



Synthesis and characterization of acrylic-grafted polyester coatings for automotive pre-coated metal

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ABSTRACT

An automotive pre-coated metal (PCM) system has been 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 stiffness to overcome the harsh conditions such as encountered in cutting, press and the stamping process. For these reasons, a series of acrylic-grafted polyester coatings (i.e., AGP-0, AGP-10, AGP-20, AGP-30) were designed to satisfy both the surface hardness and the formability for an automotive PCM. The characteristics of the resins were measured by GPC, FT-IR and ¹H NMR. The viscoelastic behavior and flexibility was evaluated using DMA and UTM. The physical properties such as pendulum hardness, pencil hardness and adhesion were measured to define the effect of incorporating acrylates. A cylindrical deep drawing tester was used to evaluate the formability of coatings.

With increasing acrylate content, the storage modulus and T_g of the coatings increased because of increasing entanglement from long chain branches of acrylates and the cross-link network between a hydroxyl function of 2-HEMA and the polyester backbone. In terms of surface hardness, AGP-30 has the maximum hardness because of the high hardness of MMA. According to the tensile strength test, the result was similar to that of DMA with increasing acrylate content. From the result of formability, some defects occurred after the 30 mm drawing test, excepting that of AGP-10. In the case of the AGP-0 system, the coating film was destroyed by die pressure because of that the maximum tensile strength is lower than 5 MPa. The large defects occurred when cross-link density of the coating increased, in this case the destruction of cross-link networks is hardly occurred. Consequently, acrylic-grafting is a powerful method affecting both the surface hardness and the formability of the polyester coatings for an automotive PCM.

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1. Introduction

Currently, the automotive industry is faced with environmental regulations such as the European Unions' Directive 2000/53/EG, the 'Registration, Evaluation, Authorisation and Restriction of Chemicals' (REACH) and the Biocidal Products Directive 98/8/EC. These regulations demand reduction of solvent or wastes of industrial products, and to reuse or recycle end of life vehicles [1]. In addition, the automotive market of developing countries, such as China, India and other nations, has increased quickly. In particular, to examine how the rush to produce smaller and cheaper cars, is being driven by the emerging markets. The world's major automakers are competing to produce the cheapest car in terms of design, methodology

and approach [2,3]. Therefore, overcoming environmental regulations and satisfying the automotive trend of developing countries are important issues in the automotive industry.

Pre-coated metal (PCM) system is manufactured in a sheet or coil coating line and assembled in factories for household electric appliances, building materials and others. In this system, a wet coating process can be eliminated by using a roll coating process, thereby the problem of solvent evaporation can be eliminated. In addition, PCM offers other advantages such as improving productivity and energy saving [4].

Based on these reasons, the automotive pre-coated metal (automotive PCM) 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 [4–8] (Fig. 1).

Polyesters are widely used in pre-coated metal sheet, especially for purposes of improved exterior durability and corrosion protection. In addition, polyesters can control physical properties and

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Table 1
Formulation of the acrylic-grafted polyester resin (unit: mole of monomer).

Contents	AGP-0	AGP-10	AGP-20	AGP-30
Propylene glycol	3	3	3	3
Neopentyl glycol	13	13	13	13
Trimethylol propane	3	3	3	3
1,6-Hexanediol	9	9	9	9
Fumaric acid	3	3	3	3
1,4-Cyclohexanedicarboxylic acid	23	23	23	23
Methyl methacrylate	0	5	10	15
2-Hydroxyethyl methacrylate	0	2	4	6
Curing agent (HMMM) ^a	1.1	1.6	2.0	2.5

^a Curing agent was used after synthesis of polyester resin.

curing conditions using various curing agents such as choice of melamine formaldehyde (MF) and blocked isocyanate. Polyesters have better adhesion to metal substrates and better impact resistance than that of acrylics. In contrast, acrylics give coatings with superior water resistance, gloss and exterior durability. Therefore, acrylics are a common material for automotive clearcoat [4,9].

In one of our previous studies, polyester resins were synthesized with polycarbonatediol to control the flexibility for an automotive PCM. The resins were designed to demonstrate the flexible chain effect using polycarbonatediol. According to results, the synthesized polyester coatings had high elongation value and good scratch resistance for the stamping, pressing and cutting process in an automotive PCM [4]. However, in terms of the surface hardness, this system is not sufficient to satisfy physical properties compared to a conventional automotive clearcoat. In this study, we designed flexible unsaturated polyester resin and grafted two kinds of acrylate (methyl methacrylate, 2-hydroxyethyl methacrylate) onto synthesized unsaturated polyester to improve surface hardness in an automotive PCM. The characteristics of the resins were measured by GPC, FT-IR and ¹H NMR. The viscoelastic behavior, flexibility and physical properties such as pendulum hardness, pencil hardness and adhesion were measured to define the effect of incorporating acrylates. A cylindrical deep drawing tester was used to evaluate the formability of coatings.

2. Experimental

2.1. Materials

Fumaric acid (Tokyo Kasei), contained a C=C bond structure was used to react with the acrylates. Propylene glycol (Samchun Chemical), neopentyl glycol (Tokyo Kasei), trimethylol propane (Tokyo Kasei), 1,6-hexanediol (Samchun Chemical), 1,4-cyclohexanedicarboxylic acid (Tokyo Kasei) were used for preparation of unsaturated polyester resins without further purification. Methyl methacrylate (Samchun Chemical) was used to improve surface hardness. 2-Hydroxyethyl methacrylate (Samchun Chemical), contained a hydroxyl functional group was used to cure with a curing agent.

Hexamethoxymethylmelamine (HMMM, Cytec), a curing agent in pre-coated metal system, was used. An amine type curing catalyst (NACURE 5925) was supplied from KING industry. Butylstannic acid (FASCAT 4100, Arkema Inc.) was used as a catalyst to catalyze polymerization and prevent a transesterification reaction during the synthesis reaction [4]. Table 1 lists the synthesis formulation of the polyester resin.

2.2. Synthesis of the acrylic-grafted polyester resin

2.2.1. Synthesis of the unsaturated polyester

Unsaturated polyester was synthesized using propylene glycol, neopentyl glycol, trimethylol propane, 1,6-hexanediol, fumaric acid and 1,4-cyclohexanedicarboxylic acid according to the following process. A 500 mL 4-neck round type reactor, fitted a temperature controller, heating mantle, N₂ 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 °C for 1 h. Subsequently, the reaction temperature was increased from 160 °C to 200 °C at 0.5 °C/min. During the synthesis process, the acid value titration was performed using a 0.1 N KOH solution [4].

2.2.2. Synthesis of the acrylic-grafted polyester resin

The resin was designed as a hydroxyl-functional acrylic-grafted polyester resin by solution polymerization technique using a free radical initiator, benzoyl peroxide (BPO, 1% based on total monomer weight). Into a 250 mL 4-necks round type reactor, fitted temperature controller, heating mantle, N₂ purge, condenser and an impeller, was placed with the unsaturated polyester resin and butyl acetate. The reactor was heated at 120 °C, the mixture of methyl methacrylate, 2-hydroxyethyl methacrylate and 1 wt% BPO were added into the reactor using a syringe pump for 2 h. During the synthesis process, the progress of the free radical reaction was followed by FT-IR by monitoring the disappearance of C=C double bond of all raw materials. Afterwards, the initiator was quenched by hydroquinone monoethylether (MEHQ). Scheme 1 shows the synthesis process of the acrylic-grafted polyester resin [4].

2.2.3. Preparation of the acrylic-grafted polyester coatings for automotive PCM

The acrylic-grafted polyester coatings were coated on galvanized steel sheet using a 40 μm bar coater and cured at 150 °C for 30 min. The cured films, prepared for DMA analysis and tensile strength test were coated on a disposable aluminum dish and cured under the same conditions. The width and thickness of cured films were 7.0 mm and 0.5 mm [4].

2.3. Methods

2.3.1. Characterization of the acrylic-grafted polyester resin

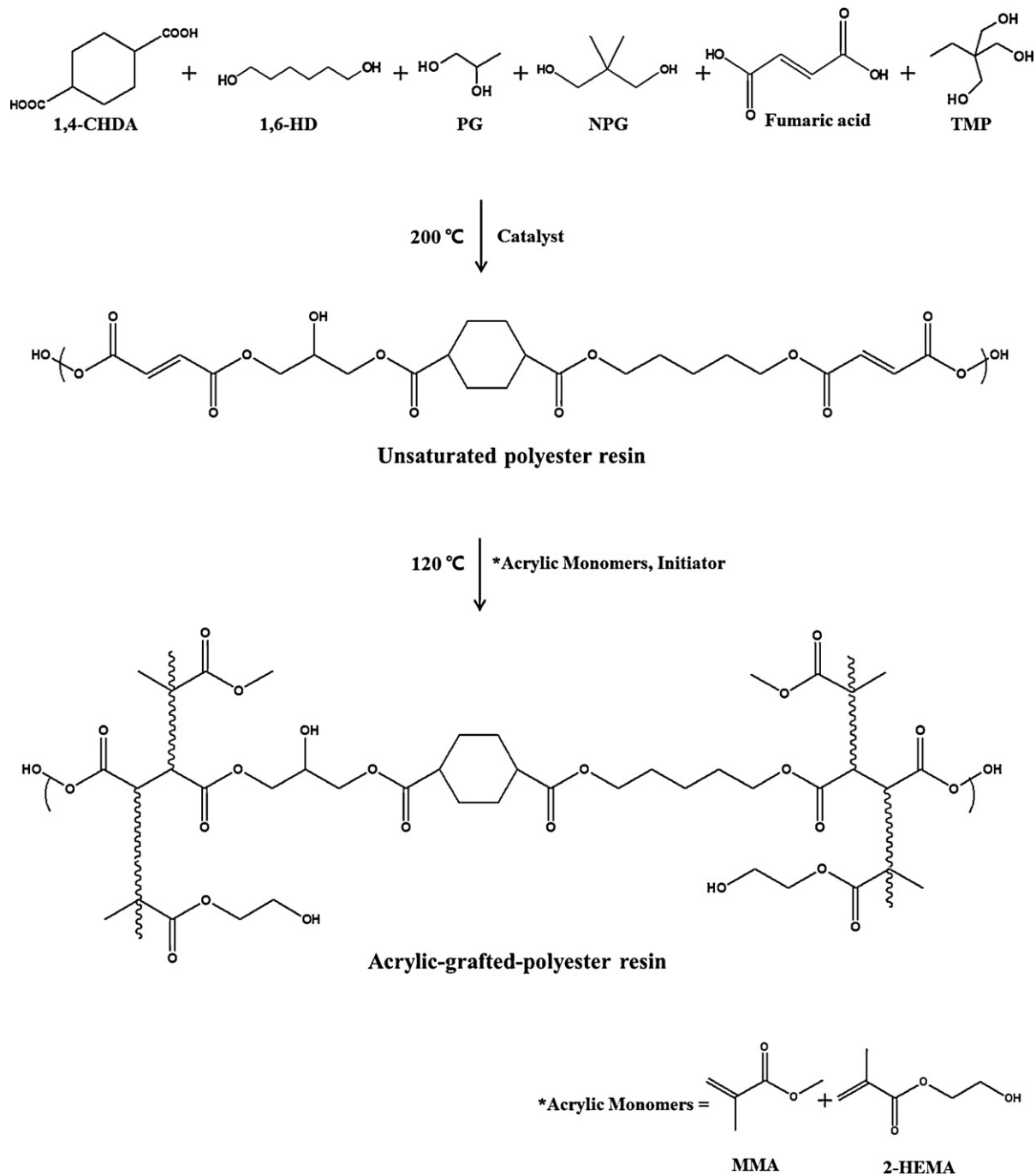
The molecular weight and polydispersity were measured using an YL9100 GPC SYSTEM (Young Lin, Korea) equipped with a pump, a RI detector and a Waters Styragel HR 5E column. The polystyrene and poly(methyl methacrylate) calibration standards were used. Tetrahydrofuran was used as the eluent, and the flow rate was 1 mL/min.

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

The ¹H NMR spectra was measured to characterize the composition of the acrylic-grafted polyester resins using a 400 MHz NMR spectrometer (JeolJNM-LA400, JEOL Ltd., Japan).

2.3.2. Dynamic mechanical analysis (DMA)

The viscoelastic behavior of the acrylic-grafted 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 cross-link density. The



Scheme 1. Synthesis process of the acrylic-grafted polyester resin.

cross-link 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 cross-link density was calculated using the following equation [4,8]:

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

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 $2^\circ\text{C}/\text{min}$.

2.3.3. Surface hardness test

To evaluate the change of the surface hardness of each cured coatings, the pendulum hardness of the 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 scratch resistance was measured using a No. 553 pencil hardness tester (Yasuda Seiki Seisakusho Ltd.). The test is in order to ASTM D3363-05 [10–12].

2.3.4. Adhesion test

The adhesion between the coating and the steel substrate was evaluated using a cross-cut tester according to the ASTM D3359-09. The distance between cuts is 1 mm with a cutting guide. The

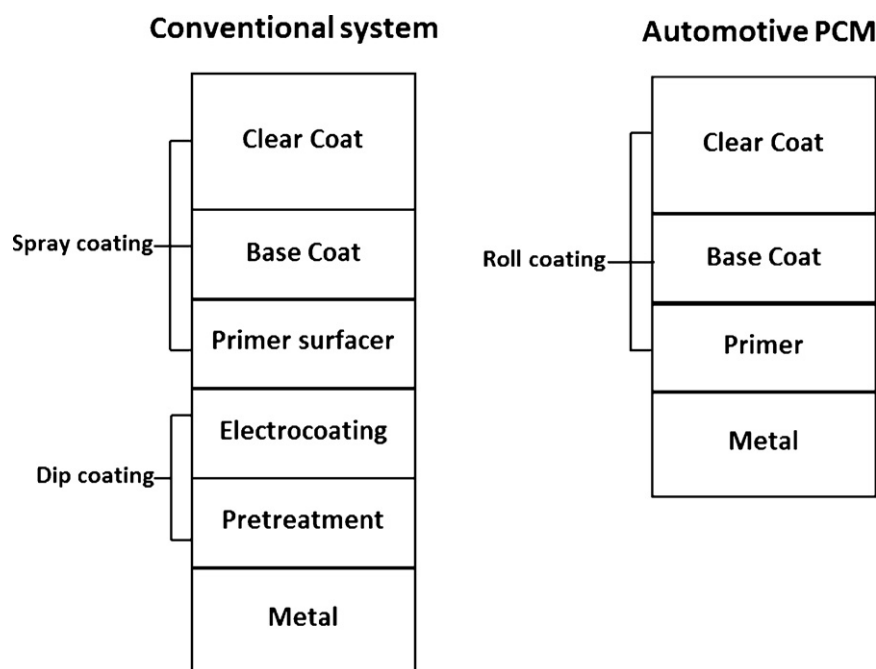


Fig. 1. The concept of an automotive pre-coated metal system comparing a conventional automotive coating system.

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].

2.3.5. Tensile strength test

The flexibility of the acrylic-grafted polyester coatings was determined from the tensile strength test using a universal testing machine (UTM, Zwick GmbH) with rectangle-shaped specimens according to the ASTM D638-10. 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 (%) [4,15].

2.3.6. Deep drawing test

A cylindrical deep drawing test was performed to examine the formability of the coated metal sheet in an automotive assembly line as shown in Fig. 2. The punch size of deep drawing was 40 diameter (mm) and the temperature of deep drawing die was 25 °C. The speed and pressure of the deep drawing machine were 20 mm/min and 4500 kg. The integrity of the coating film after deep drawing test was evaluated by observing of the appearance of formed parts. Table 2 shows the conditions of the cylindrical deep drawing test for evaluating the formability [5,16].

Table 2
Conditions of the cylindrical deep drawing test.

Contents	Conditions
Shape of punch	Cylinder
Shoulder radius of punch	5 mm
Shoulder radius of die	5 mm
Size of punch	∅40 mm
Size of PCM sheet	∅105 mm
Drawing height	30 mm
Punch speed	20 mm/min

3. Results and discussion

3.1. Characterization of polyester resin

The acrylic-grafted polyester coatings focused on the effect of acrylates for improving surface hardness of coatings. Generally, a commercial automotive clearcoat requires physical properties such as the scratch resistance, stone chip resistance and gloss. However, additional properties such as flexibility and stiffness are required to overcome harsh conditions during the cutting, pressing and stamping processes in an automotive PCM [9]. Table 3 lists the molecular weight and polydispersity of the polyester resin, determined by GPC.

In our designed formulation, theoretical hydroxyl number of the polyester resin, n_{OH} increased with the content of 2-HEMA to make cross-link network between the grafted acrylic branches and the polyester backbone. According to the result of GPC, the number average molecular weight (M_n) increased with the amount of acrylates because of increasing the length of acrylic branches onto C=C double bond of unsaturated polyester resin. In addition, the ratio between the molecular weight and hydroxyl number (M_n/n_{OH}), which is a length of the polymer chain between the cross-links was also decreased with increasing 2-HEMA content [8]. FT-IR was used to characterize the decreasing C=C double bonds in the polyester resin. As shown in Fig. 3, the C=C double bonds from fumaric acid was detected at 980 cm^{-1} and the amount of C=C double bond decreased with increasing acrylate content.

Table 3
Characterization of the acrylic-grafted polyester resin.

Property	AGP-0	AGP-10	AGP-20	AGP-30
Number of average molecular weight (g/mol)	4200	4470	4770	4900
Polydispersity (M_w/M_n)	2.2	3.9	4.6	5.1
n_{OH} (mg KOH/g) ^a	43	60	78	95
M_n/n_{OH} (g/mg KOH)	97.7	73.8	61.1	51.2
Crosslink density (10^{-3} mol/cm^3)	0.2	0.4	1.1	1.5

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

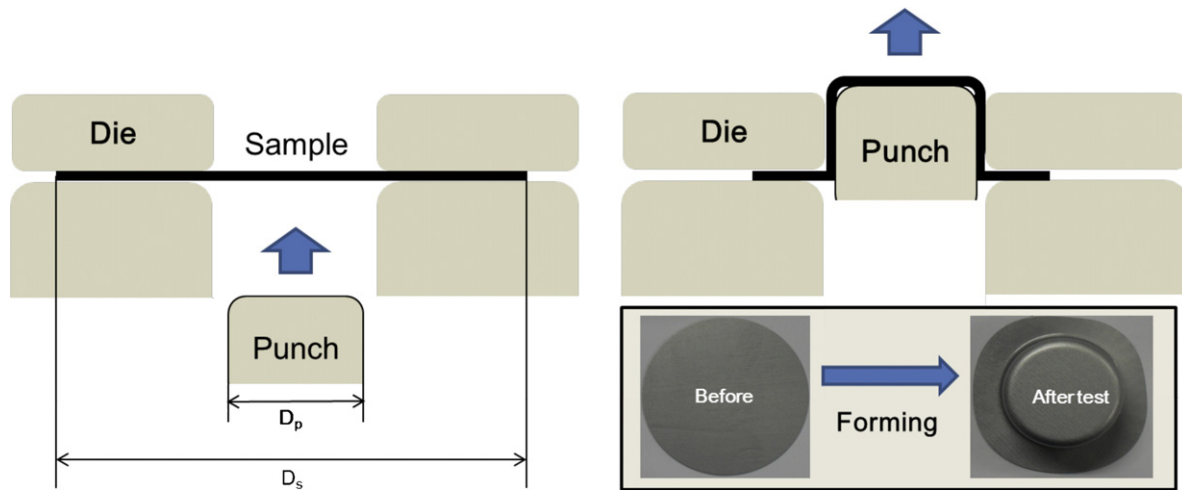


Fig. 2. The concept of a cylindrical deep drawing test. D_s , diameter of sample; D_p , diameter of punch.

The ^1H NMR spectra of AGP series with the assignments are shown in Fig. 4. The characteristic peak at 6.80 ppm is assigned to the vinyl protons of the fumaric acid. In comparison, in case of the AGP-30, 6.80 ppm peak is disappeared because of consuming the C=C double bonds after graft polymerization. The three groups of characteristic peaks at 3.67, 3.81 and 4.27 ppm are observed, which prove the existence of protons in the molecular structure of acrylates. From the ^1H NMR spectra, MMA and 2-HEMA are both introduced into the polymer chain of synthesized resin.

3.2. Viscoelastic behavior

Fig. 5 shows the storage modulus as functions of the steric hindrance of acrylic branches and the cross-link network from 2-HEMA. The stiffness increased considerably, when the content of acrylates was increased. This tendency was in the following order: AGP-30 > AGP-20 > AGP-10 > AGP-0. The result was explained by increasing entanglement from long chain branches of acrylates and the cross-link network between a hydroxyl group from 2-HEMA and the polyester backbone. In general, the improvement of

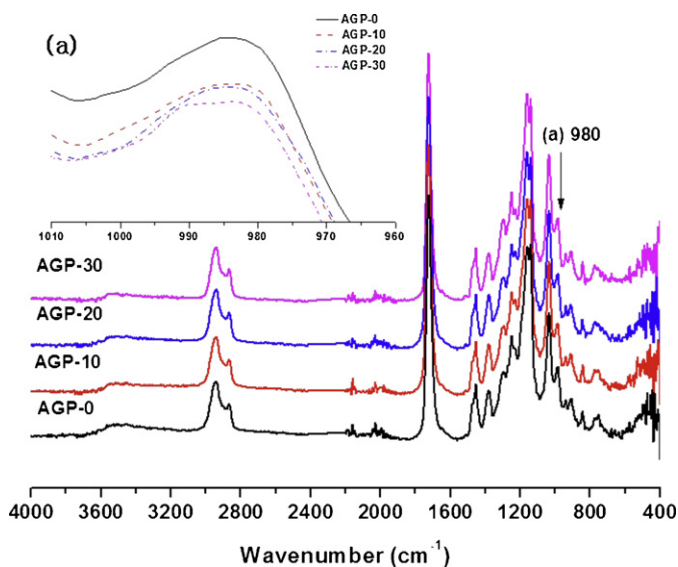


Fig. 3. IR spectra of the acrylic-grafted polyester resins: (a) the C–H bending vibration from C=C double bonds (*trans*) of fumaric acid.

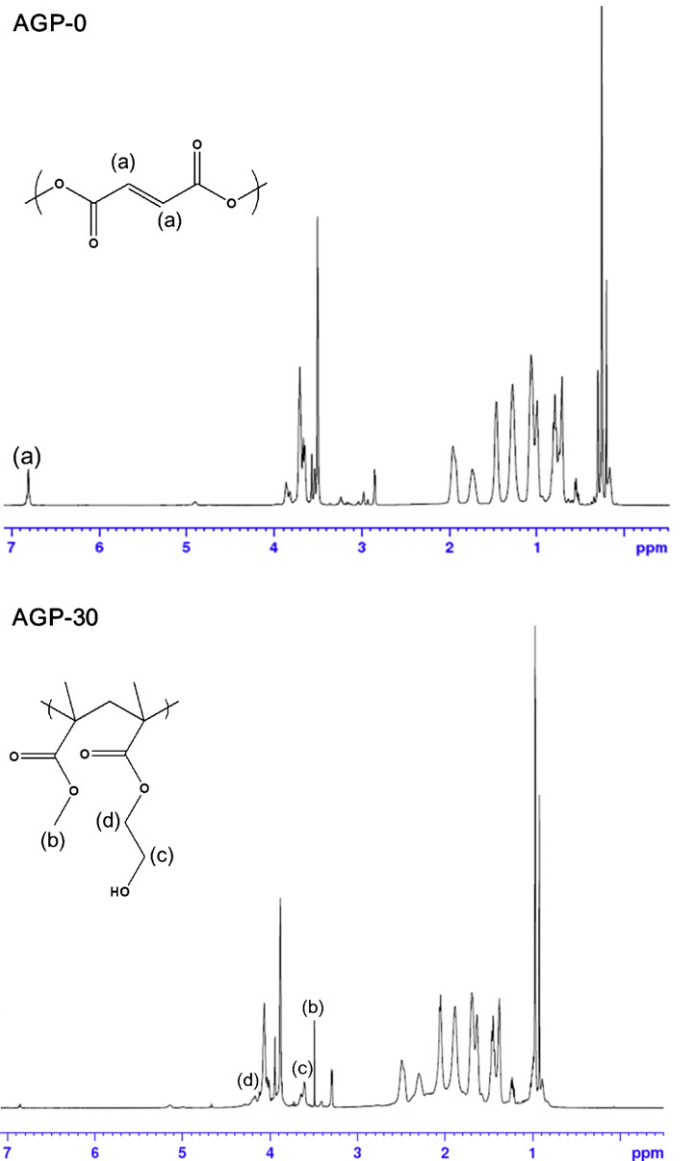


Fig. 4. ^1H NMR spectrum of the acrylic-grafted polyester resins.

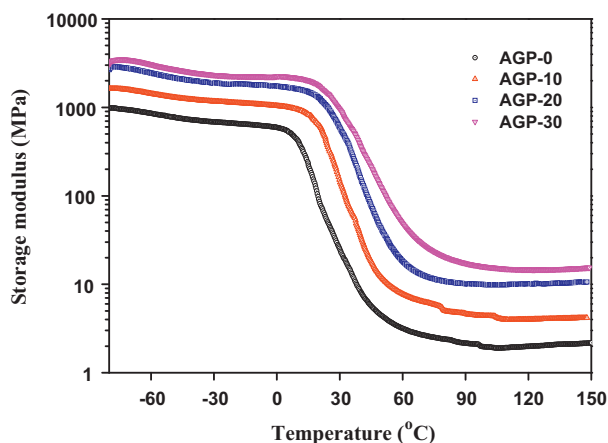


Fig. 5. Storage modulus from the DMA results of the acrylic-grafted polyester coatings.

modulus is observed with amount or length of chain branches which are caused the entanglement [17].

In addition, cross-link density is a factor to increase storage modulus of a polymer. As shown in Table 3, the cross-link density (ν_c) increased, whereas the length between the cross-links was decreased with increasing acrylate content. Generally, the mobility and flexibility of the polymer chain decreased with decreasing the ratio between the molecular weight and hydroxyl number (M_n/n_{OH}), which is a length of the polymer chain between the cross-links [8].

Fig. 6 shows that the T_g was shifted to a higher temperature due to the content of acrylates. The result is explained that high T_g of MMA and increasing cross-link density affect to the T_g of coatings [18].

3.3. Physical properties

Fig. 7 shows the surface hardness of the acrylic-grafted polyester coatings with increasing acrylate content. In the result, AGP-30 has maximum hardness around 237 sec and 2H because of high hardness of MMA. Adhesion of each coating was evaluated using a cross-cut tester. As listed in Table 4, 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.

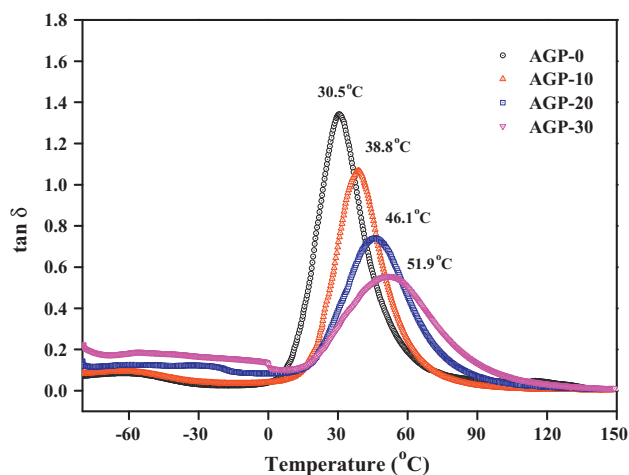


Fig. 6. Tan δ from the DMA results of the acrylic-grafted polyester coatings.

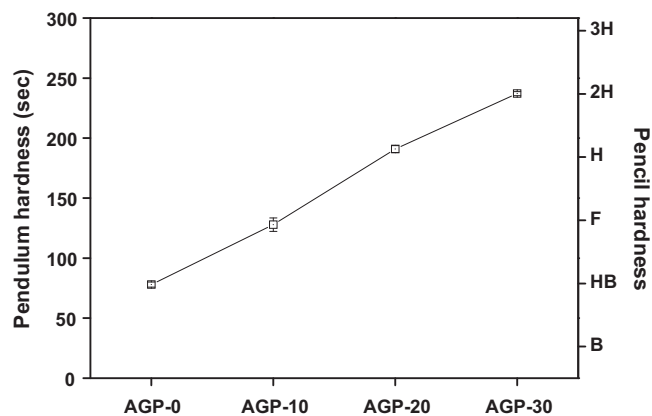


Fig. 7. Surface hardness of the acrylic-grafted polyester coatings with different acrylate content: pendulum hardness vs. pencil hardness.

3.4. Flexibility

Analysis of the tensile strength and elongation is an effective way to estimate the flexibility in the cured films. Fig. 8 shows the order of the tensile strength which was similar to that of the storage modulus ($AGP-30 > AGP-20 > AGP-10 > AGP-0$). The stress increased with acrylate content and the maximum stress of AGP-30 was approximately 17 MPa. In comparison, the elongation of coatings decreased with acrylate content. However, the rate of decreasing elongation was lower than that of increasing tensile strength with acrylate content.

In the case of AGP-30, the elongation at break was approximately 85% which is enough to apply for a forming process in an automotive PCM.

3.5. Formability

Formability of coatings is commonly evaluated using by a deep drawing tester which can control forming ratio of sample at different pressure and punch speeds. As shown in Fig. 9, the AGP series were formed to a cylindrical cup as following conditions in Table 2. After 30 mm drawing test, the side of the formed cup was tone, excepting that of AGP-10. For the detailed explanation, we recalculated the unit of die pressure from kilogram to MPa per total area of PCM sample as following equation.

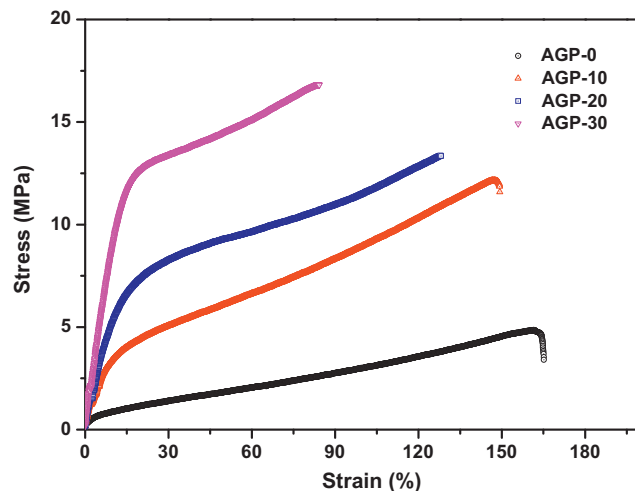


Fig. 8. Stress-strain curve of the acrylic-grafted polyester coatings.

Table 4
Physical properties of the acrylic-grafted polyester coatings.

Resins	Physical properties		
	Pendulum hardness (ANS/ISO 1522)	Pencil hardness (ASTM D3363-05)	Cross-hatch adhesion (ASTM D3359-09)
AGP-0	77.9	HB	5B ^a
AGP-10	127.9	F	5B
AGP-20	190.9	H	5B
AGP-30	237.1	2H	5B

^a 5B: when no flaking is observed after a cross-hatch adhesion test.

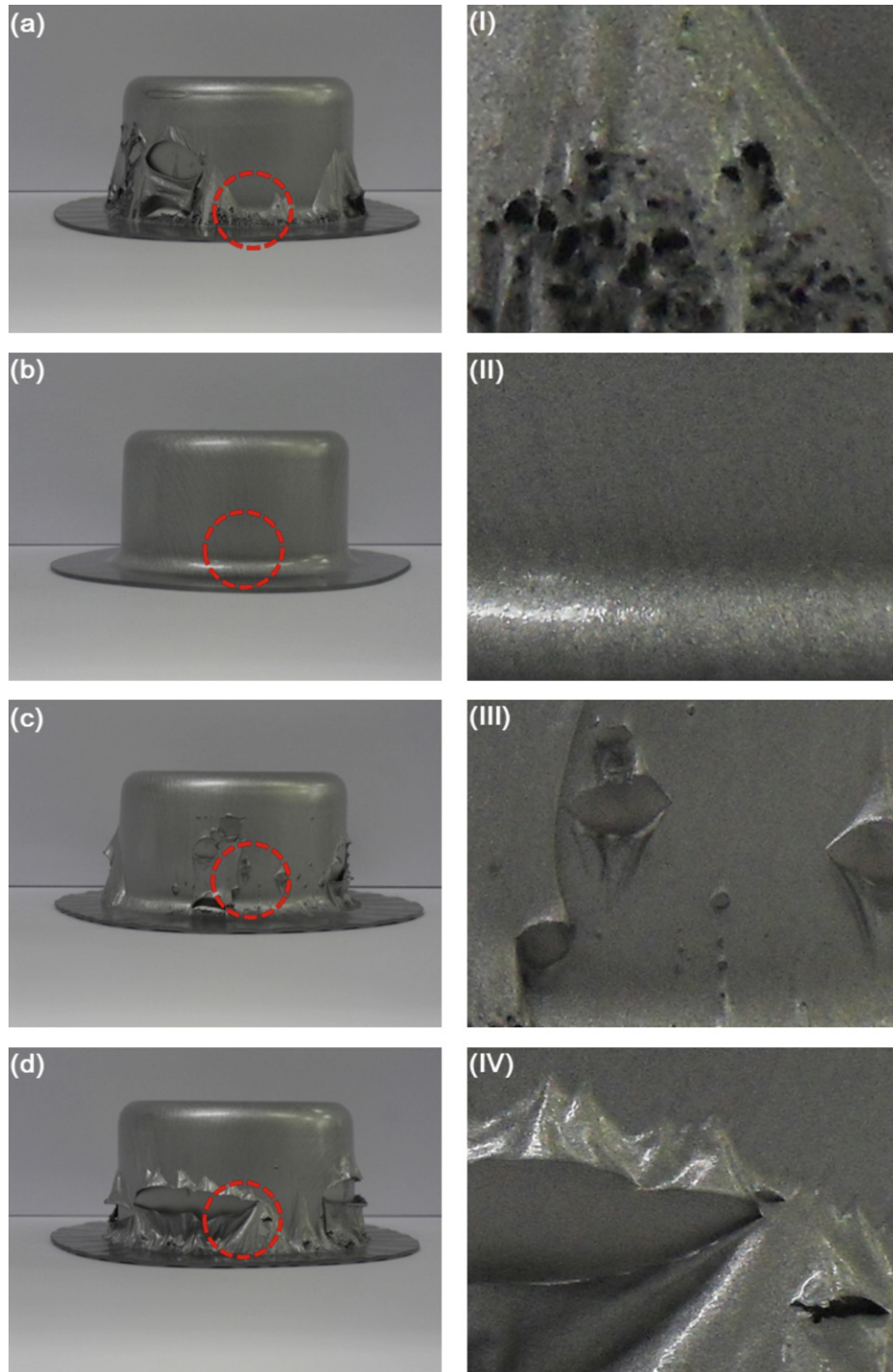


Fig. 9. Formability of AGP series on GI substrate using a cylindrical deep drawing tester: (a) AGP-0, (b) AGP-10, (c) AGP-20, and (d) AGP-30, defects of each coatings; (I) AGP-0, (II) AGP-10, (III) AGP-20, and (IV) AGP-30.

Compressive stress on PCM sample

$$= \frac{\text{die pressure (N)}}{\text{total area of sample before the drawing test (mm}^2\text{)}} \text{ (MPa)}$$

According to the equation, compressive stress on PCM sample is 5 MPa and then, the AGP-0 can be destroyed by die pressure because of that the maximum tensile strength is below 5 MPa as shown in Fig. 8. In addition, the coating film in which plastic deformation easily developed has good formability. In this case the destruction of cross-link networks occurred easily. For this reason, the large defects occurred with increasing cross-link density in the result of the AGP-20 and 30 [5,16].

4. Conclusion

We investigated an acrylic-grafted polyester resin system to improve the surface hardness satisfying formability in an automotive PCM. The resins were designed using flexible unsaturated polyester resin and grafted two kinds of acrylate (methyl methacrylate, 2-hydroxyethyl methacrylate) on synthesized unsaturated polyester. The viscoelastic behavior, physical properties, flexibility and formability were measured to determine the effect of acrylic-grafting for an automotive PCM.

Regarding the viscoelastic analysis, the stiffness increased considerably, when the content of acrylates was increased because of increasing entanglement from long chain branches of acrylates and the cross-link network between a hydroxyl group from 2-HEMA and the hydroxyl group contained polyester backbone. In terms of the $\tan \delta$ result, T_g of coatings was shifted to a higher temperature due to the content of acrylates. The result is explained based on the high T_g of MMA and increasing cross-link density affect to the T_g of coatings. In terms of surface hardness, AGP-30 has maximum hardness around 237 sec and 2H because of high hardness of MMA. According to the tensile strength test, the result was similar to that of DMA with increasing acrylate content. However, the elongation

at break of AGP-30 was approximately 85% which is enough to apply for forming process in an automotive PCM.

From the result of formability, some defects occurred after the 30 mm drawing test, excepting that of AGP-10. In the case of AGP-0, the coating film was destroyed by die pressure because the maximum tensile strength is lower than 5 MPa. In addition, the large defects occurred when the cross-link density was increased. In this case the destruction of cross-link networks is hardly occurred. Consequently, acrylic-grafting is a powerful method affecting both the surface hardness and the formability of the polyester coatings for an automotive PCM.

Acknowledgments

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