



# Synthesis and characterization of flexible polyester coatings for automotive pre-coated metal

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## ABSTRACT

An automotive pre-coated metal system has investigated to remove the wet coating process, such as pre-treatment, dip coating and spray coating for environmental regulations. However, automotive pre-coated metal sheets must have high flexibility and formability to overcome the harsh conditions such as cutting, press and stamping process. For these reasons, flexible polyester coatings were designed to control flexibility using polycarbonatediol. The characteristics, curing behavior and viscoelastic property of the resins were measured by FT-IR, GPC, rheometer, DSC, RPT and DMA. The flexibility was evaluated using a texture analyzer. A nano-scratch tester, equipped optical microscope can measure the scratch resistance of coatings and the scratched surface morphology.

With increasing polycarbonatediol content, the final frequency and the storage modulus increased and the  $T_g$  of the coatings decreased. This is related to the high mobility of the chain segment in polycarbonatediol. In terms of the flexibility and scratch resistance, CP-3 had high elongation value and good scratch resistance resulting from optimized stamping, pressing and cutting process in automotive pre-coated metal system. Therefore, polycarbonatediol is a powerful factor affecting the flexibility and scratch resistance of polyester coatings.

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## 1. Introduction

Currently, environmental issue is a major concern and problem in the automotive industry. In particular, amount of waste water and solvent, derived from wet coating process are restricted by environmental regulations. The wet coating process consists of a pre-treatment, a dip coating and a spray coating for an electrocoating, a primer, a basecoat and a clearcoat. These process discharges mixture of water and organic/inorganic materials, hence the needs for purification of waste water and solvent capturing.

Pre-coated metal system (PCM) is manufactured in a sheet or coil coating line and processed and assembled in factories for household electric appliances, building materials and others. In this system, wet coating process can be eliminated by using a roll coating process, thereby the problem of solvent evaporation can be solved. In addition, pre-coated metal system offers other advantages such as improved productivity and energy saving [1–3].

By these reasons, an automotive pre-coated metal system has been investigated to remove the wet coating process, such as pre-treatment, dip coating and spray coating. In this system, all coating layers must have high flexibility and formability to overcome the harsh conditions due to the cutting, press and stamping process [4–7].

Polyester resins have been used for automotive coatings as the a primer, basecoat and clearcoat as well as interior or exterior parts, such as air cleaners, oil filters, wheel, bumpers and many trims. This resin has good flexibility or formability and physical properties: chipping resistance and optical property [5]. In a previous our study, 1,6-hexanediol, a common raw material of polyester resin, was examined to increase the flexibility of the coatings. Generally, the chain length and crosslink density have a high correlation of flexibility and formability [6]. However, in terms of chain length, 1,6-hexanediol is difficult to overcome the flexibility and formability for an automotive pre-coated metal system.

Polycarbonatediol is an esterification product, formed by a reaction of carbonic acid with polyols. The aliphatic polycarbonates are employed as the main segment in superior polyurethane coatings due to the physical properties such as low viscosity, good toughness, weather stability and excellent hydrolysis resistance [7]. Owing to the hydroxyl group, polycarbonatediol can be used as an alcohol during the synthesis of polyester resin. In particular,

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**Table 1**  
Formulation of polyester resins with polycarbonatediol (unit: mole of monomer).

Contents	CP-0	CP-1	CP-3	CP-5
Polycarbonatediol	0	1	3	5
Trimethylol propane	5	5	5	5
Ethylene glycol	4	4	4	4
1,6-Hexanediol	15	14	12	10
Phthalic anhydride	10	10	10	10
Isophthalic acid	12	12	12	12
<sup>a</sup> Curing agent (HMMM)	1.7	1.7	1.7	1.7

<sup>a</sup> Curing agent was used after synthesis of polyester resin.

polycarbonatediol consists of a long alkyl chain which is contained many flexible rod-like group such as  $-\text{CH}_2$ . An aliphatic C–C bond is most flexible than an aromatic C–C, C–O and C–N bond because of low rotation barrier energy [8]. In addition, polycarbonate has a low glass transition temperature and a low Young's modulus, supporting flexibility and formability of the polyester coatings [9].

In this study, the polyester resin was designed to control the flexibility for an automotive pre-coated metal system using polycarbonatediol. In addition, low viscosity of polycarbonatediol can be expected to apply a high-solid coating system. The curing and viscoelastic behavior, flexibility and scratch resistance were measured to determine the flexible segment effect of polycarbonatediol for an automotive pre-coated metal system.

## 2. Experimental

### 2.1. Materials

Polycarbonatediol ( $M_w = 1000$ , Asahi Kasei Co., PCDL) was prepared to control the flexibility of the main chain. Trimethylol propane (Tokyo Kasei, TMP), isophthalic acid (Junsei Chemical, IPA), phthalic anhydride (Daejung Chemical), ethylene glycol (Samchun chemical, EG) and 1,6-hexanediol (Samchun chemical) were used without further purification.

Hexamethoxymethylmelamine (HMMM, Cytec), a common curing agent in pre-coated metal system was used. Butylstannic acid (FASCAT 4100, Arkema Inc.) was used as a catalyst to catalyze polymerization and prevent a transesterification reaction during synthesis reaction [5].

An amine type curing catalyst (NACURE 5925) was supplied from KING industries. Xylene was used as a solvent to reduce the viscosity of polyester resin. Table 1 lists the synthesis formulation of polyester resin.

### 2.2. Synthesis of flexible polyester resin

#### 2.2.1. Synthesis of polyester pre-polymer

Polyester pre-polymer was synthesized using trimethylol propane, 1,6-hexanediol, ethylene glycol, phthalic anhydride and isophthalic acid according to the following process. The resin was designed as a carboxy-excess pre-polymer. A 500 ml 4-neck round type reactor, fitted a temperature controller, heating mantle,  $\text{N}_2$  purge, condenser which was used to remove the water from esterification, was placed. All raw materials were charged into the reactor and the temperature was set to  $160^\circ\text{C}$  for 1 h. Subsequently, the reaction temperature was increased from  $160^\circ\text{C}$  to  $220^\circ\text{C}$  at  $0.5^\circ\text{C}/\text{min}$ . During the synthesis process, the acid value titration was performed using a 0.1 N KOH solution. The temperature was maintained for several hours to obtain a carboxy-excess pre-polymer.

#### 2.2.2. Synthesis of polyester resin with polycarbonatediol

With the carboxy-excess pre-polymer, the temperature was set to  $80^\circ\text{C}$  and PCDL was charged to the reactor. Subsequently, the temperature was increased from  $80^\circ\text{C}$  to  $180^\circ\text{C}$  at  $0.5^\circ\text{C}/\text{min}$ . During the synthesis process, the acid value titration was performed using a 0.1 N KOH solution. The temperature was maintained and the solvent was added over a period of several hours to remove condensed water and obtain the hydroxy-terminated polyester resin. Scheme 1 shows the synthesis process of the polyester resin.

#### 2.2.3. Preparation of polyester coatings for automotive PCM

The polyester coatings were coated on galvanized steel sheet using a  $40\ \mu\text{m}$  bar coater and cured at  $150^\circ\text{C}$  for 30 min. The cured films, prepared for DMA analysis and tensile test, were coated on a disposable aluminum dish and cured under the same condition. The width and thickness of cured films were 6.5 mm and 0.5 mm.

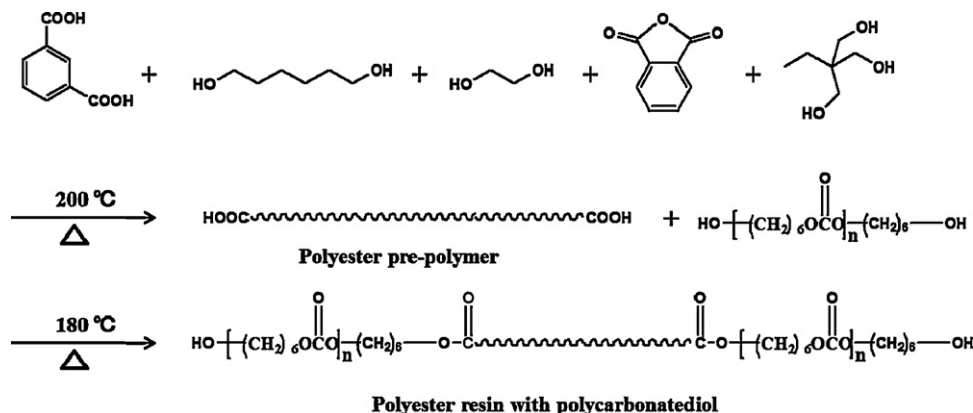
### 2.3. Methods

#### 2.3.1. Fourier transform infrared spectroscopy (FT-IR)

The IR spectra were measured using a JASCO FT/IR-6100 (Jasco, Japan) equipped with a Miracle accessory, and attenuated total reflectance (ATR). The ATR crystal was made from diamond with a refractive index of 2.4 at  $8500$ – $2500$  and  $1700$ – $300\ \text{cm}^{-1}$ . The spectra range was from  $4000$  to  $650\ \text{cm}^{-1}$  and the resolution was  $4\ \text{cm}^{-1}$ .

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

The molecular weight and polydispersity were measured using an YL9100 GPC SYSTEM (Young Lin, Korea) equipped with a pump, a RI detector and a Waters Styragel HR 5E column. The polystyrene



**Scheme 1.** Synthesis process of the polyester resin with polycarbonatediol.

**Table 2**  
Characterization of the polyester resin with polycarbonatediol.

Property	CP-0	CP-1	CP-3	CP-5
Weight average molecular weight (g/mol)	3120	3590	7350	6590
Polydispersity ( $M_w/M_n$ )	2.42	2.62	3.93	3.68
$n_{OH}$ (mg KOH/g)	100	87	70	57
$M_w/n_{OH}$ (g/mg KOH)	31.20	41.26	105	115.614
Viscosity ( $\eta$ /Pas)	1180–1300	670–680	330–350	130–135
Crosslink density ( $10^{-3}$ mol/cm <sup>3</sup> )	1.33	1.19	0.78	0.49

<sup>a</sup>  $n_{OH}$ : theoretical hydroxyl number of polyester resins.

and poly(methyl methacrylate) calibration standards were used. Tetrahydrofuran was used as the eluent, and the flow rate was 1 ml/min. Table 2 lists the molecular weight and polydispersity of the synthesized resins [10].

### 2.3.3. Rigid-body pendulum physical property testing (RPT)

A rigid-body pendulum physical property testing (RPT, A&D Co., Japan) was used to measure the curing behavior of the polyester resin. This apparatus consisted of two types of rigid-body pendulum, heating oven, steel substrate and main controller. The curing behavior was measured by detecting the movement of a knife type pendulum on the coated steel substrate with temperature. The heating oven was set from 50 °C to 200 °C at 5 °C/min, and maintained at 200 °C for 50 min [11].

### 2.3.4. Dynamic mechanical analysis (DMA)

The viscoelastic behavior of the polyester coatings is an important factor for evaluating the coating performance with temperature. Dynamic mechanical analysis (DMA) was performed using a Dynamic Mechanical Analyzer Q-800 (TA Instruments, USA). The machine was used to determine the modulus, glass transition temperature and crosslink density. 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 [4]:

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

The test method was a tension-film mode under the following conditions: a frequency of 1 Hz, strain of 0.3% and temperature from –60 °C to 160 °C at a heating rate of 2 °C/min.

### 2.3.5. Tensile strength

The flexibility of the polyester coatings was determined from the tensile strength using a Texture Analyzer (TA-XT2i) with rectangle-shaped specimens according to the ASTM D-638-10. The tensile strength was calculated to divide the maximum load in newtons (N) by the average original cross-sectional area in the gage length segment of the specimen in square meters. The percent elongation (strain %) was calculated to divide the variation in gage length by the original specimen gage length, expressed as a percent (%) [12].

### 2.3.6. Nano-scratch test (NST)

The scratch resistance is an important property in automotive clearcoat, and is related to the gloss retention and weatherability. A nano-scratch tester (CSM instruments, Switzerland) can evaluate the scratch resistance or mar resistance of coatings using a diamond stylus scratch method. The machine has several loading modes, the progressive normal force mode and constant normal force mode, which are used to measure the fracture point and penetration depth profile of the coatings. This method is performed according to the ASTM D 7187-05, and the progressive normal force mode is carried

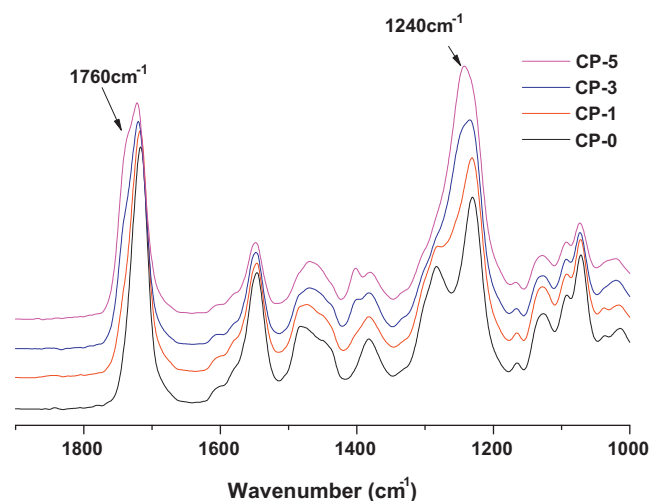
out using a sphero-conical 90 type indenter. The load ranged from 0.2 to 40 mN at a loading rate of 39.8 mN/min [13].

## 3. Results and discussion

### 3.1. Characterization of polyester resin

Polyester coatings with polycarbonatediol focused on the amount of flexible segment between the ester linkages. Generally, a commercial automotive clearcoat requires physical properties, such as the scratch resistance, stone chip resistance and gloss. However, flexibility is the most important property due to the cutting, pressing and stamping processes in automotive pre-coated metal system. FT-IR was used to characterize the carbonate group in the polyester resin. As shown in Fig. 1, the carbonate group from polycarbonatediol was detected at 1240 and 1760 cm<sup>-1</sup> and the amount of carbonate group increased with polycarbonatediol content [14]. The viscosity of the polyester resin was evaluated to determine the effect of polycarbonatediol, using a rheometer (Hakke MARS II, Thermo Electron GmbH, Germany) at ambient temperature. As shown in Table 2, the viscosity of the resin decreased with increasing polycarbonatediol content. Especially, the viscosity of CP-5 is less 10 times than that of CP-0.

Table 2 lists the molecular weight and polydispersity of the polyester resin, determined by GPC. In our designed formulation, theoretical hydroxyl number of polyester resin,  $n_{OH}$  was decreased with increasing polycarbonatediol/1,6-hexanediol ratio because of high molecular weight of polycarbonatediol. In addition, the ratio between the molecular weight and hydroxyl number ( $M_w/n_{OH}$ ), which is a length of polymer chain between the crosslinks of the synthesized polyester resin was also decreased with increasing polycarbonatediol content [4].



**Fig. 1.** IR spectra of the polyester coatings with polycarbonatediol after 1 h at 150 °C (1240, 1760 cm<sup>-1</sup>: carbonate group).

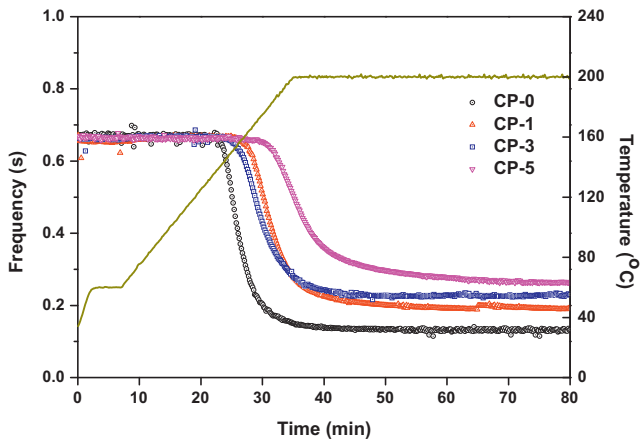


Fig. 2. Curing behavior (change of frequency(s)) of the polyester coatings with polycarbonatediol on steel substrate using a RPT instrument.

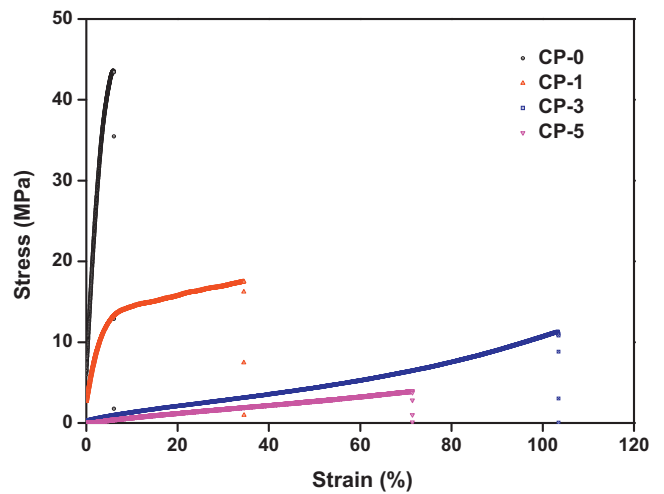


Fig. 5. Stress-strain curve of the polyester coatings with polycarbonatediol.

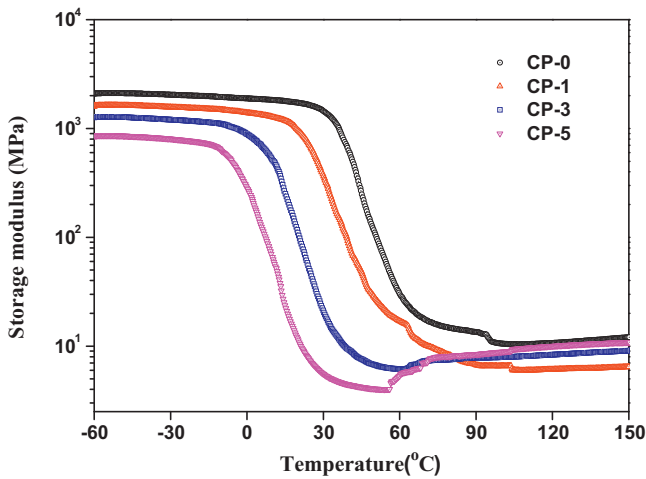


Fig. 3. Storage modulus from the DMA results of the polyester coatings with polycarbonatediol.

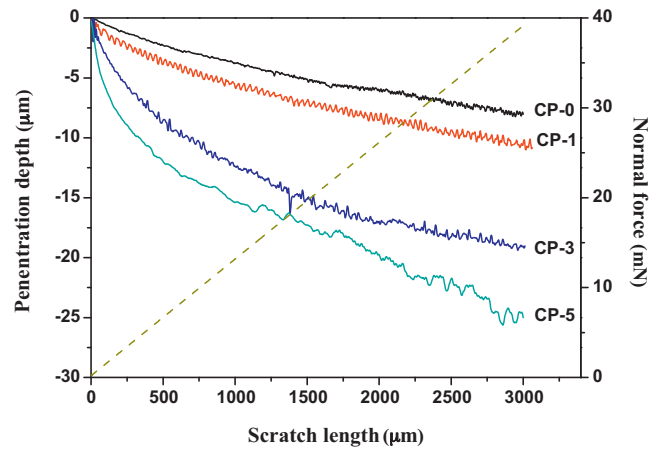


Fig. 6. Penetration depth plotted as a function of the scratch length and normal force for each cured coating.

### 3.2. Curing behavior

The curing behavior is an important property in the automotive PCM because the drying and curing zone in the roll coating process are much shorter than the conventional automotive process. The

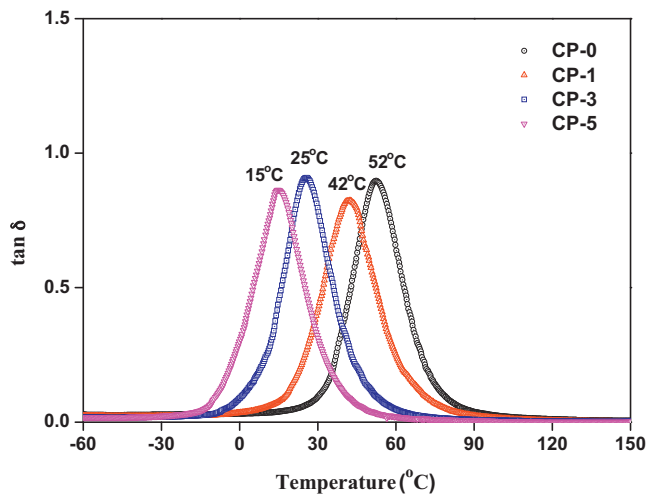


Fig. 4. Tan  $\delta$  from the DMA results of the polyester coatings with polycarbonatediol.

RPT instrument can detect the curing behavior of the coatings on the steel substrates as a function of temperature. As shown in Fig. 2, the initial curing of each coatings started at approximately 160 °C and continued to 160–200 °C, for 15 min. The change in frequency

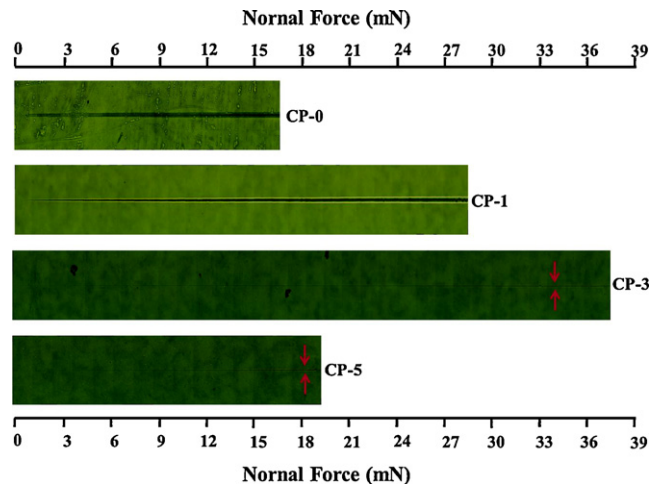


Fig. 7. Optical micrographs of the scratch paths made over the progressive load range (0–40 mN) on each cured coating.

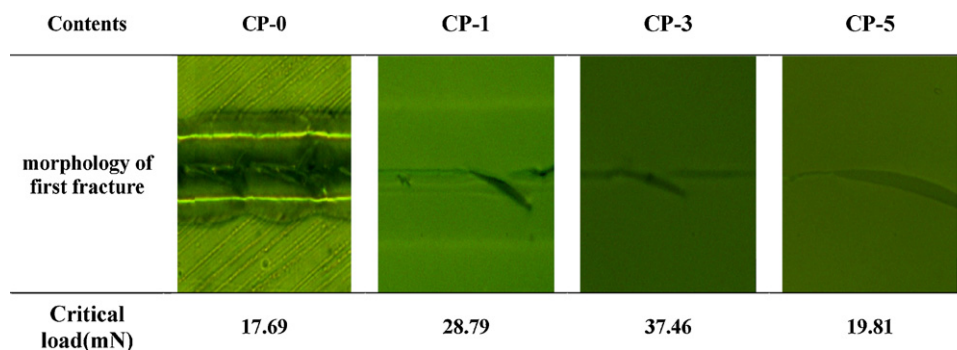


Fig. 8. Optical micrographs of the first fractures made over the progressive load range (0–40 mN) on each cured coating.

of the different coatings was similar. However, the final frequency was in the following order: CP-5 > CP-3 > CP-1 > CP-0. This suggests that polycarbonatediol is more flexible than 1,6-hexanediol.

### 3.3. Viscoelastic behavior

Fig. 3 shows the storage modulus as a function of the flexible segment from polycarbonatediol. The elasticity decreased considerably, when polycarbonatediol/1,6-hexanediol ratio increased. This tendency was in the following order: CP-0 > CP-1 > CP-3 > CP-5. The result was explained by the amount of flexible alkyl chain between the ester linkages. The molecular weight of polycarbonatediol is approximately 8 times larger than that of 1,6-hexanediol, and the continuous flexible alkyl chain was longer than that of 1,6-hexanediol. Generally, the mobility and flexibility of the polymer chain increased with linear alkyl chain segment. In addition, the storage modulus decreased and the elongation increased with increasing the ratio between the molecular weight and hydroxyl number ( $M_w/n_{OH}$ ), which is a length of polymer chain between the crosslinks [4]. As shown in Table 2, the crosslink density ( $\nu_c$ ) decreased, whereas the length between the crosslinks was increased with polycarbonatediol. Fig. 4 shows that the  $T_g$  was shifted to a lower temperature due to the content of polycarbonatediol [9].

### 3.4. Flexibility

Analysis of the tensile strength and elongation is an effective way to estimate the flexibility in the cured films. Fig. 5 shows the order of the tensile strength which was similar to that of the storage modulus (CP-0 > CP-1 > CP-3 > CP-5). The maximum stress of CP-0 was approximately 44 MPa. In contrast, the elongation of coatings increased with polycarbonatediol content. In the case of CP-3, the strain value was over 100%. However, the stress and strain value of CP-5 was poor, despite the high polycarbonatediol content. This was attributed to polycarbonatediol imparting a low crosslink density and low stiffness to the coatings because of polycarbonatediol's high weight percentage in total polyester polymer [6]. In addition, an end of a crosslink is more likely to find another segment of the same chain at short rather than long distances away from the first segment. From this reason, the short crosslink lengths between long chain segments generated intramolecular crosslinking, called loop crosslink which is a weak point of the polymer network [15,16]. Therefore, the long chain segment affects the poor functioning of the coatings in over the specific content of polycarbonatediol.

### 3.5. Scratch resistance

The scratch resistance is an important property for automotive clearcoat and it is related to the flexibility and softness of

the coatings. Fig. 6 shows the penetration depth of the coatings using the progressive normal force mode in a nano-scratch test. The greater penetration depth at the same loading means that the coating has high softness. Generally, the scratch resistance increase with increasing softness of coating surface [13].

In this result, the penetration depth with loading increased from CP-0 to CP-5 with increasing flexibility and softness as shown in the RPT, DMA and tensile strength test results.

In particular, the degree of CP-5 was approximately 5 times larger than that of CP-0 in penetration depth with loading. However, the first fracture of the coatings cannot be detected by penetration depth plotting. For the reason, an optical analysis was demanded to measure the fracture by scratching.

Fig. 7 shows the critical load at first fracture of the coatings by photographing the scratch in sections. The critical load at first fracture was an index to evaluate the scratch resistance of the coatings with the penetration depth plotting. According to the topograph, the high content of polycarbonatediol caused the narrow width and long length of scratch path with progressive loading. In the case of CP-0 and CP-3, the critical load of CP-3 was approximately 2 times larger than that of CP-0. Fig. 8 is the magnified micrograph at first fracture of coating surface by scratching. With polycarbonatediol content, the damage of the coating surface at first fracture was reduced. Generally, the surface morphology is an important factor that determines the gloss of a coating. In terms of gloss retention after scratching, the polyester coating with polycarbonatediol is more advantageous as an automotive clearcoat.

## 4. Conclusion

Polyester resins were synthesized with polycarbonatediol to control the flexibility for an automotive pre-coated metal system. The resins were designed to demonstrate the flexible chain effect, using polycarbonatediol and 1,6-hexanediol. The curing and viscoelastic behavior, flexibility and scratch resistance were measured to determine the flexible chain segment effect in an automotive pre-coated metal system.

Regarding the curing behavior and viscoelastic analysis, the synthesized polyester coatings exhibited similar curing time and temperature. However, at the end of curing, the frequency value was higher with polycarbonatediol content. This suggests that polycarbonatediol is more flexible than 1,6-hexanediol. According to DMA analysis, the elastic property decreased considerably, when the polycarbonatediol/1,6-hexanediol ratio increased. In addition, the  $T_g$  of each cured coatings was shifted to lower temperature with polycarbonatediol content. In terms of flexibility and scratch resistance, CP-3 had high elongation value and good scratch resistance for the stamping, pressing and cutting process in an automotive pre-coated metal system. Therefore, polycarbonatediol is a

powerful factor affecting the flexibility and scratch resistance of the polyester coatings.

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