



Synthesis and characterization of polyester-based nanocomposites coatings for automotive pre-coated metal

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ABSTRACT

Polyester-based nanocomposites coatings were synthesized by the in situ polymerization with high speed homogenizer process at the various contents of organic modified montmorillonite (OMMT) to disperse into the polyester matrix. The dispersion state of organoclay was examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The absence of reflection pattern of organoclay and TEM study revealed that organoclay was partially intercalated and exfoliated into the polymer matrix. Mechanical property of polyester-based nanocomposites coatings (PE/OMMT) improved the tensile strength and good formability at the deep drawing test. The viscoelastic behavior of PE/OMMT nanocomposites coatings was observed by dynamic mechanical analysis (DMA). When the content of organoclay was increased, the stiffness of the PE/OMMT nanocomposites coatings increased considerably and T_g of each cured coatings shifted to a lower temperature. Anti-corrosion property was examined by the salt spray test. CNC-3 had little rust after 600 h and it implies that nano-sized layered silicate of organoclay effectively increases the length of the diffusion pathways water molecules. And nano-sized layered silicate of organoclay might be decreased the permeability and could make higher corrosion resistance of PE/OMMT nanocomposites coatings. From those results, CNC-3 had good formability in the deep drawing and also had good anti-corrosion property. So, CNC-3 would be an appropriate coating for automotive pre-coated metal.

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1. Introduction

Pre-painted or coil-coated metals (PCM) have been used in many applications such as household electric appliances, building materials and others. In this system, 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 pre-coated metal system offers other advantages such as improved productivity and energy saving, thus the use of PCM has been spreading [1,2]. One of the most important properties of PCM is formability. If the film on the coated PCM parts is damaged, the products are rendered useless [3].

Also, the most important property of PCM is anti-corrosion property. Many researchers have been reported that the incorporation of layered silicate fillers into polymers leads to improved properties such as stiffness, strength, heat resistance, and

decreased moisture absorption and permeability, when compared to micro-scale composites [4]. One of the major properties is to decrease moisture absorption and permeability which can protect corrosion of metals which can prevent the diffusion of corrosive factors such as water and oxygen [5].

Polymer/layered silicate nanocomposites have been widely investigated. Especially polyurethane/clay nanocomposites have been tried to overcome low thermal stability and barrier property [6]. Those properties can be improved by adding clay such as organoclay to the polymer. The incorporation of organoclay into the polymer matrix improved coating properties such as adhesion [7], hardness [7,8], barrier property [9,10], and corrosion resistance [11].

Polyester has been used for automotive coatings as a primer, basecoat and clearcoat. But, polyester/clay nanocomposites coating has not been widely studied for coatings. In this study, we used organoclay such as Cloisite 30B with modified with a quaternary ammonium salt (OMMT) and Cloisite 30B has $-OH$ group. Polyester-based nanocomposites (PE/OMMT) were synthesized by the in situ polymerization with high speed homogenizer process at the various contents of organoclay. The major purpose of this paper is to study the effect of dispersed nano-layered silicates on

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corrosion performance. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were employed to characterize the state of organoclay dispersions. Another purpose of this paper is formability using polycarbonatediol which consists of a long alkyl chain with contains much flexible rod-like group such as $-\text{CH}_2$ [12].

Overall, this paper reports the design of a polyester resin for automotive pre-coated metal using organoclay and polycarbonatediol. The elongation, tensile strength and viscoelastic properties of free coated film were measured. The formability of PCM was evaluated using a cylindrical drawing test. Salt spray and electrochemical impedance spectroscopy (EIS) were employed to investigate the corrosion performance of PE/OMMT nanocomposites coatings and the effect of the concentration of organoclay into the polyester matrix.

2. Experimental

2.1. Materials

Table 1 presents the chemical structures and basic information of the raw materials used for the synthesis. A polycarbonatediol (PCDL, $M_n=500$, Asahi Kasei Chemicals Corp., Japan) was prepared to control the flexibility of the main chain. 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), trimethylol propane (TMP, Tokyo Chemical Industry, Japan), 2,2,4-trimethyl-1,3-pentanediol (TMPD, Tokyo Chemical Industry, Japan), 1,4-cyclohexanedimethanol (1,4-CHDM, Tokyo Chemical Industry, Japan), and Cloisite 30B (Southern Clay Products, Inc., USA) were used without further purification. Butylstannic acid (FASCAT 4100, Arkema Inc., USA) was used as a catalyst to catalyze

polymerization and prevent a transesterification reaction during the polymerization [13].

Hexamethoxymethyl-melamine (HMMM, Cytec Industries Inc., USA) was used as the curing agent and Nacure blocked acid catalyst (NACURE 1953, King Industries, Inc., USA) was used.

2.2. Synthesis of PE/OMMT nanocomposites coatings precursors

The formulations of PE/OMMT nanocomposites coatings precursors synthesized with Cloisite 30B and polycarbonatediol are shown in Table 2. PE/OMMT nanocomposites coatings precursors were synthesized from polybasic alcohols and polybasic acids with the following procedure which consisted of two synthesis processes. One was the fusion process and the other was the solvent process. The synthesis took place in a 500 mL round bottom flask equipped with a four-necked flask having a mechanical stirrer, thermometer, condenser and water trap. The condenser and water trap were meant to remove condensed water during the polycondensation reaction between alcohols and acids.

Organoclay dispersion: Cloisite 30B needs to disperse before using. Organoclay was dispersed in cyclohexanone with high speed homogenizer. Organoclay and cyclohexanone were charged into a vessel and dispersed for 30 min with 10,000 rpm and pre-dispersed organoclay was 10 wt.%.

Firstly, IPA, TMP, TMPD, 1,4-CHDM, and pre-dispersed organoclay (10 wt.%) were charged into a dried reactor and the reaction temperature was set to 150 °C with stirring for 2 h under N_2 purge. Subsequently, the reaction temperature was increased from 150 °C to 210 °C at the rate of 0.5 °C/min. During the fusion process, all raw materials were melted and the condensed water was collected. After that 1,4-CHDA, AA, and PCDL were charged into the reactor containing melt prepared from the preceding step and the reaction

Table 1
Raw materials used for the synthesis of PE/OMMT nanocomposites coatings precursors.

Function	Materials	Abbre.	Chemical structure	M_n (g/mol)	Supplier
Acid	1,4-Cyclohexane-dicarboxylic acid	1,4-CHDA		172	Tokyo Chemical Industry
	Adipic acid	AA		146	Samchun Pure Chemical
	Isophthalic acid	IPA		166	Junsei Chemical Corp.
Alcohol	Trimethylol- propane	TMP		134	Tokyo Chemical Industry
	2,2,4-Trimethyl-1,3-Pentanediol	TMPD		146	Tokyo Chemical Industry
	1,4-Cyclohexane dimethanol	1,4-CHDM		144	Tokyo Chemical Industry
	Polycarbonatediol	PCDL		500	Asahi Kasei Chemicals Corp.

Table 2

Formulations used for synthesis of PE/OMMT nanocomposites coatings precursors (mole).

Sample	1,4-CHDA ^a	AA ^b	IPA ^c	TMP ^d	TMPD ^e	PCDL ^f	1,4-CHDM ^g	Cloisite 30B (wt.%)
NC-0	10	2	12	3	6	1	11	0
NC-1	10	2	12	3	6	1	11	1
NC-2	10	2	12	3	6	1	11	2
NC-3	10	2	12	3	6	1	11	3

^a 1,4-Cyclohexanedicarboxylic acid.^b Adipic acid.^c Isophthalic acid.^d Trimethylolpropane.^e 2,2,4-Trimethyl-1,3-pentanediol.^f Polycarbonate diol ($M_n = 500$).^g 1,4-Cyclohexanedimethanol.

temperature was set to 130 °C with stirring for 2 h under N₂ purge. Subsequently, the reaction temperature was increased from 130 °C to 180 °C at the 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 solvent process by adding xylene. The solvent process was carried out to collect condensed water and to make low acid value. The reaction temperature was set to 180 °C. During the solvent process, the acid value was measured by 0.1 N KOH aqueous solution. The reaction temperature was maintained for several hours until the acid value was under 3 mg KOH/g resin [13]. The solid content of synthesized PE/OMMT nanocomposites coatings precursors was 70%.

2.3. Preparation of PE/OMMT nanocomposites coatings

Synthesized PE/OMMT nanocomposites coatings precursors were mixed with the cross-linker, HMMM, additives, and solvents. Four different formulations were prepared as listed in Table 3.

Free film: PE/OMMT nanocomposites coatings were cast on to an aluminum pan and dried to evaporate solvent in the oven at 60 °C for 12 h and then baked at 150 °C (oven temperature) for 1 h. The thickness of the cured films ranged from 150 to 200 μm. The resulted films became the samples for tensile strength and dynamic mechanical analysis.

PCM: The PE/OMMT nanocomposites coatings were coated on the cured pre-treated film and then baked at 150 °C for 30 min. The thickness of those cured film was 20 μm.

2.4. Characterization

X-ray diffraction (XRD) analysis of Cloisite 30B and PE/OMMT nanocomposites coatings were performed using a Bruker X-ray diffractometer (equipped with a 2-D detector) in reflection mode. Tests were carried out with 2θ scanned from 1° to 10° nickel-filtered Cu K_{α1} radiation ($k = 0.15418$ nm) under a voltage of 40 kV and a current of 40 mA. The state of clay in nanocomposites was observed with a transmission electron microscope

(TEM). Specimens with thickness of 80 nm were cut using a RMC ultra-microtome MT 7000. The morphology of PE/OMMT nanocomposites coatings was examined by a JEOL JEM-3010 TEM with operating at an accelerating voltage 300 kV.

Dynamic mechanical analysis (DMA) was used to study the variation of storage modulus and tan δ of PE/OMMT nanocomposites coatings with temperature. DMA was performed from –60 °C to 160 °C (Q800, TA Instruments). The test was performed under tensile loading at a heating rate of 2 °C/min and at a frequency of 1 Hz and strain of 0.3%. Creep and creep recovery tests were performed at a stress level of 5.1×10^6 Pa with time. The tests were performed at 25 °C, and with a loading time of 90 s followed by recovery time is 120 s. The 90 s of creep time is designed to correspond to the deep drawing testing time.

Mechanical property of tensile strength was measured using a Universal Testing Machine (UTM, Zwick Corp.) at a crosshead speed of 20 mm/min which is designed to correspond to the deep drawing testing speed. The tensile strength value was calculated by dividing the maximum load in Newton (N) by the average original cross-sectional areas in the gage length of the specimen in square meters. The percent elongation (strain %) was calculated by dividing the change in gage length by the original specimen gage length, expressed as a percentage (%) [14].

Formability of PE/OMMT nanocomposites coatings was used a cylindrical deep drawing test as shown in Fig. 1. The shape of PCM before deep drawing was a disk and its diameter was 105 mm. The shape of the punch was circle and its diameter was 40 mm, the shoulder radius of the punch and the corner radius of the punch were 5 mm. Specific conditions of the deep drawing were shown in Table 4. The speed of punch was 20 mm/min and the drawing testing time was 90 s. The blank force was 4.9×10^4 N and this test was performed at 25 °C [15].

Electrochemical impedance spectroscopy (EIS) was used to study water uptake of PE/OMMT nanocomposites coatings. The test was carried out in the unstirred 3.5 wt.% NaCl solution using a frequency range of 10⁵ down to 10^{–2} Hz using 10 mV amplitude (Solartron, SI 1260, UK). The electrical capacitance of the coatings (C) was measured every 2 min for 3 h [16]. The anti-corrosion property of PE/OMMT nanocomposites coatings was measured by the salt spray test. All specimens were first prepared on cold roll steel substrates. The salt spray test condition was according to ASTM

Table 3

Coating formulations of PE/OMMT nanocomposites coatings (wt.%).

Contents	CNC-0	CNC-1	CNC-2	CNC-3
NC-0 ^a	61.8	–	–	–
NC-1 ^a	–	61.8	–	–
NC-2 ^a	–	–	61.8	–
NC-3 ^a	–	–	–	61.8
HMMM	6.5	6.5	6.5	6.5
Additives ^b	1.0	1.0	1.0	1.0
Nacure	0.5	0.5	0.5	0.5
Solvent ^c	30.2	30.2	30.2	30.2

^a Solid content of polyester nanocomposites: 70%.^b Additives – defoamer: Afcona 3770; leveling agent: Afcona 3777.^c Solvent: solvesso #100.**Table 4**

Conditions for the deep drawing of PCM [15].

Shape of punch	Cylindrical
Shoulder radius of punch (mm)	5
Size of punch (mm)	40
Size of PCM (mm)	105
Drawing height (mm)	30
Drawing of speed (mm/min)	20

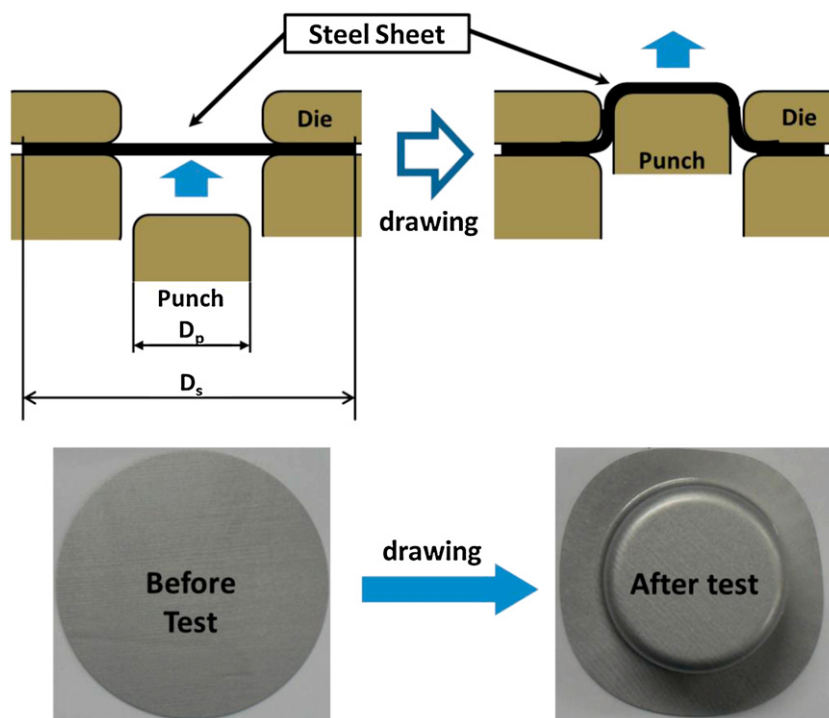


Fig. 1. Procedure of the deep drawing [15].

B-117 in a 5 wt.% NaCl solution at 35 °C. After 600 h, changes of surface morphology and surface defects were examined [17,18].

3. Results and discussion

PE/OMMT nanocomposites coatings were synthesized based on different content of pre-dispersed organoclay. The state of intercalation or exfoliation of organoclay in polyester matrix was characterized by XRD patterns as shown in Fig. 2. Cloisite 30B has one peak at $2\theta = 4.78^\circ$. This peak is related to the d-spacing of clay and d-spacing of clay is 18.48 Å by the Bragg's law. PE/OMMT nanocomposites coatings containing 1, 2 and 3 wt.% of organoclay, there is no peak at 4.78° on XRD patterns. It means that organoclay of silicate layers were dispersed into the polyester matrix during the synthesized process. The data is in a good agreement with the data reported by Heidarian et al. [5]. TEM micrograph of PE/OMMT nanocomposites coatings is shown in Fig. 3. CNC-1 has 1 wt.% and

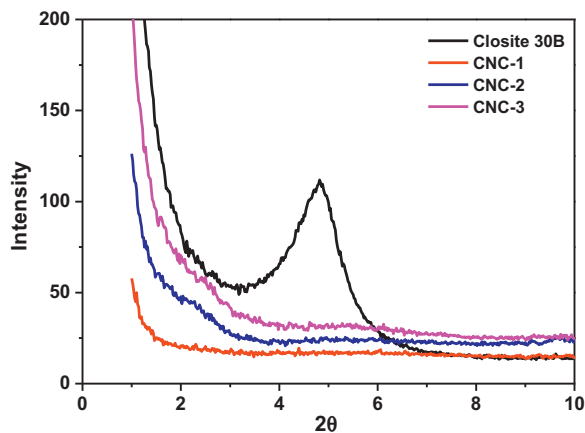
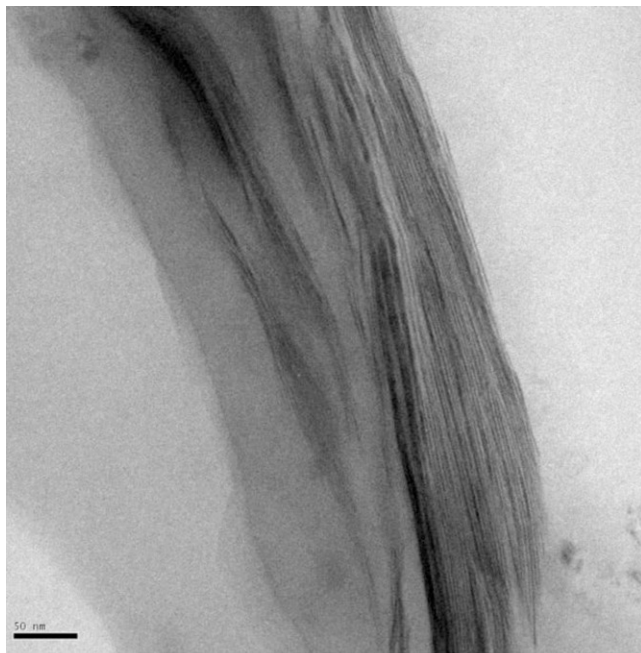


Fig. 2. XRD patterns of organoclay and PE/OMMT nanocomposites coatings.

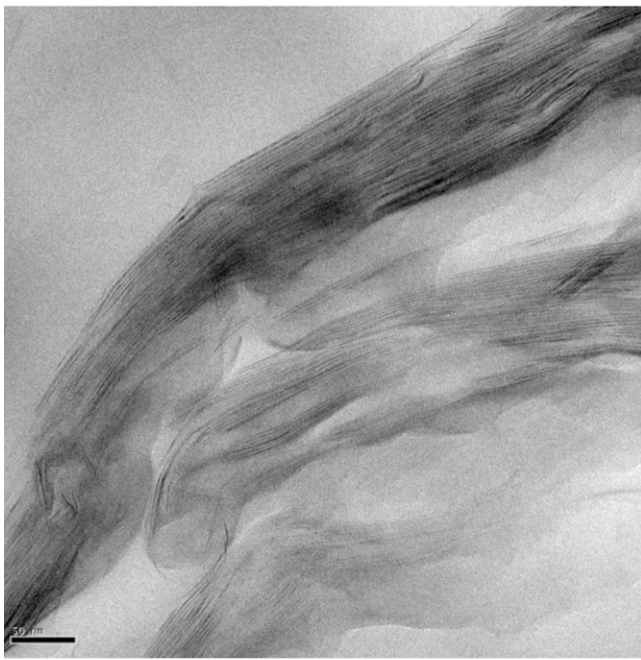
CNC-3 has 3 wt.% of organoclay. The parallel silicate layers are seen at the organoclay layers. This TEM micrograph showed the existence of well-dispersed silicate layers and organoclay was partially intercalated and exfoliated into the polymer matrix. The reason is that the strong interactions between the carboxylic ester group of polyester matrix and $-\text{OH}$ group of organoclay. From the TEM micrograph, the exhibited morphology can be classified as partially intercalation/exfoliation [19].

Dynamic mechanical analysis (DMA) is a convenient method to study thermal and mechanical viscoelastic properties of polymeric materials [20]. Fig. 4(a) shows storage modulus as a function of temperature for polyester coating and PE/OMMT nanocomposites coatings. Storage modulus increased with increasing contents of organoclay, i.e. $\text{CNC-0} < \text{CNC-1} < \text{CNC-2} < \text{CNC-3}$. With an addition of 3 wt.% of organoclay, the storage modulus of PE/OMMT nanocomposites coatings increased about 50% in the glassy state compared to no addition of organoclay. However, the glass transition temperature of PE/OMMT nanocomposites coatings is lower than PE coatings as shown Fig. 4(b). It might be reduced crosslink density and lacked surrounding entanglement between the nano-sized layered silicate of organoclay and polyester matrix at the interface. Creep behavior can estimate changes in the molecular network structure during the deformation by the stress [21]. Results of creep measurements at a stress level of 5.1 MPa and creep time is 90 s are shown in Fig. 5. Creep compliance increased with increasing content of organoclay. CNC-0 has the highest compliance among the samples investigated, and it was developed a permanent strain more easily by the stress. Conversely, CNC-3 exhibited the lowest deformation, and it was less easily developed a permanent strain by the stress. From the creep test, the compliance in an order: $\text{CPC-0} > \text{CPC-1} > \text{CPC-2} > \text{CPC-3}$, and this trend agrees with the increasing contents of organoclay of PE/OMMT nanocomposites coatings. It means that organoclay would provide stiffness to the PE/OMMT nanocomposites coatings.

Flexibility is the most important property for cutting, pressing and stamping processes in the automotive pre-coated system [22]. Fig. 6 presents effects of the contents of organoclay on the



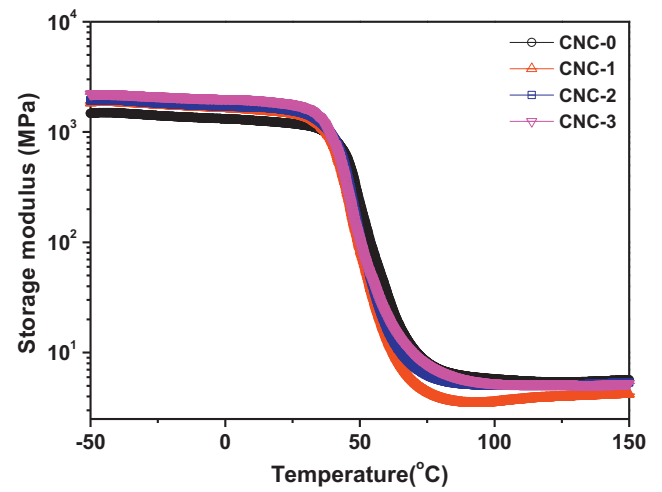
(a) CNC-1



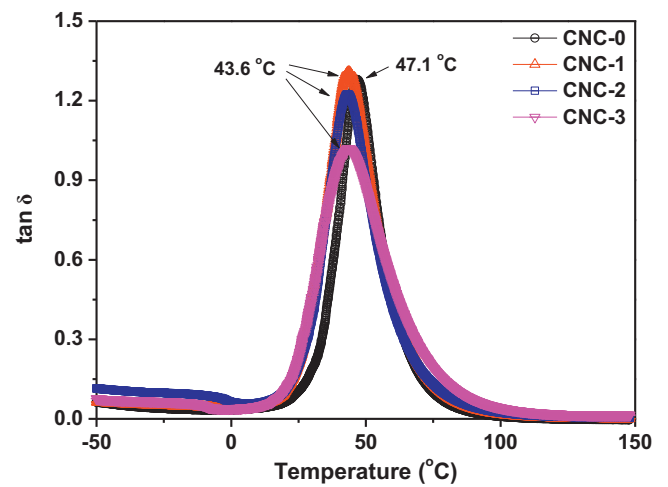
(b) CNC-3

Fig. 3. TEM images of PE/OMMT nanocomposites coatings (a) CNC-1 and (b) CNC-3.

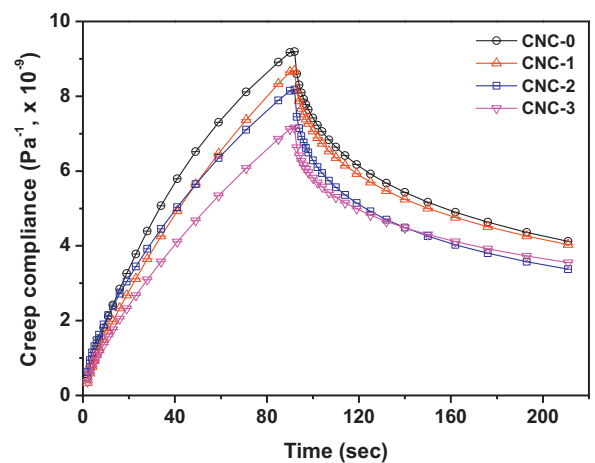
tensile behaviors of the PE/OMMT nanocomposites coatings. The tensile strength increased with an increased content of organoclay and the maximum strain decreased when the content of organoclay was increased. Compared to CNC-0 and CNC-3, the maximum tensile strength of CNC-0 was 20.2 MPa and that of CNC-3 was 22.0 MPa, with maximum strain of 185% and 166%, respectively. The maximum tensile strength of CNC-3 is increased by 8.1% and the maximum strain is decreased by 9.8% in comparison with CNC-0. It means that nano-sized layered silicate of organoclay dispersed homogeneously into the polyester matrix inhibit the mobility. This result was also reported by Chang et al. [23]. It could be implied



(a) storage modulus



(b) tan δ

Fig. 4. Viscoelastic properties of PE/OMMT nanocomposites coating (a) storage modulus and (b) tan δ.**Fig. 5.** Creep compliance of PE/OMMT nanocomposites coatings.

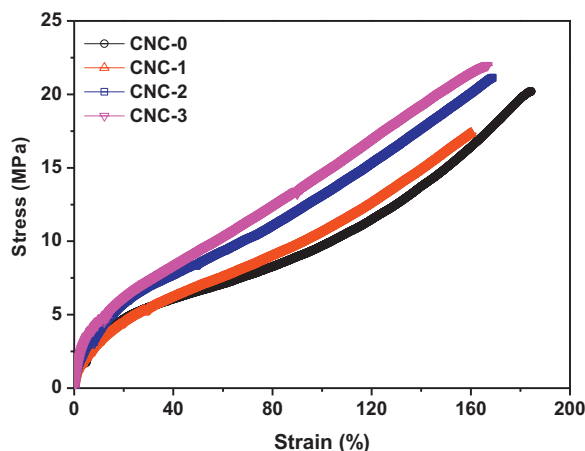


Fig. 6. Stress–strain curve of PE/OMMT nanocomposites coatings.

that organoclay can give stiffness to the PE/OMMT nanocomposites coatings.

The deep drawing test is a common method for determining formability in pre-coated metals. During the deep drawing test which took 90 s to complete, the calculated stress was 5.1 MPa and strain was 23.4% on the PCM. Stress of polyester coatings should have larger than 5.1 MPa and strain should stretch out 23.4% for 90 s to have good formability [15]. Fig. 7 shows formability resulted from the deep drawing test. All tested specimens have good formability and do not have any cracks. Because those specimens had sufficient tensile strength and elongation values based on the flexibility test. And it also had sufficient flexibility based on the creep test as shown in Fig. 8. The developed strain was over than 30% for 90 s. So, those specimens can be stretched without being damaged during the deep drawing.

One of the important roles of coatings is to block the environmental factors such as water and oxygen. Coating capacitance has been represented water uptake of coatings and it is measured by alternating current impedance method of EIS. When water is penetrating the coating, the value of coating capacitance is started. The value of water uptake of coating is calculated from Brasher–Kingbury equation [16].

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

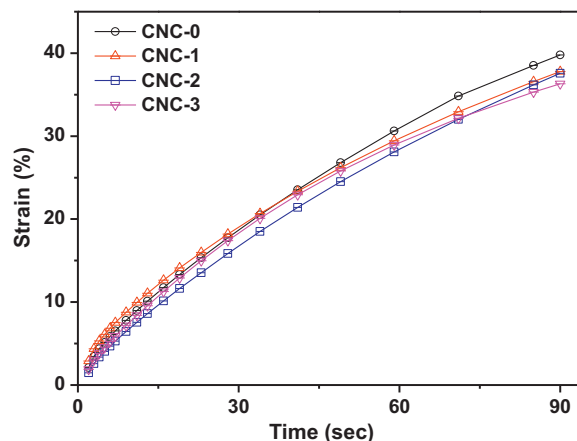


Fig. 8. Strain of PE/OMMT nanocomposites coatings by the creep test.

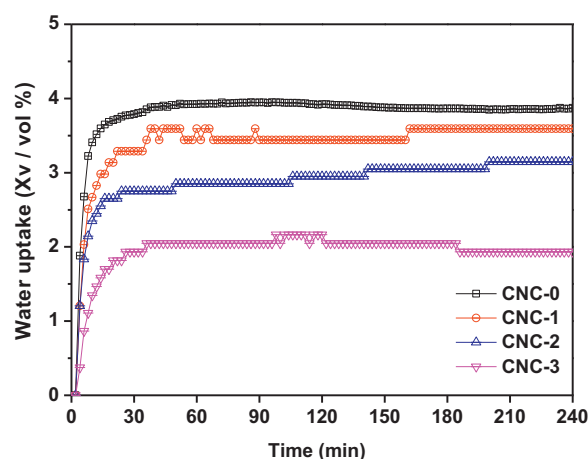


Fig. 9. Water uptake (vol.%) of PE/OMMT nanocomposites coating by the capacitance method under the immersion.

where C_t is the electrical capacitance of the coating during t time of immersion and C_0 the electrical capacitance of the coating before immersion [16]. The water uptake behavior of PE/OMMT nanocomposites coatings is shown in Fig. 9. The water uptake of PE/OMMT nanocomposites coatings was rapidly increased for 10 min and then

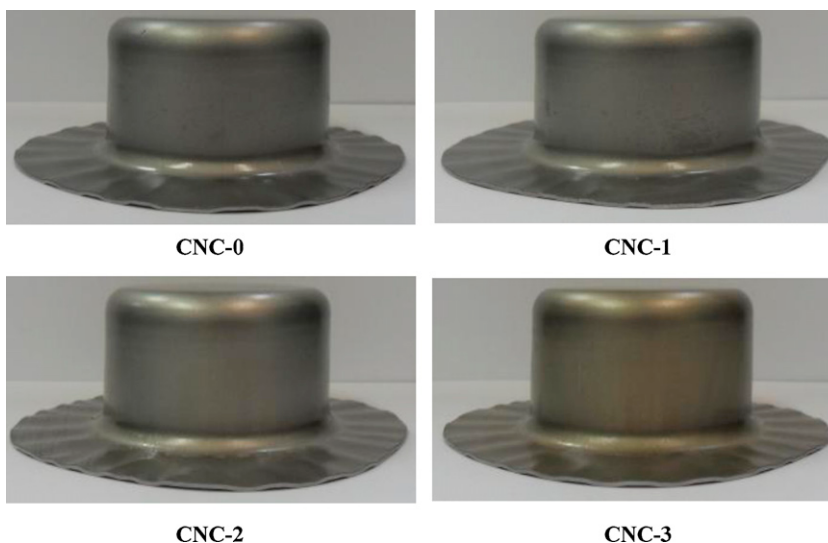


Fig. 7. Formability of PE/OMMT nanocomposites coatings on the cold roll steel.

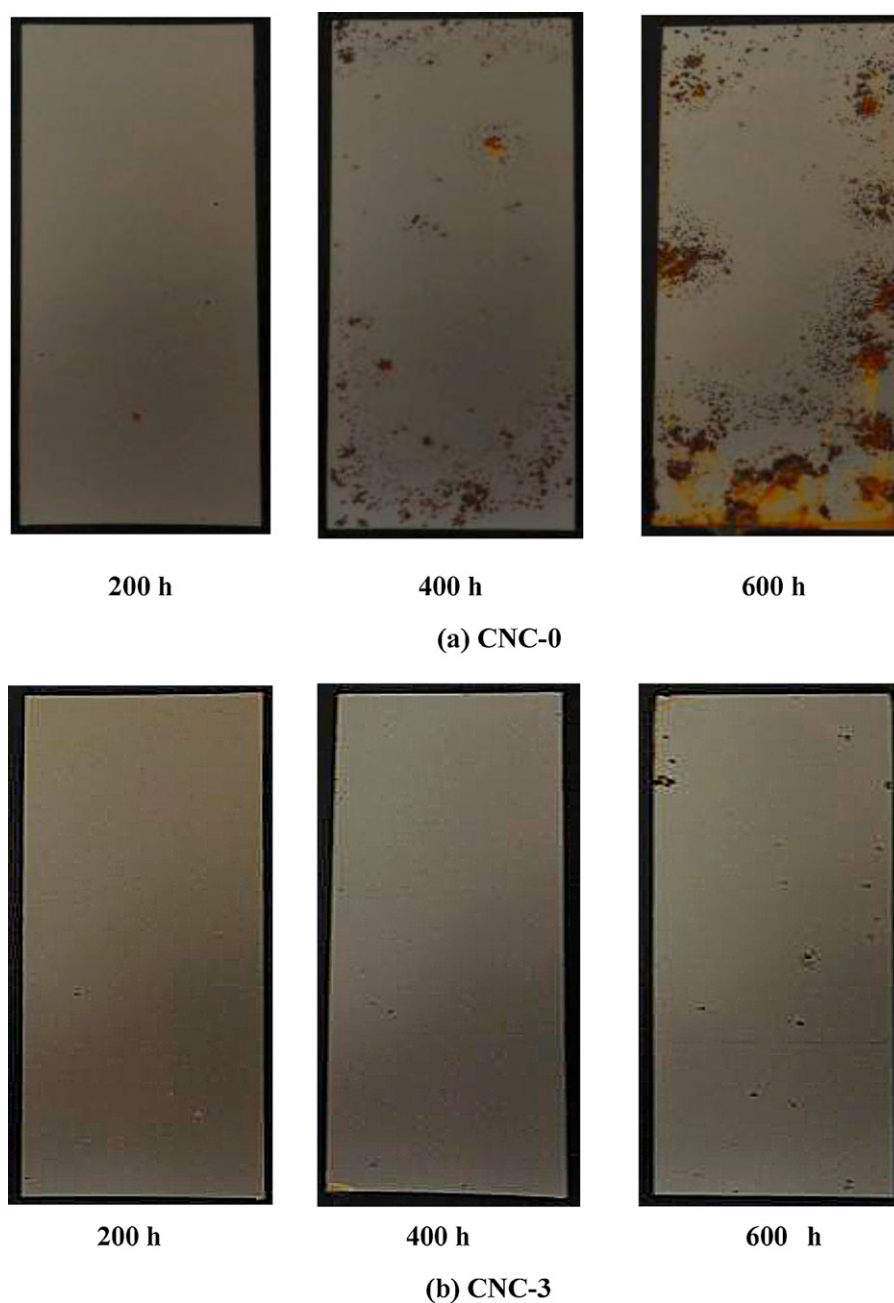


Fig. 10. Corrosion resistance of PE/OMMT nanocomposites coating by the salt spray test for 600 h (a) CNC-0 and (b) CNC-3.

was gradually increased. They were reached equilibrium state after 1 h. The value of water uptake is in order: CNC-0 > CNC-1 > CNC-2 > CNC-3. Compared to CNC-0 and CNC-3 the value of water uptake of CNC-3 was less than 2 vol.% and CNC-0 was almost 4 vol.%. It means that nano-sized layered silicate of organoclay is dispersed into the polyester matrix and can make longer pathways of water molecules to pass through the network of PE/OMMT nanocomposites coatings.

The anti-corrosion property is another physical property of automotive pre-coated metals. PE/OMMT nanocomposites coatings were tested via salt spray for 600 h. As shown in Fig. 10, CNC-0 significantly increased red rust and blistering on the surface with increasing salt spray testing time. It has lots damaged areas after 400 h. However, CNC-3 had little rust on the surface with increasing salt spray testing time. It has small damaged areas after 600 h. Those results agree with water uptake test. The value of water uptake of

CNC-3 was less than 2 vol.%, but CNC-0 was almost 4 vol.%. It implies that nano-sized layered silicate of organoclay effectively increases the length of the diffusion pathways environmental factors. And it also means that nano-sized layered silicate of organoclay might be decreased permeability and can make higher corrosion resistance of coatings.

4. Conclusion

Four types of PE/OMMT nanocomposites coatings precursors were synthesized by the in situ polymerization with high speed homogenizer process at the various contents of organoclay to disperse into the polyester matrix. The absence of reflection pattern of organoclay by XRD and TEM study revealed that organoclay was partially intercalated and exfoliated into the polymer matrix. In comparison CNC-0 and CNC-3, the maximum tensile strength of

CNC-3 was increased by 8.1% and the maximum strain is decreased by 9.8%. Because nano-sized layered silicate of organoclay was dispersed into the polyester matrix and inhibited the mobility. The viscoelastic behavior of PE/OMMT nanocomposites coatings was observed by dynamic mechanical analysis (DMA). When the content of organoclay was increased, the storage modulus of the PE/OMMT nanocomposites coatings increased considerably and T_g of each cured coatings shifted to a lower temperature.

Anti-corrosion property was examined by the salt spray test. CNC-3 had the highest amount of organoclay and it had little rust after 600 h. It implies that nano-sized layered silicate of organoclay effectively increases the length of the diffusion pathways water molecules. And nano-sized layered silicate of organoclay might be decreased the permeability and can make higher corrosion resistance of PE/OMMT nanocomposites coatings. From those results, CNC-3 had good formability in the deep drawing and also had good anti-corrosion property. So, CNC-3 would be an appropriate PE/OMMT nanocomposites coating for automotive pre-coated metal as a primer.

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