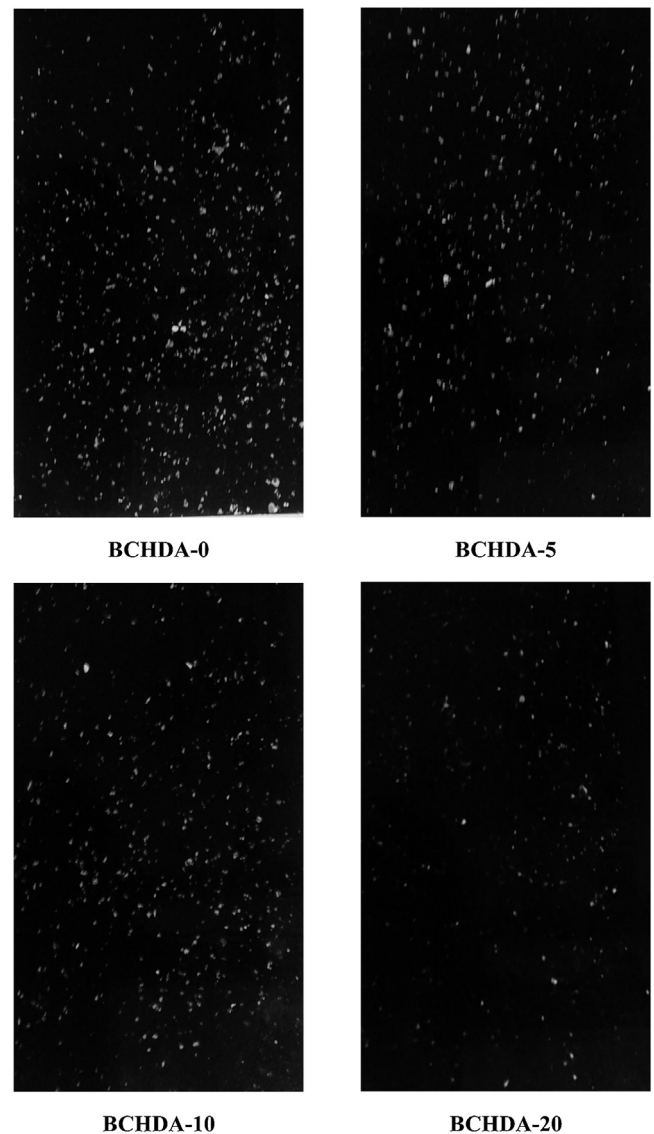


Fig. 7. Stone-chip resistance of cycloaliphatic structure of polyester coatings on the PCM (before test specimens set  $-20^\circ\text{C}$   $\times$  3 h).

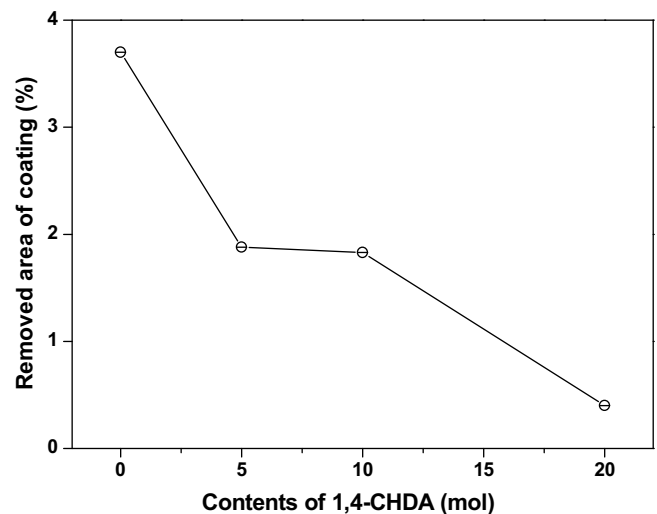


Fig. 8. Removed area of cycloaliphatic structure of polyester coatings of the stone-chip resistance by VIEEW.

#### 4. Conclusion

Four types of cycloaliphatic structure of polyester were synthesized and formulated, to control formability for pre-coated metals. Those resins were designed to show the flexibility of the cycloaliphatic structure. The viscoelastic behavior, flexibility and formability were measured to determine the cycloaliphatic structure effect on the flexibility of the pre-coated metals. When the content of cycloaliphatic structure of 1,4-CHDA was increased in the synthesizes resins, the stiffness of the product generally decreased, and the  $T_g$  of each cured polyester coatings shifted to a lower temperature. Therefore, cycloaliphatic structure is a major factor in improving the flexibility and formability of polyester coatings.

To analyze the formability, we calculated  $F_U$  (the forming coefficient based on strain energy) and  $F_\varepsilon$  (the forming coefficient based on strain).  $F_U$  of BCHDA-0 is 0.71 and BCHDA-5, BCHDA-10 and BCHDA-20 were 1.03, 1.44 and 2.42, respectively.  $F_\varepsilon$  of BCHDA-0 is 0.79 and BCHDA-5, BCHDA-10 and BCHDA-20 were 1.08, 1.27 and 1.85, respectively. When  $F_U$  and  $F_\varepsilon$  are both larger than 1, the polyester coatings have good formability. Also, BCHDA-20 had 0.44% of removed area by the chipping resistance test and it means that cycloaliphatic structure has better elasticity than aromatic structure, and can give better stone-chip resistance.

From those tests, BCHDA-20 which had 20 mol of 1,4-CHDA had good formability and also showed good stone-chip resistance. So,

cycloaliphatic structure provides lower stiffness and higher softness to the polyester coatings for automotive pre-coated metals.

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