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Synthesis and formability of long alkyl chain of polyester for automotive pre-coated metals

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Abstract

Purpose – Formability is an important property of automotive pre-coated metals (PCMs). The purpose of this study is to investigate the effect of long alkyl chains of polycarbonatediol to control the formability of polyester coatings.

Design/methodology/approach – Polyester resins with long alkyl chains were synthesized using different contents of polycarbonatediol. These resins were characterised by gel permeation chromatography (GPC), ^1H nuclear magnetic resonance (^1H NMR) and fourier transform infrared spectroscopy (FT-IR). The polyester coatings were characterised according to their viscoelastic behaviour, formability, flexibility and anti-corrosion property.

Findings – The tensile strength of PCM should be larger than 5.6 MPa of the compressive stress at a strain of 23.4 per cent to overcome the harsh condition of deep drawing. To analyse the formability, F_ε (forming coefficient based on strain) and F_U (forming coefficient based on strain energy) were calculated. When F_ε and F_U were larger than 1, the polyester coatings exhibited good formability.

Research limitations/implications – Long alkyl chains of polycarbonatediol gave flexibility and good formability to the polyester coatings.

Practical implications – There are two conditions that lead to the good formability of PCM. One is tensile strength and the other is forming coefficients based on strain and strain energy.

Originality/value – Long alkyl chains of polyester were a major factor to improve flexibility and formability. Thus, to have good formability, the tensile strength of PCM should be larger than 5.6 MPa, and the forming coefficients should be larger than 1.

Keywords Polyester, Deep drawing, Formability, Forming coefficient, Pre-coated metals

Paper type Research paper

Abbreviations

A1. Materials

1,4-CHDA	= 1,4-cyclohexanedicarboxylic acid
AA	= adipic acid
IPA	= isophthalic acid
TMP	= trimethylol propane
1,6-HD	= 1,6-hexandiol
1,4-CHDM	= 1,4-cyclohexanedimethanol
PCDL	= Polycarbonatediol
MPD	= 2-methyl 1,3-propanediol
MA 100	= mitsubishi carbon black MA 100
Shieldex C303	= SHIELDEX [®] C303
HMMM	= hexamethoxymethyl melamine
PMT	= peak metal temperature

A2. Experimental

DMA	= dynamic mechanical analysis
EIS	= electrochemical impedance spectroscopy
VIEEW	= video image enhanced evaluation of weathering

A3. Results and discussion

n_{OH}	= theoretical hydroxyl number of the polyester resin
v_c	= crosslink density
R_f	= the forming ratio
ε_c	= the developed strain for 90 s by the creep test
F_ε	= the forming coefficient based on strain
U_C	= the pure strain energy of coated film during formation to 90 s from the creep test
U_T	= the pure strain energy of coated film during formation to R_f from the tensile test
F_U	= the forming coefficient based on strain energy
EDC	= electrophoretic painting

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Introduction

Many increasingly stringent environmental policies have been implemented around the world. In the automotive industry, the amount of waste water and solvent derived from wet coating processes is restricted by environmental regulations. These regulations also affect other manufacturing sectors that use coating processes. Pre-painted or coil-coated metals (PCM) provide an opportunity to eliminate the coating processes. 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. In addition, a PCM system offers other advantages such as improved productivity and energy savings (Ueda *et al.*, 2002).

The most important property of PCM is formability. If the film on the PCM is damaged, the products are rendered useless. The characteristics of coated films for good formability are dependent on the maximum strain and tensile strength of the deep drawing. As tensile strain is mainly developed in a coating film in the forming process of PCMs, coating films with high elongation are favourable. In comparison, the strain behaviour of the coating film in a deep drawing process is more complicated because both tensile and compressive strains are developed. A published study has revealed that the formability of a material is correlated to its molecular chain length and crosslink density (Moon *et al.*, 2012). However, using polybasic alcohols, such as 1,6-hexanediol (1,6-HD) and 2-methyl 1,3-propanediol (MPD), to capitalise the chain length effect did not effectively improve the formability of the PCM systems.

In this study, polyester coatings are investigated using long alkyl chains of polycarbonatediol to control and improve formability. Polycarbonatediol has long alkyl chains, which contain very flexible rod-like groups, such as $-\text{CH}_2$ (Yin *et al.*, 1998). The elongation, tensile strength and viscoelastic properties of the polyester coatings are measured to determine the effect of long alkyl chains for automotive PCMs. The formability is evaluated using cylindrical drawing. To analyse the formability, F_e (forming coefficient based on strain) and F_U (forming coefficient based on strain energy) are calculated. The relationship between the contents of polycarbonatediol and the formability of the polyester coatings is discussed.

Experimental

Materials

Polyester resins with long alkyl chains were synthesised from 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); the polybasic alcohols used were trimethylol propane (TMP; Tokyo Chemical Industry, Japan), 1,6-hexanediol (1,6-HD; Samchun Pure Chemical, Republic of Korea), 1,4-cyclohexanedimethanol (1,4-CHDM; Tokyo Chemical Industry, Japan) and 2-methyl 1,3-propanediol (MPD; Tokyo Chemical Industry, Japan). A polycarbonatediol ($M_n = 500$, Asahi Kasei Chemicals Corp., Japan) was prepared to control the flexibility of the polymer chain. Those materials were used without further purification. Butylstannic acid (FASCAT 4100; Arkema Inc., USA) was used as a catalyst to catalyse the polymerisation and to prevent the transesterification reaction during polymerisation. Hexamethoxymethyl melamine (HMMM; Cytec Industries Inc., USA) was used as a curing agent, and NACURE 1953 (King Industries, Inc., USA) was used as a curing catalyst.

Synthesis of polyester resins with long alkyl chains

The synthesis process is shown in Figure 1, and formulations of the polyester resins with long alkyl chains using polycarbonatediol are listed in Table I. The synthesis took place in a round-bottom flask equipped with a four-necked flask with a mechanical stirrer, thermometer, condenser and water trap. IPA has two carboxyl groups, one of which reacted at approximately 190°C and the second reacted at a temperature above 210°C. It, therefore, required a high reaction temperature. Polycarbonatediol can decompose at approximately 210°C. To avoid the decomposition of polycarbonatediol, a modified synthesis process was carried out as follows.

First, IPA, TMP, 1,6-HD, 1,4-CHDM and MPD were charged into a dried reactor, and the reaction temperature was set to 150°C with stirring for 2 h under a N_2 purge. Subsequently, the reaction temperature was increased from 150°C to 210°C at a rate of 0.5°C/min. All raw materials were melted, and condensed water was collected during the fusion process. Then, 1,4-CHDA, AA and polycarbonatediol were

Figure 1 Synthesis process of polyester resin with long alkyl chains

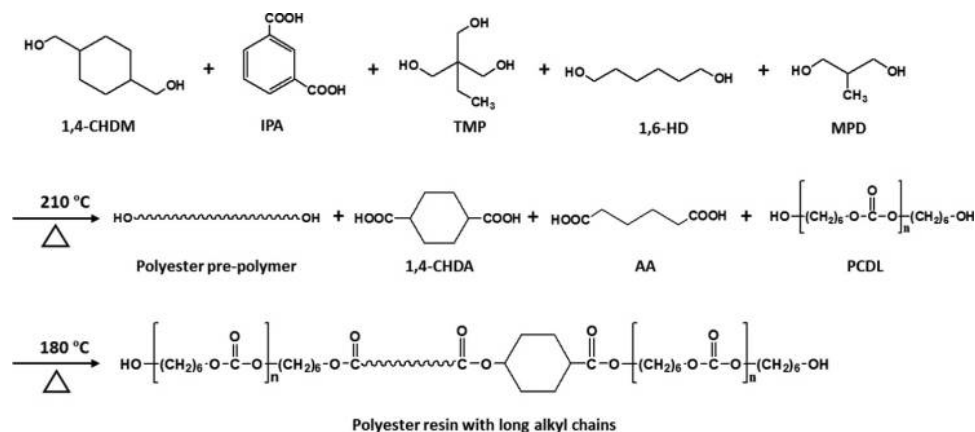


Table I Formulations of polyester resins with long alkyl chains (unit: Mole)

Sample	1,4-CHDA ^a	AA ^b	IPA ^c	TMP ^d	1,6-HD ^e	1,4-CHDM ^f	MPD ^g	PCDL ^h
PC-0	0.7	0.2	1.5	0.3	0.5	1.1	0.6	0
PC-1	0.7	0.2	1.5	0.3	0.5	1.1	0.5	0.1
PC-2	0.7	0.2	1.5	0.3	0.5	1.1	0.4	0.2
PC-3	0.7	0.2	1.5	0.3	0.5	1.1	0.3	0.3

Notes: ^a1,4-CHDA (1,4-cyclohexanedicarboxylic acid); ^bAA (adipic acid); ^cIPA (isophthalic acid); ^dTMP (trimethylolpropane); ^e1,6-HD (1,6-hexanediol); ^f1,4-CHDM (1,4-cyclohexanedimethanol); ^gMPD (2-methyl 1,3-propanediol); ^hPCDL (polycarbonate diol) ($M_n = 500$)

charged into the reactor, and the reaction temperature was set to 130°C with stirring for 2 h under a N₂ purge. Subsequently, the reaction temperature was increased from 130°C to 180°C at a rate of 0.3°C/min. The reaction temperature was maintained for several hours to collect condensed water.

The fusion process was then converted into a solvent process by adding xylene. The solvent process was carried out to collect condensed water and to induce a low acid value. The reaction temperature was set at 180°C. The acid value was measured by a 0.1 N KOH solution. The reaction temperature was maintained for several hours until the acid value was under 3 mg KOH/g resin.

Preparation of polyester coatings with long alkyl chains

Polyester resins with long alkyl chains were mixed with a cross-linker, HMMM, additives and solvents. Polyester coatings were prepared as listed in Table II:

- *Free film*: Polyester coatings were casted on to an aluminium pan and dried to evaporate the solvent in an oven at 60°C for 12 h and then baked at 150°C (oven temperature) for 1 h. The thickness of the baked films was 200 μm.
- *PCM*: Galvanised steel sheets (thickness of 0.8 mm) were coated with an alkali solution and baked at the peak metal temperature (PMT) of 220°C for 20 s for pre-treatment. The cured pre-treated films were 5 μm in thickness. A polyester coating as a primer was coated on the cured pre-treated film and then baked at a PMT of 224°C for 35 s. The thickness of those cured film was 15 μm. The total film thickness was 20 μm.

Table II Formulations of polyester coatings with long alkyl chains (unit: G)

Materials	CPC-0	CPC-1	CPC-2	CPC-3
PC-0 ^a	53.4	–	–	–
PC-1 ^a	–	53.8	–	–
PC-2 ^a	–	–	54.1	–
PC-3 ^a	–	–	–	54.3
Aromatic solvent	20.0	20.0	20.0	20.0
TiO ₂	4.0	4.0	4.0	4.0
MA 100 ^b	0.7	0.7	0.7	0.7
Shieldex C303	10.0	10.0	10.0	10.0
HMMM	5.0	4.8	4.6	4.3
Additives	1.0	1.0	1.0	1.0
Nacure	0.5	0.5	0.5	0.5
Solvent ^c	5.4	5.2	5.1	5.2

Notes: ^aSolid content of polyester resins: 75 per cent; ^bBlack pigment; ^cSolvent: Solvesso #100

Characterisation of the polyester resin

Fourier transform infrared (FT-IR) spectroscopic analysis

Infrared spectra were obtained using a JASCO FT/IR-6100 (Jasco, Japan) spectrometer equipped with a Miracle accessory and an attenuated total reflectance (ATR) setup. The ATR crystal was made of diamond, and its refractive index was 2.4 at 8,500–2,500 and 1,700–300 cm⁻¹. The spectra were collected using the ATR mode in the wavenumber range of 4,000 to 650 cm⁻¹, and the resolution of the spectra recorded was 4 cm⁻¹.

¹H nuclear magnetic resonance (¹H NMR) spectroscopic analysis

¹H NMR spectra were obtained using a 400 MHz NMR spectrometer (JEOL JNM-LA400, JEOL Ltd., Japan). The sample was dissolved in acetone-d₆.

Determination of molecular weight

The molecular weight and polydispersity of the synthesised polyesters with long alkyl chains were measured using the YL9100 gel permeation chromatography (GPC) system (Young Lin, Republic of Korea) consisting of a pump and an RI detector. Tetrahydrofuran was used as the eluent, and the flow rate was 1 mL/min.

Characterisation of the polyester coatings

Measurement of viscoelastic property

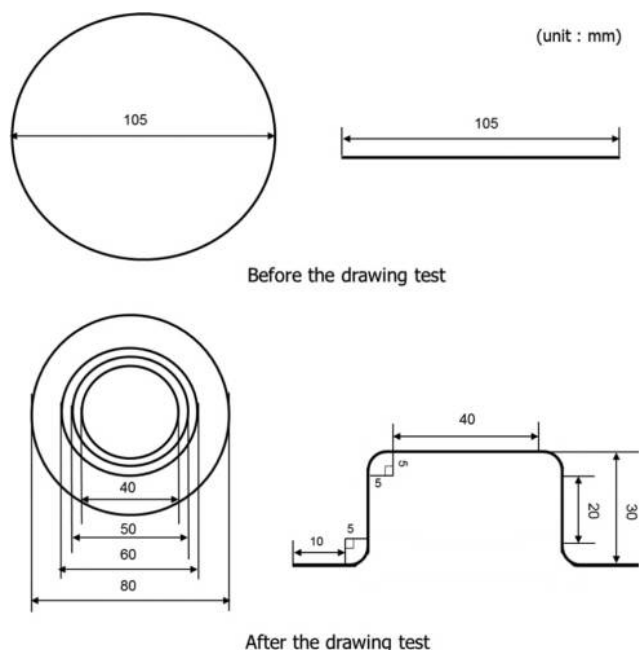
Dynamic mechanical analysis (DMA) was used to study the variation of the storage modulus and tan δ of the polyester coatings with temperature. DMA was performed from –60°C to 160°C (Q800, TA Instruments) in tension mode at a frequency of 1 Hz and strain of 0.3 per cent. The creep strain of the free films was performed by DMA at 5.6 MPa, with a loading time of 90 s, which corresponded to the deep drawing time.

Measurement of tensile strength

The tensile strength was measured using a universal testing machine (Zwick Corp). at a crosshead speed of 20 mm/min, which corresponded to the deep drawing testing speed. The tensile strength 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 meters. The per cent elongation (strain per cent) was calculated by dividing the change in gage length by the original specimen gage length.

Measurement of formability

Formability was tested using a cylindrical deep drawing, as shown in Figure 2. The shape of the PCM before deep drawing was a disk, and its diameter was 105 mm. The shape of the punch was a circle, and its diameter was 40 mm; the shoulder radius of the punch and the corner radius of the punch were 5 mm. The specific conditions are listed in Table III. The speed of the punch was 20 mm/min, and the

Figure 2 Schematic diagram of cylindrical deep drawing for PCM**Table III** Conditions of the deep drawing

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
Drawing speed (mm/min)	20

drawing time was 90 s. The test was performed at 25°C, and the blank force was 4.9×10^4 N.

Measurement of anti-corrosion property

Electrochemical impedance spectroscopy (EIS) was used to study the water uptake of the polyester coatings. The test was carried out in an unstirred 3.5 wt per cent NaCl solution using a frequency range of 10^5 down to 10^{-2} Hz at an amplitude of 10 mV (Solartron SI 1260, UK). The electrical capacitance of the coating (C) was measured every 2 min for 3 h.

The anti-corrosion property was measured using a salt spray test. All specimens were prepared on galvanised steel substrates and a cross-scratch line was made on the coating surface with a sharp instrument. The salt spray test was conducted according to ASTM B-117 in a 5 wt per cent NaCl solution at 35°C. Changes in the surface morphology, especially around the cross-line on the coating and surface defects, were examined via Video Image Enhanced Evaluation of WeatheringTM (VIEEW) digital image analyser (Atlas Electric Devices Co., USA) after 500 h. This was capable of capturing digital images of samples under various lighting schemes that were optimised to highlight and enhance surface defects to digitally process the images. The value of the specimen corrosion area was calculated by dividing the corrosion area by the tested area (%).

Results and discussion

Synthesis of polyester resins with long alkyl chains

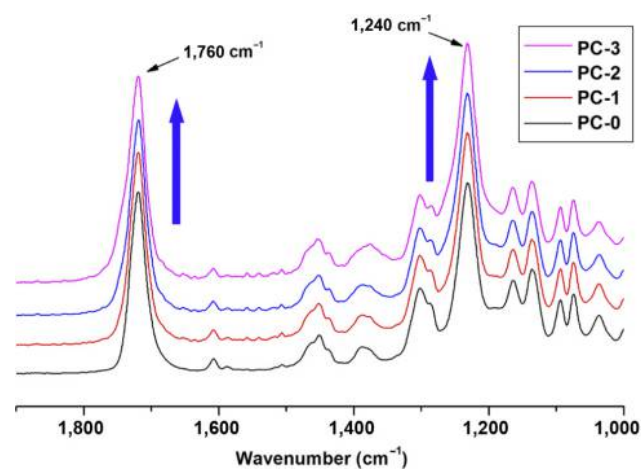
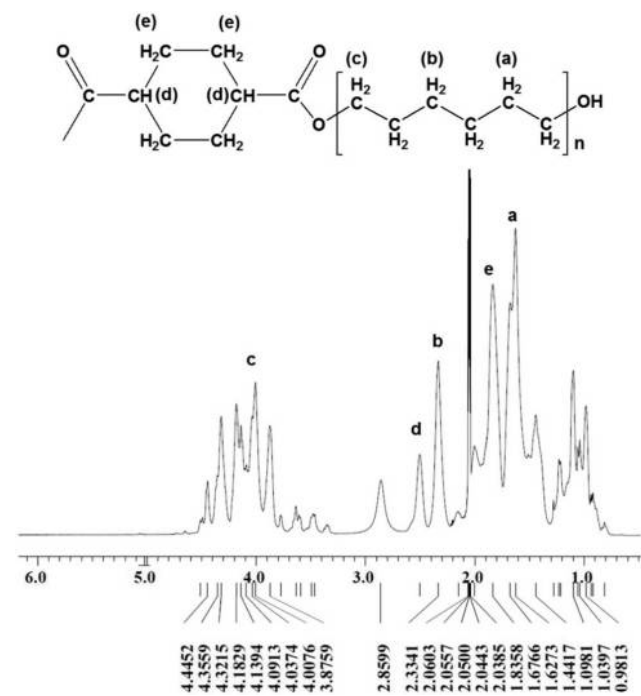
Polyester resins with long alkyl chains were synthesised with different contents of polycarbonatediol.

Chemical characteristics of the polyester resin

To characterise the chemical structure of the polyester resin with long alkyl chains, the sample was subjected to FT-IR and ¹H NMR analyses. The spectra are presented in Figures 3 and 4, and prominent peaks are identified.

Structural confirmation by the FT-IR spectrum

The carbonyl group of the polyester resin was determined using FT-IR. The carbonyl group, which was from

Figure 3 FT-IR spectra of polyester resins with long alkyl chains of polycarbonatediol (carbonyl group: 1,240 and 1,760 cm⁻¹)**Figure 4** ¹H NMR spectrum of a polyester resin with long alkyl chains (PC-3)

polycarbonatediol, was detected at 1,240 and 1,760 cm^{-1} , and the intensity of these bands increased with the increase of polycarbonatediol, as shown in Figure 3.

Structural confirmation by $^1\text{H-NMR}$ spectrum

The ^1H NMR spectrum of CPC-3 with peak assignments is shown in Figure 4. Typical resonances of polycarbonatediol were at 1.4–1.7 (δH^a), 2.2–2.3 (δH^b) and 3.9–4.1 (δH^c). Additionally, peaks at 1.45 (δH^c), 1.85 (δH^c) and 2.45 (δH^d) were observed because of the cyclohexane structure (Shih *et al.*, 2013; Liu *et al.*, 2015). From the ^1H NMR spectrum, it was clear that polycarbonatediol had been introduced into the polyester resin.

Molecular weight of the polyester resin

The molecular weight and polydispersity of the polyester resin are listed in Table IV. The theoretical hydroxyl number of the polyester resin (n_{OH}) decreased with the increase of polycarbonatediol. The ratio between the average molecular weight number and hydroxyl number (M_n/n_{OH}) indicated the length of the repeating unit in the crosslink network of the polyester resin. M_n/n_{OH} increased and the crosslinking density decreased with the increase of polycarbonatediol.

Viscoelastic properties

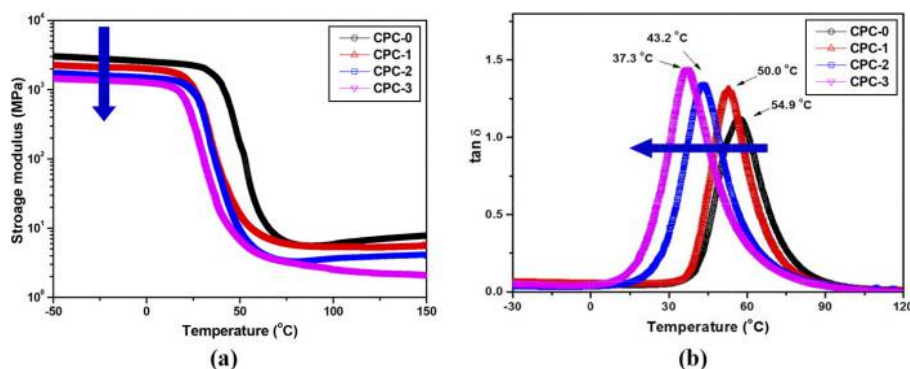
DMA is a convenient method to study the thermal and mechanical viscoelastic properties of polymeric materials. The storage modulus of the polyester coatings as a function of temperature is shown in Figure 5(a), which decreased with the increase of polycarbonatediol, that is CPC-0 > CPC-1 >

Table IV Characterisation of polyester resins with long alkyl chains

Property	PC-0	PC-1	PC-2	PC-3
Number average MW (M_n)	5,670	5,940	6,950	7,390
Polydispersity index (M_w/M_n)	4.2	4.7	4.6	4.7
n_{OH} (mg KOH/g) ^a	44.9	42.1	39.7	37.9
M_n/n_{OH} (g/mg KOH)	126	141	175	194
Crosslink density (10^{-3} mol/cm ³)	0.626	0.568	0.410	0.231

Note: ^a n_{OH} = Theoretical hydroxyl number of the polyester resins

Figure 5 Viscoelastic properties of polyester coatings with long alkyl chains



Notes: (a) Storage modulus and (b) $\tan \delta$

CPC-2 > CPC-3. Polycarbonatediol has long alkyl chains, and it is generally recognised that the mobility and flexibility of the polymer chain increase with the length of the linear alkyl chain segment.

The crosslink density (v_c) of the polyester coatings was calculated using the following equation (Stroiszniig *et al.*, 2009):

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

This equation was derived from the minimum storage modulus (E'_{min}) and the temperature at the minimum storage modulus ($T_{E'_{min}}$) in the rubbery plateau region. The crosslink density decreased with the increase of polycarbonatediol, indicating that the long alkyl chains of polycarbonatediol were introduced to the polymer chain. A longer length between crosslinks corresponded to a lower crosslink density, thus explaining the lower modulus of the polyester coatings, as listed in Table IV. Additionally, the T_g was shifted to a lower temperature with the increase of polycarbonatediol, as shown in Figure 5(b). The long alkyl chains of polycarbonatediol favourably provided a lower stiffness and higher softness to the polyester coating.

Mechanical property

Tensile strength

Flexibility is the most important property for the cutting, pressing and stamping processes in the pre-coated system. Figure 6 shows the effect of the contents of polycarbonatediol on the tensile behaviours of polyester coatings. The tensile strength decreased with the increase of polycarbonatediol (CPC-0 > CPC-1 > CPC-2 > CPC-3). In contrast, the maximum strain increased (CPC-0 < CPC-1 < CPC-2 < CPC-3). The tensile strength of CPC-2 was 16.7 MPa and that of CPC-3 was 8.7 MPa, with maximum strains of 178 and 195 per cent, respectively. These values represented high flexibility and high breaking strain, which were a consequence of the high stretchability imparted by the soft segments of the polycarbonatediol. The effect of M_n/n_{OH} on elongation and T_g is shown in Figure 7. As M_n/n_{OH} increased, elongation increased and T_g decreased. This implied that long alkyl

Figure 6 Stress–strain curves of polyester coatings with long alkyl chains (compressive strength: 5.6 MPa, forming ratio: 23.4 per cent)

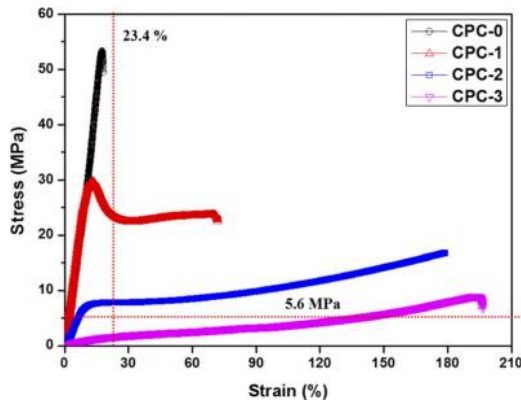
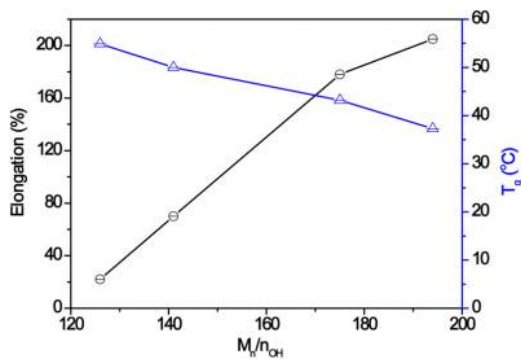


Figure 7 Elongation and T_g of polyester coatings with long alkyl chains as a function of M_n/n_{OH}



chains of polycarbonatediol gave flexibility to the polyester coating.

Formability

The deep drawing test is a common method for determining formability in PCMs. The strain behaviour of the coated film was very complicated because the tensile and compressive strains were developed during the deep drawing. The forming ratio, R_f , was calculated by measuring the size of the PCM before and after deep drawing. R_f can be calculated using equation (1):

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

where the total area before drawing test was 8,654 mm² and the total area after drawing test was 10,676 mm². Hence, the calculated R_f was 23.4 per cent. The tensile strain of polyester coatings should be larger than 23.4 per cent. The compressive stress on the PCM, σ_p , represents the die pressure on the PCM during the deep drawing and can be calculated using equation (2):

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

where the blank force was 4.9×10^4 N. The calculated σ_p was 5.6 MPa. Figure 8 shows the formability resulting from the

Figure 8 Formability of polyester coatings with long alkyl chains



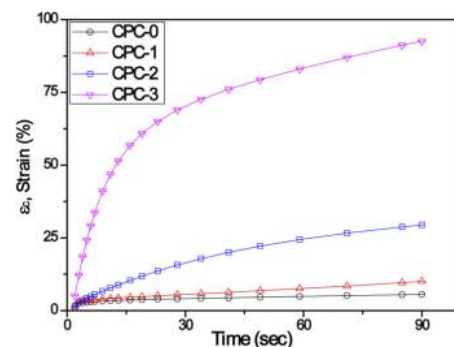
deep drawing. CPC-3 had a larger delamination because the tensile strength of CPC-3 was lower than 5.6 MPa at a strain of 23.4 per cent (Figure 6). Hence, it was not strong enough to overcome the compressive stress during deep drawing. Thus, the tensile stress of polyester coatings should be larger than 5.6 MPa to overcome the harsh stress during deep drawing.

Another route to analyse the formability is the strain related by the tensile and creep tests. The forming coefficient based on the strain, F_ε , can be calculated using equation (3):

$$F_\varepsilon = \frac{\varepsilon_c}{R_f} \quad (3)$$

where ε_c is the developed strain for 90 s by the creep test, as shown in Figure 9. The strain of creep was obtained at a stress level of 5.6 MPa, which corresponded to the compressive stress. CPC-0 and CPC-1 exhibited cracks and delamination, as shown in Figure 8, even though they exhibited higher tensile strengths. F_ε values of CPC-0 and CPC-1 were 0.24 and 0.60, respectively, and both of them were not flexible enough to be stretched out during the deep drawing. The F_ε of CPC-2 was 1.26, and it could be stretched without being damaged. Thus, F_ε should be larger than 1 to have good formability.

Figure 9 Strain of polyester coatings with long alkyl chains from the creep test



Furthermore, the formability was analysed based on the strain energy related by the tensile test and creep test. The forming coefficient based on the strain energy, F_U , can be calculated using equation (4):

$$F_U = \frac{U_C}{U_T} \quad (4)$$

where U_C was the pure strain energy of the coated film during formation to 90 s, and it can be calculated from the strain curve of the creep test. The strain energy to 90 s by the creep test (U_C) can be calculated using equation (5):

$$U_C = \int_0^{90} \text{strain - dependent stress curve } d\epsilon \quad (5)$$

where U_T was the pure strain energy of the coated film during formation to R_f , and it can be calculated from the strain curve of the tensile test. The strain energy to R_f by the tensile test (U_T) can be calculated using equation (6):

$$U_T = \int_0^{R_f} \text{strain - dependent stress curve } d\epsilon \quad (6)$$

The F_U values of CPC-0 and CPC-1 were 0.11 and 0.32, respectively. CPC-0 and CPC-1 were not flexible enough to be stretched out during the deep drawing. The F_U of CPC-2 was 1.49, and it was able to be stretched without being damaged. Thus, F_U should be larger than 1 to have good formability. The calculated values are listed in Table V. Therefore, the tensile stress should be larger than 5.6 MPa at 23.4 per cent, and F_ϵ and F_U should be larger than 1 to have good formability.

Anti-corrosion properties

Water uptake

One of the important roles of coatings is to block environmental factors such as water and oxygen. Coating capacitance represents water uptake of coatings, and it can be measured by the alternating current impedance method of EIS. When water penetrated the coating, the value of coating capacitance was initiated. The water uptake of coatings can be calculated from the Brasher–Kingbury equation:

Table V Calculated values obtained from the tensile test and creep test for polyester coatings with long alkyl chains

Sample	ϵ_C (%)	F_ϵ (ϵ_C/R_f)	U_C	U_T	F_U (U_C/U_T)
CPC-0	5.55	0.24	28.30	253.10	0.11
CPC-1	14.09	0.60	71.87	227.58	0.32
CPC-2	29.42	1.26	150.9	101.15	1.49
CPC-3	92.55	3.96	472.01	20.23	23.33

Notes: ϵ_C = The developed strain for 90 s by the creep test; R_f = The forming ratio, 23.4 per cent; F_ϵ (ϵ_C/R_f) = The forming coefficient based on strain; U_C = The pure strain energy of coated film during formation to 90 s from the creep test; U_T = The pure strain energy of coated film during formation to R_f from the tensile test; F_U (U_C/U_T) = The forming coefficient based on strain energy

$$\text{Water uptake} = \frac{\log(C_t/C_0)}{\log 80}$$

where C_t is the electrical capacitance of the coating during time t of immersion and C_0 is the electrical capacitance of the coating before immersion.

The behaviour of water uptake is shown in Figure 10. The coating thickness of the electrophoretic painting (EDC) was 15 μm , and the water uptake of EDC continuously increased for 2 h. However, the polyester coatings greatly increased for 10 min and then gradually increased. The equilibrium state was reached after 1 h. The water uptake of EDC was 20.5 vol per cent, whereas that of CPC-0, CPC-1 and CPC-2 was almost the same at 4 vol per cent. However, the water uptake of CPC-3 was 6 vol per cent, which was larger than that of the other polyester coatings, because CPC-3 had the highest amount of polycarbonatediol, leading to a weaker polyester coating because of intramolecular crosslink (Simon *et al.*, 1991).

Salt spray test

The anti-corrosion property is one of the important properties of PCMs. EDC and polyester coatings were tested via salt spraying for 500 h. All specimens had red rust around the X-cut, as shown in Figure 11. EDC had a much greater amount of red rust around the X-cut, but the surface was clear. CPC-3 exhibited a large amount of blistering around the X-cut. However, CPC-2 had a relatively clear surface around the X-cut. These results agreed with the water uptake results. EDC had the highest

Figure 10 Water uptake (vol per cent) of EDC and polyester coatings with long alkyl chains by the capacitance method under immersion

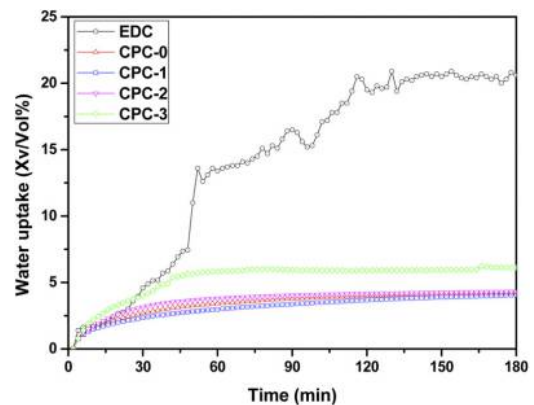


Figure 11 Corrosion resistance of EDC and polyester coatings with long alkyl chains by the salt spray test for 500 h

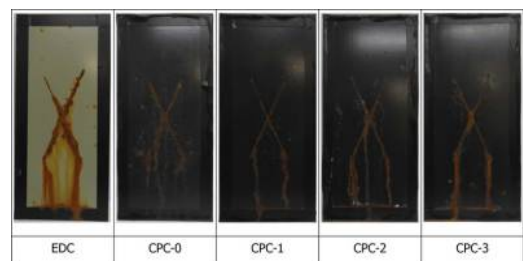
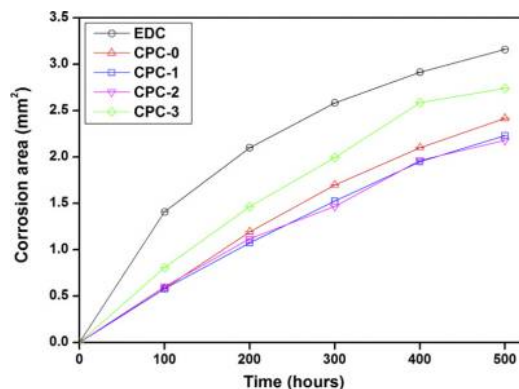


Figure 12 Corrosion area of EDC and polyester coatings with long alkyl chains



value of water uptake, so it was not able to block corrosion factors during the salt spray test. Figure 12 shows the values of the corrosion area of the specimens, which were calculated by dividing the corrosion area around the X-cut by the tested area from VIEEW. This was evaluated every 100 h, and the corrosion area gradually increased with the increase of the salt spray test time. All specimens exhibited the same tendency. The corrosion area of EDC was 3.3 per cent and that of polyester coatings was less than 3.0 per cent. From the salt spray test, the polyester coatings had a better anti-corrosion property than EDC.

Conclusions

Polyester coatings were investigated to control formability using long alkyl chains of polycarbonatediol for automotive PCMs. The viscoelastic behaviour, flexibility and formability were measured to determine the long alkyl chain effect of the PCM. When the long alkyl chain of polycarbonatediol increased in the polyester coating, the stiffness was considerably decreased and the T_g was shifted to a lower temperature. Therefore, long alkyl chains of polycarbonatediol were a major factor to improve flexibility and formability. The tensile stress of the polyester coating should be larger than 5.6 MPa at R_f to overcome harsh stress to have good formability. Moreover, the formability was analysed based on the strain and strain energy. It was found that F_s and F_U should be larger than 1 to have good formability. The F_s and F_U values of CPC-2 were 1.26 and 1.49, respectively, and

the tensile stress was 7.5 MPa at R_f . Thus, CPC-2 exhibited good formability, as well as a good anti-corrosion property, compared to EDC. From these tests, CPC-2 is an appropriate coating for automotive PCMs as a primer.

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