



Synthesis of elastomeric polyester and physical properties of polyester coating for automotive pre-primed system

Je-Ik Moon^a, Yong-Hee Lee^{a,b}, Hyun-Joong Kim^{a,b,*}, Seung-Man Noh^c, Jun-Hyun Nam^c

^a Laboratory of Adhesion and Bio-Composites, Program in Environmental Materials Science, Seoul National 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 PPG Industries (Korea) Inc., Cheonan 330-912, Republic of Korea

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ABSTRACT

An automotive pre-primed system has been investigated to remove wash and pre-treatment processes using a roll coating application for environmental regulations. However, automotive pre-primed sheets must have high flexibility and formability to overcome harsh conditions such as cutting, press and stamping processes. For these reasons, elastomeric polyester resins were designed to improve flexibility and formability in terms of high molecular weight, low crosslink density and content of flexible segment. The curing, viscoelastic behavior, flexibility, formability and physical properties of resins were measured to evaluate suitability of the synthesized primers for an automotive pre-primed system.

Regarding the curing and viscoelastic behavior, CE-PE-I and III have good stiffness and elasticity due to the high molecular weight and crosslink density comparing CE-PE-II which was designed for low crosslink density. In terms of the $\tan \delta$ result, T_g of primers was similar to each other, thus surface hardness of CE-PE series was around 120–140 s. For tensile results, CE-PE-I and III have good tensile strength and elongation values. From the result of drawing, no defects were observed at the side of all drawn samples after 48 mm drawing. However, the side of drawn cup was tone, excepting that of CE-PE-I after 57 mm drawing. Consequently, high molecular weight and the content of flexible segment are powerful factors affecting the formability for an automotive pre-primed system.

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1. Introduction

Currently, environmental regulation and productivity is a major concern and problem in the automotive industry. In particular, emission of waste water and solvent, derived from wet coating process are restricted by environmental regulations. The wet coating 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 a consolidate system in a sheet or coil coating line for household electric appliances, building materials and others. This system consists of roll coating application which can be eliminated thereby the problem of solvent emission can be solved using solvent capture equipment. In addition, pre-coated metal system can be improved productivity and energy saving [1–3].

By these reasons, an automotive pre-primed system has been investigated to remove wash, pre-treatment and electrocoating processes using a roll coating application. However, the pre-primed sheets must have high flexibility and formability to overcome the harsh conditions such as the cutting, press and stamping processes [4]. The concept of pre-primed system is shown in Fig. 1.

Polyester resins have been used for automotive coatings as 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].

We mentioned three types of elastomeric polyester resins to overcome harsh conditions for an automotive pre-primed system. One of the elastomeric polyester, elastomeric polyester type resin I (E-PE-I) was designed to increase the molecular weight for formability. Elastomeric polyester type resin II (E-PE-II) was contained low hydroxyl number to reduce crosslink density due to its flexibility. In a previous study, high molecular weight and low crosslink density are good factors for formability in deep drawing [6]. Finally, elastomeric polyester type resin III (E-PE-III) was designed to increase the content of flexible segment such as 1,6-hexanediol and adipic acid which were contained many flexible rod-like $-CH_2$ group supporting flexibility and formability [7].

* 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.

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

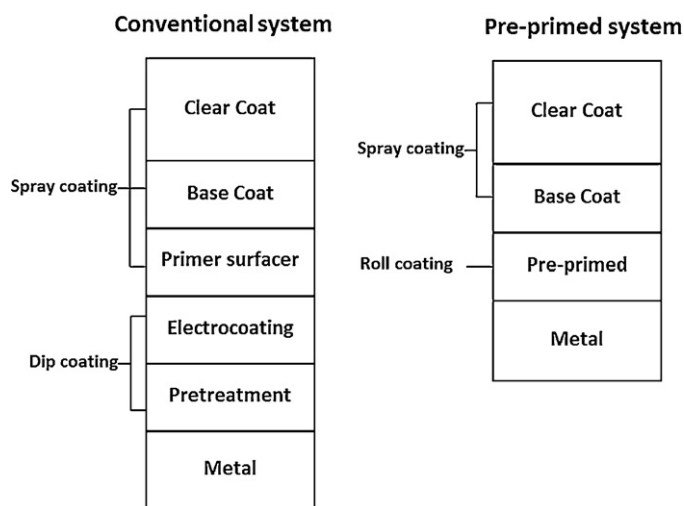


Fig. 1. The concept of an automotive pre-primed system.

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. In addition the T_g of resins were targeted to be above the drawing temperature (25 °C) to prevent the effects of softening which occurs above T_g [8].

The curing behavior was measured to determine suitable curing condition in a pre-coated metal system. Subsequently, the formability and physical properties such as pendulum hardness, adhesion, tensile strength, and anti-corrosion property were evaluated to apply in the automotive primers.

2. Experimental

2.1. Materials

2-Methyl-1,3-propanediol (2-MPD), trimethylol propane (TMP), isophthalic acid (IPA), phthalic anhydride, adipic acid (AA), 1,6-hexanediol, neopentyl glycol (NPG), ethylene glycol (EG), terephthalic acid (TPA) were purchased from Samchun Chemicals (South Korea) and used without further purification. Hexamethoxymethylmelamine (HMMM, Cytec) and blocked isocyanate (Desmodur BL 3175 SN, Bayer MaterialScience) were used as a curing agent. An amine type curing catalyst (NACURED 5925) was supplied from KING industries.

Butylstannic acid (FASCAT 4100, Arkema Inc.) was used as a catalyst to catalyze polymerization and prevent a transesterification reaction during the synthesis reaction [9]. Galvanized steel (GA) and an electrocoating were supplied from PPG Korea. Table 1 lists the synthesis formulation of polyester resins.

Table 1
Synthesis formulation of the elastomeric polyester resins (unit: wt%).

Contents	E-PE-I	E-PE-II	E-PE-III
Ethylene glycol	0	3.4	3.7
Neopentyl glycol	8.8	16.0	12.5
2-Methyl-1,3-propanediol	26.6	11.8	0
Trimethylol propane	3.6	1.5	6.2
1,6-Hexanediol	0	5.2	18.7
Adipic acid	7.7	11.2	31.2
Phthalic anhydride	23.5	0	0
Isophthalic acid	29.8	38.2	22.4
Terephthalic acid	0	12.7	5.2
Total	100	100	100

Table 2

Formulation of the elastomeric polyester automotive primers (solid content of resins: E-PE-I: 65%, E-PE-II: 50%, E-PE-III: 50%) (unit: wt%).

Contents	CE-PE-I	CE-PE-II	CE-PE-III
Resin	44.7	37.0	38.0
HMMM (melamine type)	2.8	1.0	1.8
Desmodur BL 3175 SN (block isocyanate type)	1.0	1.0	1.0
Catalyst	0.2	0.2	0.2
TiO ₂	7.0	7.0	7.0
^a Anticol yellow tint paste	20.0	20.0	20.0
Solvent	26.0	26.0	26.0
Additives	1.1	1.1	1.1

^a A corrosion inhibitor.

2.2. Synthesis of elastomeric polyester resin

A 500 mL 4-neck round type reactor, fitted with a temperature controller, heating mantle, N₂ purge, and condenser (for removing the water from esterification) was placed. All raw materials were charged into the reactor and the temperature was set to 160 °C for 1 h. Subsequently, the reaction temperature was increased from 160 °C to 220 °C at 0.5 °C/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 [9].

2.3. Preparation of polyester coatings for automotive pre-primed sheet

The formulations of the elastomeric polyester coatings are listed in Table 2. In addition, the formulated primers renamed from E-PE to CE-PE to classify between resins and primers. Polyester primers were coated onto a galvanized steel sheet using a 30 μm bar coater and cured at 150 °C for 30 min. The cured films, prepared for DMA analysis and tensile tests, 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 0.1 mm [9].

2.4. Methods

2.4.1. Gel permeation chromatography (GPC)

The molecular weight and polydispersity were measured using an Agilent 1100 equipped with a pump, and a RI detector. Tetrahydrofuran was used as the eluent, and the flow rate was 1 mL/min. Table 3 lists the molecular weight and polydispersity of synthesized resins [10].

2.4.2. Rigid-body pendulum physical property testing (RPT)

The curing behavior of the polyester resin was measured using a rigid-body pendulum physical property testing instrument (RPT, A&D Co., Japan). Fig. 2 shows two types of rigid-body pendulum – a knife edge type pendulum which is used to measure the curing behavior and a cylindrical edge type to analyze physical properties, such as T_g of the cured coatings. The curing behavior

Table 3
Characterization of the elastomeric polyester resins.

Property	E-PE-I	E-PE-II	E-PE-III
Number average molecular weight (M_n)	10,000	6500	4100
Polydispersity (M_w/M_n)	3.0	2.7	2.3
^a n_{OH} (mg KOH/g)	36	20	35
^b ν_c (10^{-3} mol/cm ³)	0.75	0.30	0.53

^a Theoretical hydroxyl value of the E-PE resins.

^b Crosslink density of the CE-PE primers.

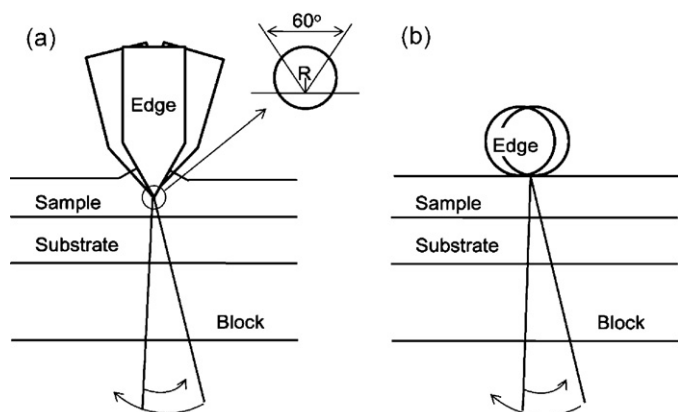


Fig. 2. Rigid-body type pendulums in a RPT instrument; (a) knife edge type for the curing process, and (b) cylindrical edge type for physical properties [9].

was measured by detecting the movement of a knife type pendulum on the coated steel substrate 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. This apparatus consists of heating oven, steel substrate and main controller. To examine curing the polyester coatings were coated on the steel substrate (50 mm × 20 mm × 0.3 mm) using a 40 μm coating tool. The heating condition was set from 30 °C to 200 °C at 5 °C/min, and maintained at 200 °C for 30 min [9,11].

2.4.3. Dynamic mechanical analysis (DMA)

The viscoelastic behavior of the synthesized polyester coatings is an important factor for evaluating the coating performance as a function of 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 (ν_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 [4,7]:

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

The test method was a tensioilm mode under the following conditions: a frequency of 1 Hz, strain of 0.1% and temperature from –80 °C to 200 °C at a heating rate of 2 °C/min.

2.4.4. Physical properties

To evaluate the change of surface hardness of each cured primers, the pendulum hardness was measured by a pendulum hardness tester (Ref. 707PK, Sheen Instruments Ltd.) according to the König method (ANS/ISO 1522) at 23 ± 1 °C and $50 \pm 2\%$ [12]. The adhesion between the primer and the steel substrate was evaluated using a cross-cut tester according to the ASTM D 3359-09. The distance between cuts is 1 mm with a cutting guide. The classification of adhesion test results is 0B when over 65% flaking of the crosscut area is occurred and 5B when no flaking is observed. The degree of 1–4B was determined between 0B and 5B [13,14].

2.4.5. Tensile strength

The flexibility of the polyester primers was determined from tensile tests using a Texture Analyzer (TA-XT2i) with rectangle-shaped specimens according to the ASTM D-638-10 method. The tensile strength was calculated by dividing the maximum load in newtons (N) by the average original cross-sectional area (mm²) in the gage length segment of the specimen. The percent elongation (strain %) was calculated by dividing the change in gage length by the original specimen gage length, expressed as a percentage (%) [9,15].

2.4.6. Deep drawing test

Rectangular deep drawing test was performed to examine the formability of the coated metal sheet as shown in Fig. 3. The cup size of the punch was 50 mm × 50 mm and the shoulder radius of the die were 5 mm. The test was performed at 25 °C and the speed of punch was 17 mm/s. After drawing, defects to the coated films of samples were observed via optical microscope [16].

2.4.7. Salt spray test

The anti-corrosion property was measured using a salt spray tester. 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 °C. After 1000 h, the changes of surface morphology, especially around the cross-line on the coating was measured based on ASTM D 610-08 [17,18].

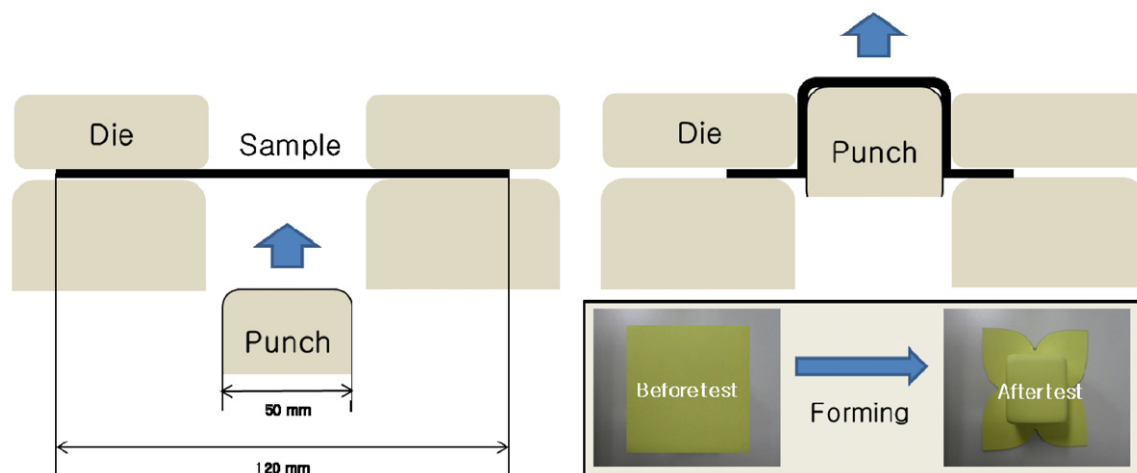


Fig. 3. The concept of a rectangular deep drawing test.

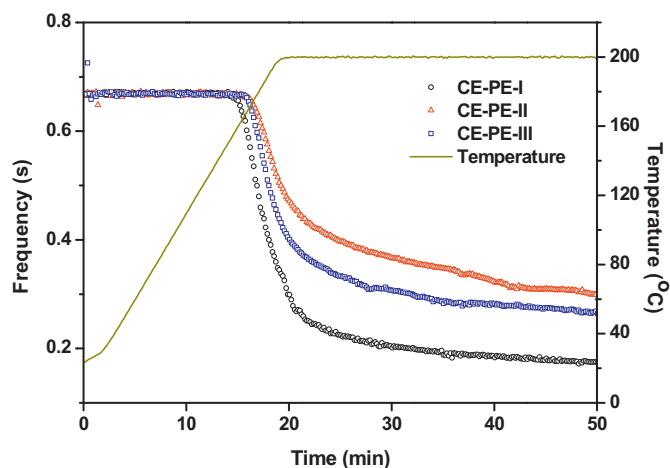


Fig. 4. Curing behavior (change of frequency(s) and initial curing point) of elastomeric polyester primers on steel substrate using a RPT instrument.

3. Results and discussion

3.1. Characterization of polyester-based resin

Generally, a commercial automotive primer was required physical properties, such as the stone chip resistance, anti-corrosion, good adhesion to the basecoat, etc. The E-PE series focused on high molecular weight, low crosslink density and linear structure to overcome harsh conditions during the cutting, pressing and stamping processes in an automotive pre-primed system. Table 3 lists the characteristics of synthesized resin such as molecular weight, polydispersity, theoretical hydroxyl value, and crosslink density. In our designed formulation, the theoretical hydroxyl number of polyester resins, n_{OH} , was designed from 20 to 35. As the result of GPC, we prove that E-PE-I has the highest average molecular weight comparing other resins as following our design.

3.2. Curing behavior

Curing behavior is an important property in automotive pre-primed system because drying and curing zone in the roll coating application are much shorter than the conventional automotive process. The RPT instrument detects the curing behavior of the coatings on the steel substrate as a function of temperature. As shown in Fig. 4, the initial curing of each coating began at approximately 165 °C and continued to 165–200 °C for 15 min. The change in the frequency of each coating was similar. However, at final frequency was in the following order: CE-PE-II > CE-PE-III > CE-PE-I. Generally, the final frequency is related to the stiffness of coating, thus the result suggests that CE-PE-I is stiffest than other samples [9].

3.3. Viscoelastic behavior

Fig. 5 shows the storage moduli as a function of temperature. The CE-PE series were in the following order: CE-PE-I > CE-PE-III > CE-PE-II. CE-PE-I had highest elasticity than that of the other resins and CE-PE-III has also good elastic property in spite of flexible segment from the 1,6-hexandiol and adipic acid which is contained many flexible rod-like group such as $-CH_2$. However, storage moduli of CE-PE-II were lower than those of other resins. Generally, steric effects depending on the size or number of the pendant group hinder the rotation about backbone and cause increasing of T_g . In addition, crosslink density is a factor to increase storage modulus of a polymer [19]. Comparing CE-PE-II to CE-PE-III, steric effects of CE-PE-II are larger than those of CE-PE-III because of high content of

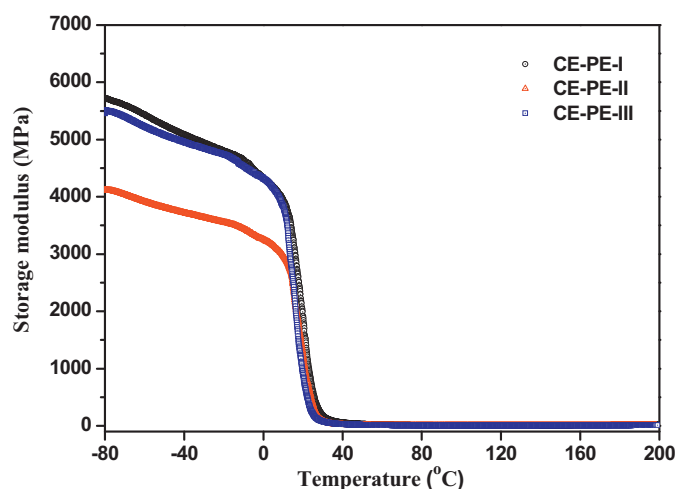


Fig. 5. Storage modulus from the DMA results of the elastomeric polyester primers.

neopentyl glycol and isophthalic acid which are caused hindrance of rotation about backbone. However, crosslink density of CE-PE-III is higher than that of CE-PE-II. Hence, crosslink density is more effective factor to storage modulus in this study. According to Fig. 6, the T_g of each cured coating was similar at 29 °C, thus the result suggests that synthesized resins can prevent the effect of softening which occurs above T_g by the drawing temperature (25 °C).

3.4. Physical properties

Fig. 7 shows the pendulum hardness of each cured coatings on GA substrates. Surface hardness of CE-PE series was around 120–140 s because of that the T_g of CE-PE series was similar to each other. In general, the T_g of an amorphous polymer is an excellent probe of its chain stiffness, which is related to its hardness [20]. As shown in Fig. 8, the adhesion between the coating and the substrate is 5B which was no flaking observed. For this reason, all coatings have high adhesion on the galvanized steel sheet.

3.5. Flexibility

Tensile strength and elongation are an effective factor to estimate the flexibility and stiffness of the cured coatings Fig. 9 shows a plot of the results of a stress–strain test, in which a coating film is

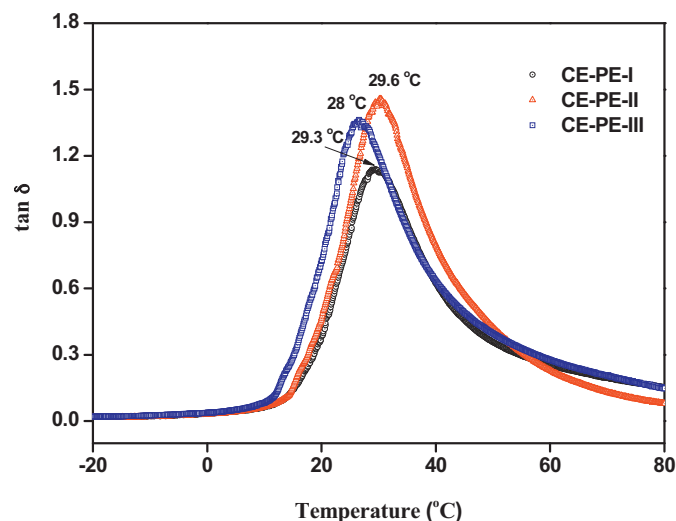


Fig. 6. $\tan \delta$ from the DMA results of the elastomeric polyester primers.

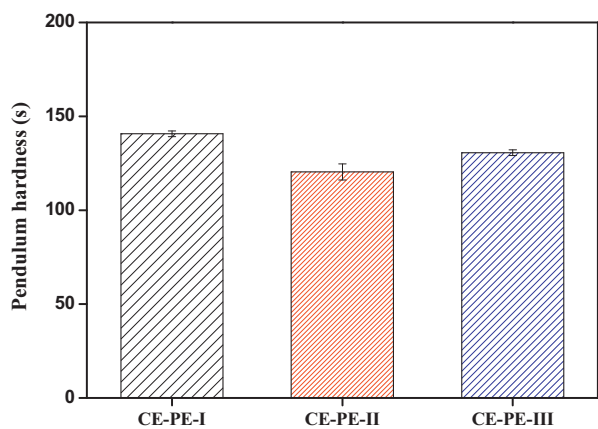


Fig. 7. Pendulum hardness of the elastomeric polyester primers on GA substrates (pendulum type: König).

elongated at a constant rate and the resulting stress is recorded. This result shows the order of tensile strength which was similar to that of the storage modulus (CE-PE-I > CE-PE-III > CE-PE-II). CE-PE-I and III have high stress and elongation values, and the maximum stress of CE-PE-I was approximately 11.3 MPa. In terms of elongation, CE-PE-I and III were stretched approximately twice than CE-PE-II. In contrast, the stress and strain value of CE-PE-II was poor, despite the low crosslink density. Generally, the long crosslinks would permit molecular slippage and hence allow better load distribution and higher elongation [21]. However, a low crosslink density, made from a low hydroxyl number, caused low elongation that 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 [22,23].

3.6. Formability

Formability of coatings is commonly evaluated using by a deep drawing tester which can control forming ratio of sample at different punch speed. As shown in Fig. 10, the CE-PE series were formed

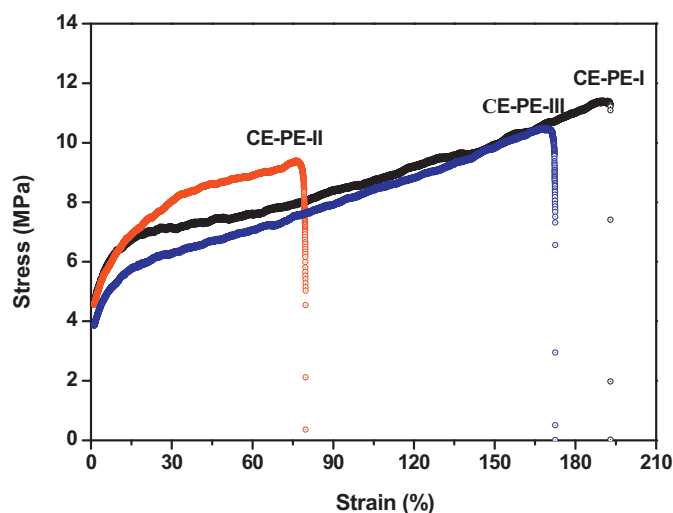


Fig. 9. Stress–strain curve of the elastomeric polyester primers.

to a rectangular cup with 17 mm/s. After 48 mm drawing, defects such as cracks and tears were not observed at the side of all drawn samples. However, the side of drawn cup was tone, excepting that of CE-PE-I after 57 mm drawing. According to these result, CE-PE-I has better formability in deep drawing than that of CE-PE-II and III. In addition, the defects of CE-PE-III were smaller than those of CE-PE-II.

3.7. Anti-corrosion property

Anti-corrosion property is an important property in automotive coatings. In the automotive pre-primed system, primers must be satisfied to anti-corrosion property because of deleting dip coating process such as an electrocoating. Fig. 11 shows that the CE-PE series and an electrocoating which were appeared a clear morphology after 1000h exposure time in the salt spray condition. According to these results, CE-PE series had good anti-corrosion property comparing that of an electrocoating.

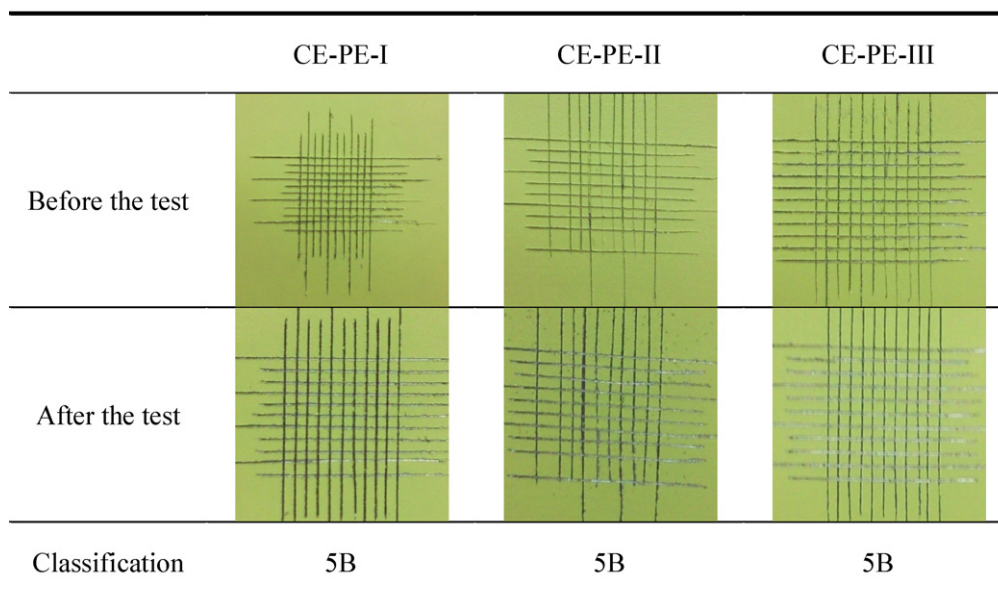


Fig. 8. Adhesion of the elastomeric polyester primers using a cross-cut tester.

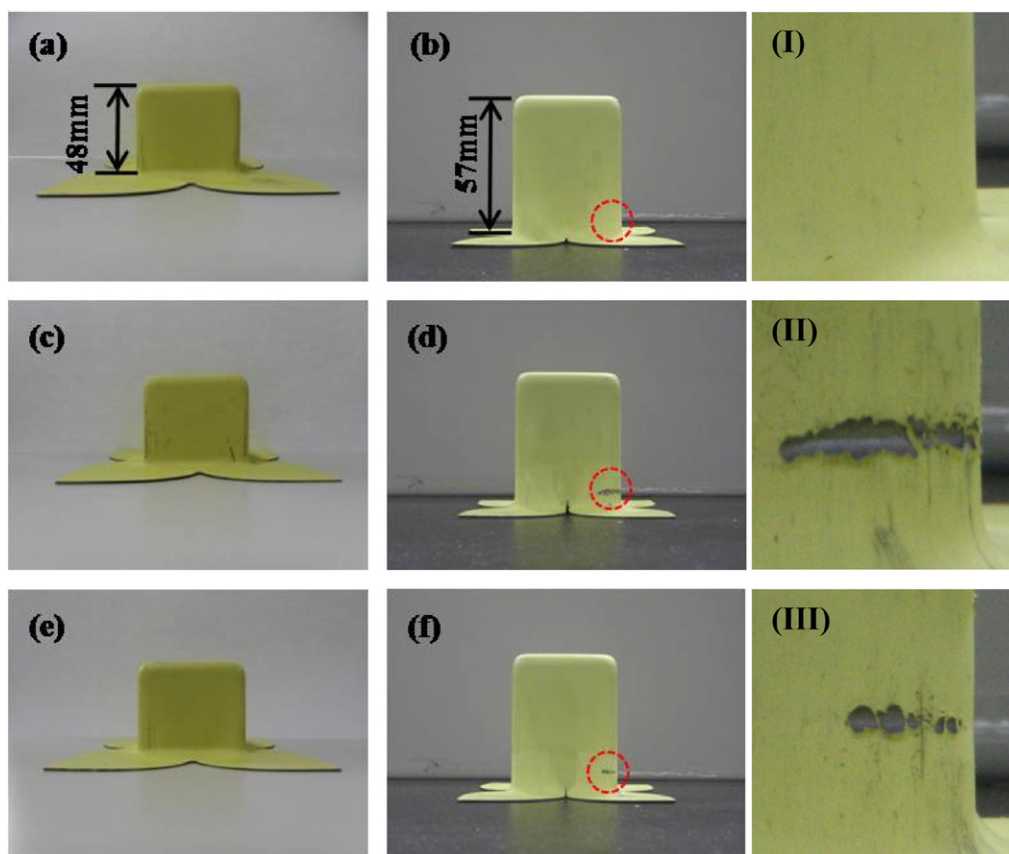


Fig. 10. Formability of the elastomeric polyester primers on GA substrate using a rectangular deep drawing tester; (a) and (b), CE-PE-I; (c) and (d), CE-PE-II; (e) and (f), CE-PE-III, defects of each coatings; (I) CE-PE-I, (II) CE-PE-II, (III) CE-PE-III.

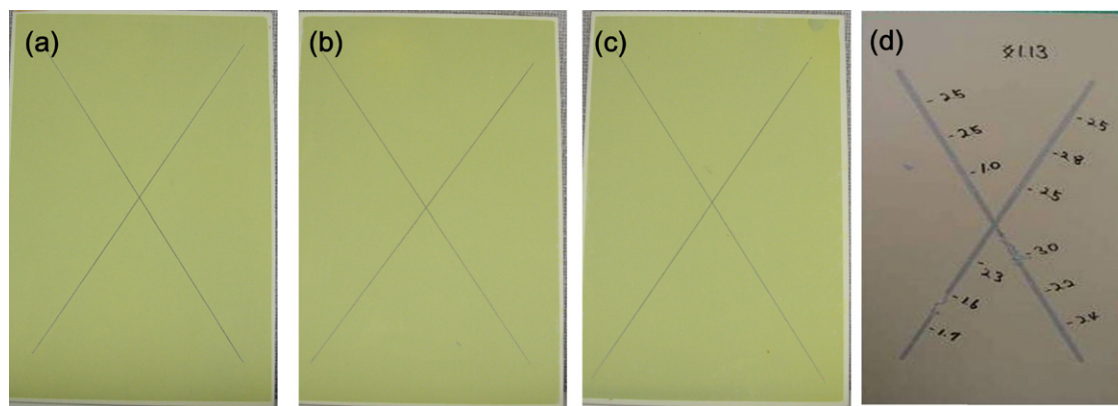


Fig. 11. Anti-corrosion property of automotive pre-primed coatings on GA substrates using a salt spray test method (1000 h); (a) E-PE-I, (b) E-PE-II, (c) E-PE-III, and (d) electrocoating.

4. Conclusion

We designed automotive primers to replace dip coating processes using a roll coating application for an automotive pre-primed coating system. Three resins were focused on high molecular weight, low crosslink density and content of flexible segment to improve flexibility and formability. The curing and viscoelastic behavior, physical properties, flexibility, formability, and anticorrosion property were measured to evaluate the factors of investigated primers for an automotive pre-primed system.

Regarding the curing behavior, the synthesized primers exhibited a similar curing time and curing temperature. However, at the end of curing, the frequency was different to each other as following

order (CE-PE-II > CE-PE-III > CE-PE-I). The final frequency is related to the stiffness of coating, thus the result suggests that CE-PE-I is stiffest than other samples. According to DMA analysis, CE-PE-I had the highest elasticity than that of the other resins and CE-PE-III has also good elastic property in spite of flexible chain segment from the 1,6-hexandiol and adipic acid which are contained many flexible rod-like group such as $-\text{CH}_2$. In terms of the $\tan \delta$ result, T_g of primers was similar to each other, thus surface hardness of CE-PE series was around 120–140 s. For tensile results, CE-PE-I and III have good tensile strength and elongation values. From the result of drawing test, no defects were observed at the side of all drawn samples after 48 mm drawing. However, the side of drawn cup was tone, excepting that of CE-PE-I after 57 mm drawing. In addition,

the defects of CE-PE-III were smaller than those of CE-PE-II. Consequently, high molecular weight and the content of flexible segment are powerful factors affecting the formability for an automotive pre-primed system.

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