



공학박사학위논문

Enhancing Interfacial Adhesion of Steel/Plastic Composites via Molecular Adhesion

분자 접합을 통한 강판/플라스틱 복합재료의 계면 접합력 향상

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재료공학부

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Abstract

Enhancing Interfacial Adhesion of Steel/Plastic Composites via Molecular Adhesion

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Steel/plastic composites (SPCs) have attracted much attention for a long time since they display multifunctional characteristics such as thermal insulation, reduction in noise, vibration, and harshness (NVH) as well as multifarious advantages of high rigidity, fatigue resistance, and impact resistance while significantly reducing their weight. These advantages increase the demand for the employment of SPCs, especially in the automobile industry where weight reduction is an urgently leading issue during the period of energy crisis. To the best of our knowledge, the commercially available SPC is the only Smartsteel[®] developed by Material Sciences Corporation (US), and unfortunately, related researches are insufficient compared to the need for development.

The most challenging key factor in the development of SPCs is the interfacial adhesion between steel and plastic. For an actual structural material, robust and sustainable adhesion is required. Conventional physical adhesion which permeates to the roughness of the substrate causes a deterioration in durability and applicability because of a decrease in interfacial adhesion due to external conditions such as temperature, humidity, and stress and also the occurrence of a peeling effect at the interface. Recently, several emerging techniques such as laser welding and direct bonding by injection molding have been developed for attaching steel and plastic. However, the wide application of these techniques is still thwarted because of their high cost and limitations in adopting various materials.

For enhancing the interfacial adhesive properties, an impeccable understanding of the steel/plastic interface is essential. Factors that affect the interfacial adhesion are generally classified into four types: the viscosity (wettability) of plastic, the surface roughness of the substrate, and physical /chemical interaction. Among those factors, the viscosity (wettability) of plastic and surface roughness can be easily handled by the manufacturing method. Interfacial adhesion is enhanced by completely adsorbing plastic onto the surface roughness of steel via the hot-press process. Besides, physical and chemical interaction at the interface is mostly improved through surface treatment or modification of each substrate. In chapter 2, chemical and physical modification of the plastic surface was conducted to improve interfacial adhesion between steel and plastic. Physico-chemical treatment of the plastic surface and the introduction of a copolymer layer which has a polar functional group on the main chain of plastic were adopted for modifying the surface chemistry. The adhesion strength was greatly increased in both strategies, and these strategies were developed further for follow-up study.

In chapter 3, for improving the interfacial adhesion between the steel and the plastic, functional groups capable of forming a covalent bond under the hot-press process were introduced onto both surfaces of the steel plate and the plastic film. The primary amine and maleic anhydride were applied as reactive functional groups. The adhesion strength was significantly enhanced in all plastic candidates. Three types of presumable adhesion mechanisms were proposed called molecular adhesion in this study.

In chapter 4, both process simplification and development of weldable SPCs were conducted for improving the industrial applicability of SPCs. Carbonyl-containing plastic candidates were examined and polyketone which exhibited high adhesive properties via molecular adhesion without surface modification was singled out. The processing time of the steel surface was also effectively reduced by more than 80 % while maintaining adhesive properties above 90 %. Moreover, SPC with remarkably high adhesive properties and thermal resistance was developed using polyetheretherketone as the plastic core layer. The conductive fillers were embedded in the plastic surface through mechano-chemistry, and the steel fiber mesh was also adopted for the development of weldable SPCs. In summary, we believe that SPCs with molecular adhesion have sufficient potential to be applied in various industrial fields requiring weight reduction.

Keywords: metal/plastic hybrid materials, steel/plastic composites, sandwich structured laminates, interfacial adhesion, direct bonding, surface treatment/modification, lightweighting materials

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Chapter 1.

Introduction

1.1. Steel/Plastic Composites for Weight Reduction

In recent years, weight reduction of material is becoming a major trend in the automobile industry with strict fuel economy standards during the period of energy crisis^[1]. For improving fuel efficiency, various attempts have been conducted from the change of power source to changes in designs of vehicles and materials. Obviously, the change in power source from internal combustion engine (ICE) to electric vehicles (EVs) is the most desirable solution to energy problems. However, since EVs are typically 125 % heavier than ICE equivalents, the need for weight reduction is also growing to enhance battery efficiency^[2-3]. As automotive lightweighting is an urgently leading issue in both ICE vehicles and EVs, the strategies for change in materials are becoming more prominent. Although adopting lightweight metals such as aluminum, titanium, and magnesium^[4-6] or hotstamping steel that exhibits higher mechanical properties compared to conventional steel^[7-8] is mostly attempted for recent automobiles, the wide use of these materials is still thwarted because of their high cost and limitations to apply for the powertrain. Such approaches cause the irrationality of the natural frequency matching, leading to an increase in noise, vibration, and harshness (NVH) which have a major impact on the

quality of the ride^[9].

Steel/plastic composites (SPCs) have attracted much attention since they display specific advantages of high rigidity^[10], high stiffness^[11], fatigue resistance, and impact resistance^[12-13] as well as significantly reducing their weight^[14]. Especially, SPCs with a sandwich structure (steel-plastic-steel) exhibit multifunctional characteristics such as heat shielding, energy absorption, and reduction in NVH^[15-17] due to the plastic layer in the core. These advantages increase the demand for the employment of SPC, not only in the automobile industry but also electronics, aerospace, defense, and medical industries.

Classification of SPC. The sandwich structured SPCs consist of two high-strength skin steel sheets which are connected by a lightweight plastic core layer. They are generally classified into two types according to their main purpose of applications in automobiles, low NVH and weight reduction^[18]. The former has a quite thin plastic core, typically less than 10 % of the total thickness, and has already been commercialized known as Quiet steel[®], vibration damping steel, noiseless steel, etc^[19]. Besides, A thick aluminum foam sandwich (AFS) is also adopted for this type of SPCs. The highly porous aluminum alloy foam core and two aluminum skin sheets are

bonded with metallic bonding^[20-21]. The latter has a relatively thick plastic core, normally more than 30 % of the total thickness. To the best of our knowledge, the commercially available SPC for weight reduction is the only Smartsteel[®] developed by Material Sciences Corporation (MSC) in the United States^[22], and related researches are insufficient compared to the need for development.

1.2. Interfacial Adhesion

The most challenging key factor in the development of SPC is the interfacial adhesion between heterogenous materials. A robust and sustainable adhesion is required for practical structural materials. Conventional physical adhesion which permeates to the roughness of the substrate surface causes a deterioration in durability and applicability^[23]. Figure 1-1 exhibits three different types of phenomena which can be occurred at the steel/plastic interface. When heterogenous materials, steel, and plastic, with different characteristics such as physical properties, surface energy, and dimensional stability are attached, the peeling effect occurs at the interface as shown in Figure 1-1 (a)^[24]. In addition, these different properties cause the generation of internal stress during the forming process

of SPCs, resulting in separation at the interface in Figure 1-1 (b). These delaminations at the interface lower the applicability and formability of SPCs^[25]. Lastly, the interfacial adhesion is reduced by the change in the external environment, temperature, or humidity^[26]. The combined action of those factors exceedingly weakens the durability of SPC.



Figure 1-1. Three different types of phenomena at the steel/plastic interface (a) peeling effect, (b) delamination by internal stress, and (c) reduction in adhesion strength by changes in the external environment^[24-26].

Factors Affecting Interfacial Adhesion. For enhancing the interfacial adhesive properties, an impeccable understanding of the steel/plastic interface is required. Figure 1-2 illustrates four major factors affecting interfacial adhesion. Among those factors, the viscosity (wettability) of plastic and surface roughness can be easily handled by the manufacturing method. Interfacial adhesion can be maximized by completely adsorbing plastic onto the surface roughness of steel via the hot press process with the melting of plastic^[27]. On the other hand, physical and chemical interaction at the interface is mostly improved through surface treatment or modification of each substrate in other studies^[28-30]. Herein, the interfacial adhesion is enhanced by adjusting these four factors, which will be described in detail in section 1.4, research objectives.



Figure 1-2. Schematic illustration of four major factors affecting interfacial adhesion at the steel/plastic interface, (a) chemical interaction, (b) physical interaction, (c) surface roughness, and (d) viscosity (wettability) of plastic.

Evaluation of Interfacial Adhesion of SPC. Evaluation methods for measuring various mechanical properties of SPC are listed in Table 1-1. To completely understand the mechanical properties of SPC which have a sandwich structure, it was essential to evaluate the cohesive strength of the core plastic layer as well as the interfacial adhesion between steel and plastic. Especially for structural composites, the lap shear test is generally conducted that can determine both cohesive strength and adhesive strength since delamination at each interface and collapse of the core layer are directly related to the durability of SPCs^[31]. The peel test, which can measure the interfacial adhesion more precisely, is difficult to evaluate when the mechanical properties of the plastic are lower than the interfacial adhesion. Therefore, the single lap shear test is carried out for the evaluation method in this study.

Evaluation Method	Schematic Illustration	Characteristics	Standard
Peel Test		Interfacial Adhesion	ASTM D1876
Lap Shear Test		Interfacial Adhesion, Cohesion of Core Layer	ASTM D1002
Erichsen Test	3	Formability of SPC	DIN 50101
Bending Test		Ductility of SPC	ASTM D790

 Table 1- 1. Evaluation method candidates for mechanical properties of SPC.

1.3. State-of-The-Art in Adhesion Techniques for SPC

As the importance of metal/plastic hybrid materials increases, techniques for attaching the two different materials have been developed in multifarious ways. The state-of-the-art in adhesion techniques for SPC is categorized as follows:

Plastic Welding. Plastic welding is originally a manufacturing process for the plastic part by joining different types of compatible thermoplastics^[32]. The process proceeded with the preparation of two different parts of plastic, pressing them to weld joints, and heating them with several techniques. These techniques rely primarily on the applied plastic and are classified by how heat is provided, for example, ultrasonic, laser, vibration, friction, etc ^[33-35]. Since these techniques do not require extra consumables such as mechanical fasteners, solvents, and adhesives, it is easy to simplify the process and reduce the cost. Moreover, the welding process is suitable for any complex shapes from curved to irregular types ^[32].

Recently, direct laser welding of metals and plastics called LAMP (Laser-Assisted Metal and Plastic) welding is developed by the Joining and Welding Research Institute, Osaka University^[36]. Semiconductor lasers

(laser diode) with a 0.8 to 1.0 µm wavelength, YAG lasers with a 1.03 to 1.09 µm wavelength, fiber lasers, and disk lasers are majorly adopted for joining metals and transparent thermoplastics. In the LAMP welding process, after fastening overlapped plastic and metal, the laser is irradiated to the metal surface for melting the plastic at the joint interface via reflected high energy which can generate internal voids in the plastic layer. High adhesion strength is achieved due to the anchoring effect at the joint interface caused by the high pressure accompanying the rapid expansion of the generated internal voids and pushing the molten plastic into the minute gaps on the metal surface. Although LAMP welding exhibits greatly fast processing within 1 s and excellent adhesive properties, the initial cost of investment is high and deformation in plastic can be induced by the generation of internal stress caused by voids in the plastic layer. In addition, it is difficult to apply in thick plastic (above 1.2 cm) and only a few metals with high reflectivity (Al or Mg) shows high adhesive properties^[37].

Direct Bonding by Injection Molding. The injection molding technique is a direct bonding method (without the application of adhesive) like plastic welding and proceeds in two continuous steps by forming a plastic part and attaching it to the metal part simultaneously^[38]. Diverse

approaches have been conducted to improve the adhesive properties by modifying the chemical and physical properties of the metal surface. Chemical treatment of the metal surface is represented by primer (also known as adhesion promoter) coating, and past studies on coating agents such as organosilane^[39-40] or triazine trithiol-based^[41-42] have been reported. On the other hand, the adhesion strength can be improved by physicochemical treatment with both increase in surface roughness and modifying the surface chemistry, for example, abrasion^[43], etching^[44], plasma or laser treatment^[45-46]. In the late 2010s, combining the above two treatments, primer coating on surface-treated metal, has become the most widely applied process for manufacturing polymer-metal hybrid material. However, this technique has not only little capability of improvement by solely change in the metal surface but also low applicability to fabricate complicated shapes since plastic is directly injected onto the metal surface.

Adhesive for Structural Materials. Strong adhesion, high resistance to the external environment, and elasticity are required for adhesive applied in structure materials. Resin type adhesives and silicon-based elastomer type adhesives are majorly employed for manufacturing sandwich structural material^[47]. The former has low resistance to peel stress

and high resistance to shear stress in general, and the latter has the opposite characteristics^[48]. Resin type adhesives, epoxy- and acrylate-based types, exhibit high adhesion strength of ca. $15 \sim 25$ MPa which are measured by lap shear test^[49]. However, there are many restrictions for adopting specific applications which operate at high-temperature conditions, since these adhesives are generally restricted to temperature in the range of 66 \sim 99 °C^[50]. Silicon-based elastomer type adhesives can be adopted in the hightemperature range, however, they show relatively low adhesion strength (ca. $1 \sim 10$ MPa) and applicability because of their high cost^[49]. Other works are also conducted to reduce the residual stress by controlling the coefficient of thermal expansion (CTE) of the adhesive to match the dimensional stability between the metal and plastic^[51-52]. Above all, the use of adhesives increases the heterogeneity between metal/plastic interfaces making it difficult to achieve reproducible adhesion and expect long-term durability.

1.4. Research Objectives

The development of sandwich-structured laminate (steel-plasticsteel) called SPCs with robust and sustainable adhesion was conducted in this study. For overcoming fundamental issues in the current adhesion technique, novel concepts of adhesion were applied. Plastic was completely adsorbed to the steel surface assisted by the hot-press process as described in Figure 1-3. Surface treatment and modification of each substrate with wet chemistry were also performed with a complete understanding of steel/plastic interfaces. Finally, through these series of processes, all the factors affecting interfacial adhesion classified into four categories were improved in this study. In chapter 2, chemical and physical modifications of the plastic surface were carried out to improve interfacial adhesion between steel and plastic. Physico-chemical treatment of the plastic surface and the introduction of a copolymer layer that had a polar functional group on the main chain of plastic were adopted. The adhesion strength was greatly increased in both strategies, and these strategies were developed further for follow-up study.

In chapter 3, for improving the interfacial adhesion between the steel and the plastic, functional groups capable of forming a covalent bond under the hot-press process were introduced onto both surfaces of the steel plate and the plastic film. The primary amine and maleic anhydride were applied as reactive functional groups. Confirmation of the introduction of functional groups on each substrate was conducted and the adhesion strength of the manufactured SPCs was evaluated. Three types of presumable adhesion mechanisms were proposed called molecular adhesion in this study.

In chapter 4, both process simplification and development of weldable SPCs were conducted for improving the industrial applicability of SPCs. Carbonyl-containing plastic candidates were examined and polyketone which exhibited high adhesive properties without surface modification was singled out. Time reduction of the established process (Chapter 3) for steel surface was performed, in company with bio-inspired coating treatment. At last, for the development of the conductive plastic core layer, the conductive fillers were embedded in the plastic surface through mechano-chemistry^[53], and the steel fiber mesh (SFM) was also adopted for maximizing the electrical conductivity.



Figure 1-3. Schematic illustration of designed adhesion system in this study.

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Chapter 2.

Chemical/Physical Modification of Plastic Surface and Understanding Adhesive

Properties Between Steel and Plastic

2.1. Introduction

Steel/plastic composites (SPCs), especially sandwich-structured laminate, display multifunctional abilities such as heat shielding, energy absorption, reduction in noise, vibration, and harshness (NVH) as well as multifarious advantages of high stiffness, fatigue, and impact resistance while significantly reducing their weight. These advantages increase the demand for the employment of SPCs, particularly in the automobile industry where weight reduction is an urgently leading issue during the period of energy crisis. To the best of our knowledge, the commercially available SPC is the only Smartsteel[®] developed by Material Sciences Corporation (US), and unfortunately, related researches are insufficient compared to the need for development.

The most challenging key factor in the development of SPCs is the interfacial adhesion between different materials. For a practically usable structural material, robust and sustainable adhesion is required. Factors that affect the interfacial adhesion of SPCs are generally classified into four types: viscosity (wettability) of plastics, the surface roughness of steel substrate, physical interaction, and chemical interaction. Among these factors, the wettability of plastics is improved by the hot-press process at a

temperature higher than the melting temperature of plastic^[1]. Plastic can be adsorbed into the non-uniform and rough steel interface by the complete melting of the plastic. Moreover, modifying the surface chemistry of plastic can enhance both physical and chemical interaction at the steel/plastic interface^[2-3].

Physico-chemical surface treatments of plastic are applied to modify the surface chemistry of plastic for improving the wetting characteristics as well as enhancing physical and chemical interaction at the interface without affecting the properties of bulk material^[4-5]. Such surface pretreatment methods represented by corona discharges^[6], plasma^[7-8], and ultraviolet/ozone (UV/O₃)^[9-10] are widely employed in various industrial fields by allowing effective adhesion such as paints, printings, or laminates. UV/O₃ treatment can be conducted under relatively mild conditions, atmospheric pressure, and room temperature, compared to the above two treatments which are based on high kinetic energy. Therefore, numerous studies have been performed to investigate the combined effects of UV and including polyolefin^[11], ozone on multifarious plastic substrates polyethylene terephthalate^[12], polystyrene^[13], and fabric surfaces^[14].

Herein, we designed adhesion between electro-galvanized iron steel and plastics, polyethylene (PE), and Nylon 6, extensively adopted as interior materials for automobiles. Both plastics were completely adsorbed into the steel surface via the hot-press process. The interfacial adhesion was improved by modifying the surface chemistry of Nylon 6 through UV/O₃ treatment. For PE, introducing a copolymer layer having a polar functional group, maleic anhydride (MA), on the steel surface was also adopted for enhancing physical/chemical interaction at the steel/plastic interface. Finally, the adhesion strength was evaluated through the lap shear test method.



Figure 2-1. Graphical abstract of strategies applied in this study (a) increase in physical interaction and (b) complete adsorption of plastic via hot-press.

2.2. Experimental

Materials. Two steel (EG: 0.6 mm thickness, PL: 0.4 mm thickness, electro-galvanized iron steel) steel sheets were kindly provided by POSCO (Pohang Iron and Steel Co., Ltd, KR). The sheets were cut into a plate with the dimension of 100 mm x 25 mm, washed several times with absolute ethanol, and stored in a desiccator before use. The HDPE (High-Density Polyethylene) film (ET323100, 1 mm thickness, Named PE) and Nylon 6 film (AM301200, 0.2 mm thickness) were purchased from Goodfellow Cambridge Ltd (UK). The HDPE-graft-maleic anhydride (HDPE-g-MA, 1.0 wt % of introduced MA) was obtained from TWOHCHEM PROPOLDER Ltd (KR).

Surface Analysis of Steel Plate. Scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDS, JSM-7800F, JEOL Ltd, JP) was applied for elemental analysis of the steel surface. Elemental mapping of the steel surface was performed under 3.0 kV and x3,000 (magnification) conditions and three elements with the highest fraction were recorded. The measurement of surface roughness through the

three-dimensional structural information was conducted with Atomic Force Microscope (AFM, NX-10, Park Systems, KR). Tapping mode AFM with single module flexure XY-scanner with closed-loop control was adopted for tomographic imaging of steel surface (Resolution: 0.05 nm). Both analyses were carried out at room temperature without pretreatment.

Surface Treatment of Nylon 6 Film. The surface of the Nylon 6 film was cleaned using ultrasonication in ethanol before treatment. Photosensitized oxidation was then performed through UV/O₃ treatment. UV/O₃ treatment was carried out with a small-scale (15 cm x 15 cm) bench top photoreactor (AC-12, AhTech LTS, KR) using a UV lamp (UVJ-42, Jelight, US). The Nylon 6 films were treated at a distance of 1 cm from the UV grid lamps, and the irradiated wavelengths were 184.9 and 253.7 nm for both sides of the films respectively for 30 min with 28 mW/cm² at room temperature. Optimization of irradiation time was established through SEM-EDS with the same device as mentioned above. The surface-treated Nylon 6 films were kept in a desiccator after rinsing with ethanol and named as UVO-Nylon 6.

Preparation of Specimens for Evaluation of Adhesion Strength.

The preparation of specimens for the lap shear tests was conducted in two different methods, surface treated type (Nylon 6), and electrostatic spray type (HDPE/PE-MA). First, surface treated type specimens were fabricated as follows: two steel plates (PL as representative) were placed in contact with each other in a 1.2 mm thick frame for fixation during the hot-press process. The contact area was adjusted to $12.5 \times 25 \text{ mm}^2$ and Nylon 6 films with the same dimension were filled with a thickness of 0.4 mm between steel plates. Pieces of PTFE sheets with a 0.1 mm thickness were inserted into the space excluding the contact area in order to avoid unintentional adhesion between the steel plate and Nylon 6 film. The frame was then placed on the hot pressing machine (Hydraulic Press, SAMDOO, Korea) and PTFE sheets were also inserted between the frame and stage, both top and bottom, to prevent contamination and adhesion to the stage. After setting both sides of the frame in close contact with the stage, the temperature was increased to the corresponding processing temperature for Nylon 6 as listed in Table 1. At the processing temperature, the frame was kept for 10 min to allow the Nylon 6 to melt sufficiently and the pressure was raised to 5 MPa while a hot-press process was performed for an additional 30 min. The frame was released from compression, removed from the machine, and cooled to room temperature.

The electrostatic spray type specimens were prepared as follows (Figure 2-2 (a)): PE-g-MA powder was sprayed onto the steel surface to have a uniform thickness (below 0.1 mm) by using an electrostatic spray gun (DJ10A, DJS, KR). The obtained steel plates were placed in a convection oven and heated above the melting point (180 °C) for 30 min followed by cooling at room temperature. The specimens were then fabricated using neat HDPE films in the same procedure as the surface-treated type.

Evaluation of Adhesion Strength. A single-lap shear test was adopted for measuring the adhesion strength of steel/plastic composites. The adhesion strength of prepared specimens was evaluated using a universal testing machine (QUASAR 5, GALDABINI SPA, IT). The conditions of lap shear tests were the same as described in ASTM D1002 using a 5 kN load cell. For PL plates, the width of the contact area of the specimens and the thickness of the contact area were set up to 12.5 x 25 mm² and 1.2 mm, respectively (Figure 2-2(b)). Both ends of the specimen were firmly fixed by the clamp of the jig, and the upper clamp was pulled with a speed of 0.15 MPa/s. The lap shear tests were conducted at two different time intervals:

immediately after the preparation of specimens (0 d aging) and three days after the preparation of specimens (3 d aging). The average values obtained from three repeated tests were reported and all the tests were performed at room temperature.

Plastic Structure T_m (°C) Modification **Specimen Preparation** Tp(°C) Introduction of HDPE/ 135 180 copolymer layer Electrostatic spray type PE-MA (1.0 wt % grafted) UV/O3 treatment Nylon 6 220 250 Surface-treated type (30 min exposure)

Table 2-1. Plastic candidates adopted in this study.



Figure 2-2. (a) Preparation of electrostatic spray type specimens and (b) schematic (i) diagram of lap shear test and (ii) dimensions of the specimen (PL steel).

2.3. Results and Discussion

Surface Analysis of Steel Plate. The elemental fraction and surface roughness of each steel plate was listed in Table 2-2. Since both EG and PL steel were electro-galvanized steel, Zn exhibited the highest elemental fraction. As shown in the layer structure of the steel surface (Table 2-2), a post-treatment, phosphate conversion coating (PCC) was carried out in advance on the surface of PL steel to improve paintability^[15]. Because of PCC, PL steel showed a relatively high oxygen fraction at the surface (22.9 %) and surface roughness (92.2 nm on the micro-scale and 0.76 on the nano-scale) compared to EG steel, 2.1 % of oxygen fraction, 62.3 and 0.22 nm on micro/nano-scale respectively. In Figure 2-3, the surface of PL steel was more irregular and rough compared to EG steel by topographical AFM images based on 3D structural information and SEM images.

Product	Layer Structure	Thickness (mm)	EDS Elemental Analysis (mass %)			AFM Surface Roughness (nm)	
			Zn	Fe	0	Micro Scale	Nano Scale
EG	Zinc Steel	0.6	83.8 ± 0.4	3.0 ± 0.2	2.1 ± 0.1	62.3	0.22
PL	Phosphate Zinc Steel	0.4	38.1 ± 0.2	1.6 ± 0.1	22.9 ± 0.2	92.2	0.76

 Table 2-2. Characteristics of steel plates employed in this study.



Figure 2-3. Topographical AFM images of (a) EG steel (b) PL steel and SEM images of (c) EG steel (d) PL steel (3,000x mag, scale bar: 500nm).

Surface Treatment of Nylon 6 Film. UV/O3 treatment, a photosensitized oxidation process, allowed modification of physico-chemical properties of the plastic surface according to the following four-step mechanisms^[16-19]. Firstly, UV radiation in the low wavelength (184.9 nm) changed atmospheric oxygen molecules into an excited-state, 0_2^* . An excited-state oxygen molecule then dissociated into two ground-state oxygen atoms, O^G. Ozone molecule was generated from the conjugation between the ground-state oxygen atom and the oxygen molecule, O₃. Lastly, the photolysis of ozone molecules occurred upon high wavelength UV radiation (253.7 nm) resulting in the generation of atomic oxygen. The generated atomic oxygen was a significantly reactive and short-lived species. Therefore, carbon radicals were produced by an immediate reaction between plastic and atomic oxygen through the abstraction of hydrogen from a plastic chain. Hydroxyl radicals were also produced in the presence of water vapor within the UV/O₃ chamber. As a result, various polar functional groups such as hydroxy- and carboxy- were generated. As depicted in Figure 2-4, the photocleavage of the plastic chain occurred concurrently to form larger grains at the surface^[20-21].

The optimized exposure time was determined by oxygen fraction at

the surface of Nylon 6 measured with SEM-EDS elemental analysis. Figure 2-5 exhibited the oxygen fraction of the Nylon 6 surface after varying exposure times from 0 to 60 min. As the exposure time of UV increased, the oxygen fraction of the Nylon 6 surface increased due to the formation of polar functional groups. Up to 30 min of exposure, the oxygen fraction increased by 131 % from 21.2 % (0 min) to 27.9 %, however, even when additional exposure for 30 min, the increase was only 102 % (28.5 % at 60 min). Consequently, the optimized exposure time was selected as 30 min in this work.



Figure 2-4. Schematic illustration of UV/O_3 treatment to Nylon 6 film.



Figure 2-5. Oxygen fraction of Nylon 6 surface depending on the exposure time.

Evaluation of Adhesion Strength. The lap shear test specimens were prepared with the same dimension as shown in Figure 2-2 (b). In Figure 2-6, for pristine PE, the adhesion did not occur at all in both EG and PL steel. However, when a copolymer layer (PE-MA) was introduced at the interface, the adhesion strength of steel/PE composites dramatically increased from 0 to 6.9 MPa at 3 d aging (EG) and 8.9 MPa at 3 d aging (PL) respectively. Similarly, the adhesion strength of steel/Nylon 6 composites increased from 7.7 to 10.3 MPa at 3 d aging (EG) and 7.1 to 12.7 MPa at 3 d aging (PL) as shown in Figure 2-7 and Table 2-3. The increase in adhesion strength was considered as the combined action of an increase in physical/chemical interaction at the steel/plastic interface and the complete adsorption of plastic onto the steel surface.

In particular, the adhesive strength was high in the case of PL steel was adopted as the skin material of SPCs for both plastics. The phosphate layer formed on the PL steel surface via PCC induced high roughness and oxygen fraction, and therefore it is judged that the anchoring effect at the interface and the interaction with the polar functional group of the plastics were enhanced compared to EG steel. Besides, the adhesion strength generally increased under 3 d aging than 0 d aging conditions because of the effect of the relaxation time. These phenomena were explained by understanding the behavior and shape of the plastic chain near the steel/plastic interface^[22-23]. The plastic chains on the surface of the plastic layer extended away from the steel/plastic interface and were entangled inward toward the plastic layer at the initial stage after the hot-press process. As time advanced after external pressure was removed, plastic chains in the region adjacent to the steel/plastic interface were rearranged toward the interface, and the entangled chains became closer to the substrate. As the interfacial interactions between the adsorbed plastic and steel substrates were more dense over time, the adhesion strength was improved.



Figure 2-6. Adhesion strength of steel/PE composites depending on the introduction of copolymer layer († non-measurable).



Figure 2-7. Adhesion strength of steel/Nylon 6 composites (Steel/Non: applying non-treated Nylon 6, Steel/UVO: applying UV/O₃-treated Nylon 6).

Polymer /		Pristi	ne PE	PE / PE-MA (1.0 wt % grafted)		
Stee	1	0 d (MPa)	3 d (MPa)	0 d (MPa)	3 d (MPa)	
	EG	0	0	4.8 ± 0.05	6.9 ± 0.8	
PE	PL	0	0	7.3 ± 0.4	8.9 ± 0.5	
Polymer /		Non - UV/O ₃ Treatment		UV/O ₃ Treatment (30 min)		
Polyme	er /	Non - UV/O	₃ Treatment	UV/O ₃ Treat	ment (30 min)	
Polyme Stee	er / l	Non - UV/O 0 d (MPa)	3 Treatment 3 d (MPa)	UV/O ₃ Treata 0 d (MPa)	ment (30 min) 3 d (MPa)	
Polymo Stee	er / l EG	Non - UV/O 0 d (MPa) 6.4 ± 1.6	3 Treatment 3 d (MPa) 7.7 ± 0.4	UV/O ₃ Treats 0 d (MPa) 9.4 ± 0.3	ment (30 min) 3 d (MPa) 10.3 ± 0.7	

 Table 2-3. Adhesion strength of steel/PE and steel/Nylon 6 composites.

2.4. Conclusion

In this work, we designed direct bonding without the application of adhesive between steel and plastics. Two employed plastics, PE and Nylon 6, were completely adsorbed into the steel surface via the hot-press process. For enhancing the interfacial adhesion at the steel/plastic interface, modification of the surface chemistry of plastics was conducted. The adhesion strength of steel/plastic composites significantly increased by modifying physical and chemical interaction at the steel/plastic interface. Finally, based on the understanding of adhesive properties obtained in this study, further research was conducted in the next chapter.

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Chapter 3.

Development of Interface Treatment to Enhance Adhesive Properties in Steel/Plastic Composites

3.1. Introduction

As the importance of metal/plastic hybrid materials increases, adhesion techniques between different materials such as metals and plastics have become more prominent in automobiles, aerospace, electronics, defense, and medical industries. The demand for the employment of plastic-metal hybrid materials significantly increases in the automobile industry where weight reduction is an urgently leading issue during the period of energy crisis. Various studies on adhesion techniques, laser welding, or direct injection molding, have been reported, however, several issues to be improved still remain. For example, laser welding can be applied to only a few metals with high reflectivity for high adhesive properties, and direct injection molding is unsuitable to fabricate complicated shapes since plastic is directly injected onto the metal surface.

Therefore, novel concepts of adhesion need to be applied for the development of practically usable metal/plastic hybrid materials. The possibility that molecular-sized bonding can be applied to adhesion between macroscopic materials has been demonstrated according to diverse studies^[1-8]. For instance, mussel-inspired polydopamine and a

catechol functional group derived therefrom have the potential to be applicable techniques^[1-3]. In addition, organosilane chemistry is frequently adopted to improve adhesive properties^[4-10]. In particular, aminosilane is known to be easily hydrolyzed in an aqueous solution to form self-assembled monolayers (SAMs)^[11-12], and many approaches have been conducted to apply aminosilane as an adhesion enhancer. The surface treatment of Al with aminosilane improves the adhesive properties with polyamide as the formation of hydrogen bonding and also effectively increases adhesive properties even with chemically nonreactive thermoplastics like polyolefins^[4-6]. Besides, there is a study combining aminosilane SAMs formed on the Ti surface and polyimide activating carboxyls with 1-(3-(dimethylamino)-propyl)-3its ethylcarbodiimide (EDC) /N-hydroxysuccinimide (NHS) through a hotpress process^[7].

In our previous study, we aim to increase the physical/chemical interaction at the steel/plastic interface by modifying solely the plastic surface. Herein, for improving the interfacial adhesion between the steel and the plastic, functional groups capable of forming a covalent bond under the hot-press process were introduced onto both surfaces of steel and plastic. The primary amine and maleic anhydride (MA) were applied as reactive functional groups, which were known to reproducibly form a well-defined covalent bond layer on various types of solid substrates such as glass/wafer, polyurethane, polyethylene terephthalate^[13-15].

In this work, we designed the adhesion between electro-galvanized iron steel anchored with SAMs of 3-aminopropyltriethoxysilane (APTES) and high-density polyethylene (HDPE), acrylonitrile butadiene styrene (ABS) and Nylon 6 which were widely used as interior materials for the automobile. The MA was introduced into the main chain of plastic candidates through photo-initiated grafting. Confirmation of the introduction of amine onto the steel plate and quantitative analysis of the amount of introduced MA onto the plastic surface was conducted, and the adhesive properties of the manufactured steel/plastic composites (SPCs) were evaluated. Based on these results, three types of presumable adhesion mechanisms were proposed called molecular adhesion in this study.



Figure 3-1. Graphical abstract of molecular adhesion applied in this study.

3.2. Experimental

Materials. Steel (PL, electro-galvanized iron steel, 0.4 mm thickness) sheets were kindly donated by POSCO (Pohang Iron and Steel Co., Ltd, KR). The sheets were cut into 100 mm x 25 mm, washed several times with absolute ethanol, and stored in a desiccator before use. The HDPE film (ET323100, 1 mm thickness, Named PE) and Nylon 6 film (AM301200, 0.2 mm thickness) were purchased from Goodfellow Cambridge Ltd (UK). The ABS pellets (ER 461) were kindly provided by LG Chem Co., Ltd (KR). APTES (99 %), benzophenone (BP, 99 %) and MA (99 %) were obtained from Sigma-Aldrich. All reagents were used as received without further purification.

Surface Treatment of Steel Plates (Steel-NH₂). The surfaces of steel plates were cleaned using ultrasonication in ethanol and distilled water. The plates were placed in a small-scale (15 cm x 15 cm) bench top photoreactor (AC-12, AhTech LTS, KR) using a UV lamp (UVJ-42, Jelight, US) for UV/O₃ treatment. The steel plates were treated at a distance of 1 cm from UV grid lamps, and the irradiated wavelength were 184.9 and 253. 7

nm respectively for 1 h with 28 mW/cm² at room temperature. The plates were then soaked into 5 wt % KOH aqueous solution for 10 min, followed by rinsing using ultrasonication in ethanol and distilled water. After the plates were immersed in 5 wt % APTES aqueous solution for an additional 30 min, the plates were washed with ethanol and dried in ambient air. The surface-treated plates were kept in a desiccator before use and named Steel-NH₂. All the treatments were performed at room temperature.

Surface Modification of Plastic Films (Plastic-MA). Since the ABS film was not commercially available, the ABS pellets were made into a film with a thickness of 200 µm using a hot pressing machine (Hydraulic press, SAMDOO, KR) at 250 °C. PE, Nylon 6, and ABS films were washed several times using ethanol and dried in a vacuum oven before modification. The films were immersed for 3 min in methanol solution which was prepared by dissolving the same molar ratio of MA and BP at concentration of 10 and 20 w/v % based on the weight of MA. The films were then dried in a 50 °C oven until methanol was completely removed and exposed to UV irradiation (UVJ-42 lamp, Jelight, US). Irradiation of UV was conducted on both sides of the film for 5 min each with the same device as mentioned above. The surface-modified plastic films were kept in a desiccator after

rinsing with ethanol and named a plastic-MA film such as PE-MA, Nylon 6-MA, and ABS-MA film. All the treatments were conducted at room temperature.

Surface Analysis of Steel Plates and Plastic Films. Scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDS, JSM-7800F, JEOL Ltd, JP) was adopted for the analysis of nitrogen fraction in the steel surface. Elemental mapping of steel surfaces was performed under 3.0 kV and x3000 (magnification) conditions. A ninhydrin test was performed to confirm the existence of amine functional groups on the surface of the steel plate. Ninhydrin solution was prepared by dissolving 0.2 g ninhydrin in 100 ml n-butanol and 3 ml acetic acid. FT-IR (TENSOR 27, Bruker, DE) spectra were obtained using a single-reflection attenuated total reflection (ATR) method to quantitatively analyze the amount of introduced MA on the surface of the plastic film based on the two-point baseline method. The spectra were recorded in the range of 4,000 to 400 cm⁻¹ at a spectral resolution of 4 cm⁻¹, and 32 scans were taken per sample.

Preparation of Specimens for Evaluation of Adhesion Strength.

The specimens for the lap shear tests were fabricated as follows: two steel plates were placed in contact with each other in a 1.2 mm thick frame for fixation during the hot-press process. The contact area was adjusted to 12.5 x 25 mm^2 and plastic films with the same dimension were filled with a thickness of 0.4 mm between steel plates. Pieces of PTFE sheets with a 0.1 mm thickness were inserted into the space excluding the contact area in order to avoid unintentional adhesion between the steel plate and plastic film. The frame was then placed on the hot pressing machine and PTFE sheets were also inserted between the frame and stage, both top and bottom, to prevent contamination and adhesion to the stage. After setting both sides of the frame in close contact with the stage, the temperature was increased to the corresponding processing temperature for each plastic as listed in Table 3-1. At the processing temperature, the frame was kept for 10 min to allow the plastic to melt sufficiently and the pressure was raised to 5 MPa while a hot-press process was performed for an additional 30 min. The frame was released from compression, removed from the machine, and cooled to room temperature.

The specimens for the 90° peel tests were prepared as follows: The
steel plate was placed in a 0.8 mm thick frame and two sheets of Nylon 6 films of the same size as the plate were placed on the steel plate. A piece of PTFE sheets ($25 \times 25 \text{ mm}^2$) was inserted between the plate and film to facilitate the subsequent peeling of Nylon 6. The hot-press process was conducted in the same method as mentioned above. After removing a piece of PTFE sheet inside the fabricated specimen, the non-adhesive part of the Nylon 6 film was set upright at 90 degrees to proceed with the 90° peel tests.

Evaluation of Adhesion Strength. Adhesion strengths of prepared specimens were evaluated using a universal testing machine (QUASAR 5, GALDABINI SPA, IT). The lap shear tests were conducted according to ASTM D1002 using a 5 kN load cell. The width of the contact area of the specimens and the thickness of the contact area were set up to 12.5 x 25 mm^2 and 1.2 mm, respectively. Both ends of the specimen were firmly fixed by the clamp of the jig, and the upper clamp was pulled with a speed of 5 mm/min. The lap shear tests were performed at two different time intervals: immediately after the preparation of specimens (0 d aging) and three days after the preparation of specimens (3 d aging).

The 90° peel tests were carried out according to ASTM D1876

using a 250 N load cell. The specimen was fixed on a horizontally movable jig and the non-adhesive part of Nylon 6 film was fastened with the upper clamp. The upper clamp was pulled with a speed of 5 mm/min and the movable jig was continuously moved to maintain the angle between the fixed specimen and the pulling direction was exactly 90 degrees. The 90° peel tests were performed by adding 7 d aging conditions to the previous 0 d aging and 3 d aging conditions. The average values obtained from three repeated tests were reported and all the tests and aging process were conducted at room temperature.



Scheme 3-1. Schematic illustration of surface treatment on (a) steel plate, (i) KOH aqueous solution, 10 min (ii) APTES aqueous solution, 30 min, and (b) plastic film (iii) MA, BP in methanol, dipping, (iv) UV radiation (λ : 254 nm, 28 mW/cm²), 5 min.

3.3. Results and Discussion

Surface Treatment and Analysis of Steel Plate. The primary amine groups were introduced on the surface of the steel plate through an organosilane coupling reaction^[16-17]. Firstly, the steel plates were immersed into a basic KOH aqueous solution to introduce hydroxyl groups on the surface which provided the necessary anchoring point for the coupling reaction. The steel plates were then treated with APTES aqueous solution to form stable bonds of steel-O-Si-C as described in Scheme 3-1 (a). The ethoxy groups in APTES were easily hydrolyzed to silanols in an aqueous solution. The coupling reactions proceeded with two sequential steps; from a state of physisorption through the formation of a hydrogen bond to a formation of a covalent bond by dehydration between silanols of APTES and hydroxyls of the steel surface^[18].

Steel-OH + HO-Si(OH)₂-R
$$\longrightarrow$$
 Steel-OH IIIII HO-Si(OH)₂-R
 \longrightarrow Steel-O-Si(OH)₂-R + H₂O

The existence of amines on the steel surface was confirmed through the ninhydrin test as shown in Figure 3-2, however, the amount of introduced amine was hardly analyzed since the amount of amine and the degree of color expression by the ninhydrin reaction were not proportional. In addition, water contact angle measurement and surface analysis using FT-IR were also attempted to validate the change in the steel surface. Unfortunately, it was extremely difficult to properly prove the differences. Because the steel had already been subjected to the hydrophilization treatment (PCC, mentioned in Chapter 2) in advance, the water contact angle did not show significant differences depending on the introduction of amines on the steel surface. Furthermore, the introduced monomolecular layer buried in the bulk substrate was too thin to analyze quantitatively using conventional FT-IR ATR spectral measurements with a calculated penetration depth of $0.664 \mu m$.



Figure 3-2. Positive result of ninhydrin test supporting the introduction of amine groups on the surface of the steel plate.

Surface Modification and Analysis of Plastic Film. As a counterpart of the amines, MAs were grafted into the main chain of plastic through photo-initiated grafting with BP as an initiator (Scheme 3-1 (b)). BP was a typical Norrish type II photo-initiator, which generally required donor molecules such as amine synergists^[19]. In the photo-initiation process, BP molecules were excited to the excited singlet state and then underwent intersystem crossing (ISC) to the excited triplet state. These excitations led to the formation of the excited triplet state of MA which acted like donor molecules and electron transfer followed by proton transfer between MA and the benzopinacol radical to initiate grafting (Figure 3-3)^[20-21].

The introduction of MA on the main chain of Nylon 6 (as representative) was confirmed by FT-IR based on the presence of a cyclic anhydride group in MA (C=O, stretch, 1750 cm⁻¹) and the absence of a double bond in MA (C=C, bend, 900 cm⁻¹). In particular, it was confirmed that MA was successfully introduced into the main chain of Nylon 6 without ring opening through the disappearance of the double bond in MA while maintaining the cyclic anhydride group as shown in Figure 3-4. Quantitative analysis of the amount of introduced MA was carried out by comparing the peak intensity ratios (PIRs) of the carbonyl group of the amide bond (C=O,

stretch, 1680 cm⁻¹) and the cyclic anhydride group in MA. The relative intensities were quantified by the two-point baseline method^[22-24]. The intensity of each peak was measured from the baseline, which was corrected by drawing a straight line from each peak as depicted in Figure 3-5. A vertical line from the top of the peak to the baseline represented the peak intensity.

PIRs
$$(x) = \frac{C = O (Ester), Stretch, Peak Intensity}{C = O (Amide), Stretch, Peak Intensity}$$

Introduced MA (wt %) = $79.55 x - 3.73 \times 10^{-1}$

FT-IR spectra were recorded by mixing Nylon 6 with 1,3 and 10 wt % of MA in a molten state without reaction to derive the PIRs and above formula for calculating the amount of introduced MA on Nylon 6 (Figure 3-5, $R^2=0.999$). The amount of introduced MA on each plastic was summarized in Table 3-1. The amount of introduced MA on ABS was 4.9 and 6.6 wt %, respectively, which was the highest amount among the three plastics because of the double bond in the structure. In the case of Nylon 6, 3.8 and 5.8 wt % of MA were introduced which were quite high similar to ABS due to the presence of the carbonyl group, electron-withdrawing group, that lowered the stability of the β -carbon radical. On the other hand, PE

exhibited a relatively low amount of introduced MA, 1.0 and 2.0 wt %, compared to ABS and Nylon 6 since there was no functional group in its structure that could affect the reactivity of the radical.



Figure 3-3. Reaction mechanism of photo-initiated grafting to plastic using BP and MA (K_q : quenching constant)^[20].



Figure 3-4. FT-IR spectra of (a) Nylon 6-MA and Nylon 6 film and (b) pristine maleic anhydride.



Figure 3-5. Establishment of the reference value to derive the formula for quantitative analysis of introduced MA on Nylon 6 film.

Polymer	T _m (°C)	T _p ^a (°C)	Introduced MA (wt %)	Adhesive Strength (MPa)	
				Non-treated	Surface-treated ^b
PE	135	180	1.0, 2.0	≈0	11.5 ± 0.5
ABS	220	250	4.9, 6.6	2.5 ± 0.6	11.1 ± 0.6
Nylon 6	220	215	3.8, 5.8	13.0 ± 0.4	14.1 ± 0.2

 Table 3-1. Properties of plastics used in this study.

^a Processing temperature for the fabrication of SPCs

^b Maximum adhesion strength of SPCs after 3 d aging

Adhesion strength of Steel/PE and ABS composites. The lap shear test specimens were prepared with the same dimension as shown in Figure 3-6 (a). For reliable measurement of cohesion and adhesion strength, it was necessary to fabricate a uniform plastic core layer without internal voids. Therefore, specimens were prepared by the hot-press process for 30 min at 5 MPa after sufficient melting of plastic at a processing temperature (Table 3-1) higher than the melting point of PE and ABS to inhibit the formation of internal voids. In Figure 3-6 (b), for PE, when the surface modification was not performed, the adhesion did not occur at all. However, the adhesion strength of PE-MA (1.0 wt %) dramatically increased from 0 to 8.8 MPa at 0 d aging and 11.5 MPa at 3 d aging. Likewise, the adhesion strength of ABS-MA (4.9 wt %) increased from 2.5 to 8.4 MPa at 0 d aging and 1.5 to 11.1 MPa at 3 d aging compared to non-treated ABS as can be seen in Figure 3-6 (c).

The increase in adhesion strength was considered as the combined interaction of three possible adhesion mechanisms which was called molecular adhesion in this study. Firstly, the primary amine on the steel and introduced MA on plastic reacted to form a chemical covalent bond during the hot-press process as described in Figure 3-7 (a) and (c). Primary amines formed an amide bond with MA under heating conditions, and when heat is applied further, the amide bond and an adjacent carboxylic acid additionally react to form succinimide by dehydration^[25]. In Figure 3 (b), electrostatic attraction by hydrogen bonding between amine and carboxylic acid of the ring-opened MA due to the above reaction was considered to be the last possible adhesion mechanism. However, these three types of presumable adhesion mechanisms were extremely difficult to validate precisely since they were molecular-sized interfacial interactions between two bulk substrates. Obviously, the feasibility of forming covalent bonds between reactive functional groups at a solid/plastic interface has been demonstrated in several studies^[6,7,13,21]. Only a few studies using an unmodified and neat solid interface such as glass or wafer were able to analyze the bond formation at the interface^[13], and most studies were limited to indirect verification based on the results^[6,7,21]. Similar to our previous study (Chapter 2), the adhesion strength of both PE and ABS increased under 3 d aging than 0 d aging conditions because of the effect of relaxation time.



Figure 3-6. (a) Schematic (i) diagram of the lap shear test and (ii) dimensions of the specimen. Adhesion strength of (b) steel/PE composites and (c) steel/ABS composites depending on the amount of introduced MA by the lap shear test ([†]non-measurable)



Figure 3-7. Presumable three types of adhesion mechanisms and examples of the formation of (a) amide, (b) electrostatic attraction by hydrogen bond, and (c) succinimide.

Adhesion Strength of Steel/Nylon 6 Composites. Nylon 6 could be an excellent alternative for a plastic core layer in SPC except for its high hygroscopicity. High hygroscopicity, which was a crucial disadvantage for the core layer of sandwich composites, not only affected the mechanical strength and dimensional stability but also caused the occurrence of a peeling effect at the interface which led to delamination^[26-27]. Since the molecular adhesion had a formation of a covalent bond as the main adhesion mechanism, it was expected that the moisture absorption did not affect the adhesion unlike secondary bonds such as electrostatic attraction and hydrogen bonding.

Processing temperature was more carefully controlled for preparing the Nylon 6 layer of SPC. When the hot-press process was conducted at a temperature higher than the melting point (220 °C), internal voids were generated on the surface and inside of the Nylon 6 layer as shown in Figure 3-8 (a). It was determined that the high hygroscopicity of Nylon 6 caused the formation of internal voids. Therefore, the optimization of processing temperature was carried out by gradually changing the temperature condition based on the melting point. As a result, the hot-press process for 30 min at 5 MPa and 215 °C was effective to suppress the formation of internal voids (Figure 3-8 (b)). For more direct confirmation of the effect of the hygroscopicity, a 90° peel test was performed. The 90° peel test measured only the adhesion strength at the interface excluding the cohesive strength, and the effect of moisture absorption was evaluated more accurately by exposing one side as shown in Figure 3-9 (a).

In Figure 3-9 (b), the adhesion strength of Nylon 6-MA (3.8 wt %) increased from 13.0 to 13.9 MPa at 0 d aging and 12.7 to 14.1 MPa at 3 d aging compared to non-treated Nylon 6. Similar to PE and ABS, Nylon 6 showed higher adhesion strength as the molecular adhesion was applied. Especially, the adhesion strength of Nylon 6-MA (3.8 wt %, 3 d aging) was superior to the tensile strength of the steel plate, whereupon the fracture of the steel plate was observed while maintaining the adhesion as can be seen in Figure 3-10. Nylon 6 exhibited high adhesion strength regardless of the application of the molecular adhesion in contrast with PE and ABS on account of its excellent mechanical properties and electrostatic interaction by hydrogen bonding between amide bonds in the structure.

As expected, the adhesion strength of Nylon 6 did not increase considerably even if relaxation time was given unlike in the case of PE and ABS. It could be confirmed more clearly via the 90° peel test. In Figure 3-9 (c), the peel strength of non-treated Nylon 6 decreased significantly by less than half from 111.5 to 53.3 N/cm after 7 d aging. When the molecular adhesion was applied, the peel strength was maintained to some extent (80.2 % (3 d), 89.0 % (7 d), respectively) though moisture absorption occurred over time. These slight decreases in adhesion were presumed to occur due to the weakening of the secondary bonding which was vulnerable to moisture absorption corresponding to figure 3-7 (b) among the suggested adhesion mechanisms. On the other hand, above a certain amount of introduced MA, a modest decrease in adhesion strength was observed for all plastics used in this study, which was judged to be due to a decrease in mechanical properties of the plastics as the amount of introduced MA increased and the insufficient amount of amines on the steel surface compared to the amount of MA on the plastic surface.



Figure 3-8. (a) Image showing the formation of internal voids in Nylon 6 layer fabricated at the temperature condition above the melting point and (b) Image showing void-free Nylon 6 layer fabricated at the optimized condition.



Figure 3-9. (a) Schematic (i) diagram of the 90° peel test and (ii) dimensions of the specimen. Adhesion strength of steel/Nylon 6 composites depending on the amount of the introduced MA by (b) lap shear test and (c) 90° peel test ([†]the fracture of the steel plate while maintaining the adhesion of steel/Nylon 6 composites).



Figure 3-10. (a) Image showing the fracture of the steel plate while maintaining the adhesion of steel/Nylon 6 composites (Introduced MA: 3.8 wt %, 3 d aging) and (b) Stress-strain curves of specimens fractured the steel plate while maintaining the adhesion of steel/Nylon 6 composites.

3.4. Conclusion

In this study, for the development of SPCs, commercially available electro-galvanized steel and plastic candidates which were frequently used as interior materials for automobiles were adopted. A molecular-sized layer was formed on the surface of each substrate through the surface treatment of steel plates and the modification of plastic films. The amines on the steel surface were confirmed with the ninhydrin test, and the quantitative analysis of the amount of introduced MA was conducted using FT-IR. Three types of presumable adhesion mechanisms were proposed called molecular adhesion in this study. When the molecular adhesion was applied, the adhesion strength was increased in all the plastics. Especially for Nylon 6, the adhesion strength was maintained over time despite the moisture absorption. The high adhesion strength in Nylon 6 even when the molecular adhesion was not applied, was judged to be due to the effect of the carbonyl groups in the plastic structure, and further studies to apply carbonyl-containing plastics were carried out, which will be described in the next chapter.

3.5. References

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Chapter 4.

Development of Steel/Plastic Composites with High Adhesive Properties and Industrial Applicability via Molecular Adhesion

4.1. Introduction

For applying steel/plastic composites (SPCs) directly to the current automobile industry, several issues related to industrial applicability need to be improved. Industrial applicability is mainly divided into two categories: process miniaturization and in-process tailorability. Process miniaturization, especially for wet chemistry, refers to designing a process 'bigger' from labscale method to scale-up and 'smaller' the step of the process, simplification^[1]. Since SPC is prepared in an uncomplicated process through hot-press, simplifying the process condition of steel and plastic surface is mainly focused. On the other hand, in-process tailorability is represented by weldability because structural materials for automobiles called body-in-white (BIW) are mainly manufactured through the welding process^[2].

In our previous studies, it was revealed that the cohesive strength of the core plastic layer as well as the interfacial adhesion at the interface is significant for high adhesive properties. In particular, carbonyl-containing plastics such as Nylon, polycarbonate (PC), polyethylene terephthalate (PET), polyurethane (PU), and polyketone (PK) exhibit excellent mechanical properties because of strong inter/intra-chain polar interaction between carbonyl groups. This strong polar interaction induces the crystallinity of plastic which imparts high cohesive strength and also plays an important role in adhesion at the interface. In addition, ketone and carboxylic acids can form covalent bonds with a primary amine under high-temperature conditions^[3]. Therefore, carbonyl-containing plastic candidates are discovered for high adhesive properties via molecular adhesion without surface modification.

For the surface treatment of steel, mussel-inspired surface chemistry can be a splendid alternative approach. Catechol-based derivatives, the origin of adhesive properties of mussels, are exceedingly characterized through substrate-indepnedency^[4], remarkable simplicity^[5], and mild conditions ^[6]. Moreover, tannic acid (TA), which is a type of polyphenol with multifunctional groups similar to catechol, is a water-soluble natural polyphenol and easily coated onto the substrate surface by immersing in a few minutes^[7-8]. These versatilities have attracted immense interest in adopting wet adhesives and coatings from inorganic to organic substrates.

Spot welding is a type of electric resistance welding applied to various metal sheets. Generally, more than 400 pressed panels are welded to manufacture BIW by using spot welding^[9]. In the spot welding process,

contacting metal sheets are welded by heat generated from resistance to electric current. Consequently, it is essential to develop a conductive plastic core layer for adopting spot welding to SPCs. Carbon-based graphitic material, graphite nanoplatelets (GNPs), and carbon nanotube (CNT) which is widely applied as conductive filler are embedded in plastic through mechano-chemistry. Mechano-chemistry is a much more effective way to bind conductive filler with plastic through mechanical force-involved chemical coupling^[10-12].

In this study, both process simplification and development of weldable SPC were conducted for improving the industrial applicability of SPC. Galvanized iron steel (GI), which was widely used in BIW manufacturing, was newly adopted for SPCs. Carbonyl-containing plastic candidates were examined and PK which exhibited high adhesive properties without surface modification was singled out. In addition, polyetheretherketone (PEEK) which had a similar structure to PK was applied for high heat resistance and mechanical properties of SPC. Time reduction of the established process for steel surface was conducted, in company with bio-inspired coating treatment. At last, for the development of the conductive plastic core layer, the conductive fillers were embedded in the plastic surface through mechano-chemistry, and the steel fiber mesh (SFM) was also adopted for maximizing the electrical conductivity.

4.2. Experimental

Materials. Steel (PL, electro-galvanized iron steel, 0.4 mm thickness and GI, galvanized iron steel, 0.3 mm thickness) sheets and steel fiber mesh (SFM, vertical: 0.85 mm, horizontal: 0.3 mm thickness) were kindly donated by POSCO (Pohang Iron and Steel Co., Ltd, KR). The sheets were cut into 100 mm x 25 mm, washed several times with absolute ethanol, and stored in a desiccator before use. The Nylon 6 film (AM301200, 0.2 mm thickness) and PC film (CT301352, Lexan[®] 8B28, 0.5 mm thickness) were purchased from Goodfellow Cambridge Ltd (UK). The PET film (RB175, 0.175 mm thickness) and PK powder (POKETONE, M640P) were provided by HYOSUNG (KR). The PU film (Soft, VB2085, 0.2 mm thickness and hard, VB3095FR, 0.2 mm thickness) was obtained from Ventwin (KR). The PEEK film (APTIV[®] 1000, 0.5 mm thickness) was purchased from VICTREX plc (UK). The polyimide (PI) film (Kapton[®] 0.1 mm thickness) was purchased from DuPont (US). TA (403040, > 99%) and catechol (CA, 135011, > 99%) were purchased from Sigma-Aldrich (US). HDPE-based black masterbatch (NB9925, 30 wt % of carbon black) was obtained from Woosung Chemical Co., Ltd (KR). A multiwall carbon nanotube (MWCNT-6A, outside diameter: $5 \sim 7$ nm, length: $50 \sim 150 \mu$ m)

was purchased from JEIO Co., Ltd (KR). GNPs (M25 grade, 6 nm thickness, 25 μ m lateral size and N008-P40, 5 nm thickness, 50 ~ 100 nm lateral size) were purchased from XG Sciences, lnc (US) and Angstron Materials, lnc (US), respectively.

Surface Treatment of Steel Plates. The surfaces of steel plates were cleaned in advance, using ultrasonication in ethanol and distilled water. The surface treatment of steel plates was conducted in two different methods, organosilane, and bio-inspired coating. Firstly, surface treatment with organosilane was performed as follows: The plates were placed in a small-scale (15 cm x 15 cm) bench top photoreactor (AC-12, AhTech LTS, KR) using a UV lamp (UVJ-42, Jelight, US) for UV/O₃ treatment. The steel plates were treated at a distance of 1 cm from UV grid lamps, and the irradiated wavelength were 184.9 and 253. 7 nm respectively for 1 h with 28 mW/cm^2 at room temperature. The plates were then soaked into 5 wt % KOH aqueous solution for 10 min, followed by rinsing using ultrasonication in ethanol and distilled water. After the plates were immersed in 5 wt % APTES aqueous solution for an additional 30 min, the plates were washed with ethanol and dried in ambient air. The time condition of each step was varied to perform time reduction of the above process. The surface-treated plates were kept in a desiccator before use and named PL-NH₂ and GI-NH₂.

The bio-inspired coating was conducted with only PL plates as follows: The plates were immersed in 5 wt % KOH aqueous solution for 10 min, followed by rinsing using ultrasonication in ethanol and distilled water. The plates were then treated with 5 wt % of CA and TA aqueous solution for 5 min, respectively. The resulting plates were washed several times with distilled water and dried in ambient air. The bio-inspired coated steels were kept in a desiccator before use and named PL-TA and PL-CA.

Preparation of Specimens for Evaluation of Adhesion Strength.

The specimens for the lap shear tests were fabricated as follows: two PL plates were placed in contact with each other in a 1.2 mm thick frame for fixation during the hot-press process. The contact area was adjusted to 12.5 x 25 mm² and plastic films with the same dimension were filled with a thickness of 0.4 mm between PL plates. On the other hand, a 1.0 mm thick frame was used in the case of GI plates. The contact area was adjusted to 5 x 25 mm² and plastic films with the same dimension were filled with a thickness of 0.4 mm between GI plates. Pieces of PTFE sheets with a 0.1 mm thickness were inserted into the space excluding the contact area in order to avoid unintentional adhesion between the steel plate and plastic film. The frame was then placed on the hot pressing machine and PTFE sheets were also inserted between the frame and stage, both top and bottom, to prevent contamination and adhesion to the stage. After setting both sides of the frame in close contact with the stage, the temperature was increased to the corresponding processing temperature for each plastic excluding PEEK in Table 4-1. At the processing temperature, the frame was kept for 10 min to allow the plastic to melt sufficiently and the pressure was raised to 5 MPa while a hot-press process was performed for an additional 30 min. The frame was released from compression, removed from the machine, and cooled to room temperature.

Preparation of Specimens for Evaluation of Adhesion Strength of Steel/PEEK composites. The specimens for steel/PEEK composites were prepared with only GI steel plate as follows: The same dimensions of specimens were adjusted for preparing steel/PEEK composites as described above. PI sheets were applied in place of PTFE sheets to prevent contamination and unintentional adhesion. The hot-press process was carried out in the same process with two different temperature and pressure conditions as listed in Table 4-1.

Evaluation of Adhesion Strength. Adhesion strengths of prepared specimens were evaluated using a universal testing machine (QUASAR 5, GALDABINI SPA, IT). The lap shear tests were conducted according to ASTM D1002 using a 5 kN load cell. The width of the contact area of the specimens and the thickness of the contact area were set up to 12.5×25 mm² and 1.2 mm for PL and 5×25 mm² and 1.0 mm for GI, respectively. Both ends of the specimen were firmly fixed by the clamp of the jig, and the upper clamp was pulled with a speed of 5 mm/min. The lap shear tests were performed at two different time intervals: immediately after the preparation of specimens (0 d aging) and three days after the preparation of specimens (3 d aging). The average values obtained from three repeated tests were reported and all the tests and aging process were conducted at room temperature.

Preparation of Electrical Conductive Plastic Core Layer. The HDPE-based black masterbatch was made into a film with a thickness of
200 µm using a hot pressing machine at 180 °C. PK and conductive fillers, GNPs and CNT, were dried in a 50 °C vacuum before use. PK and each conductive filler were then injected into the chamber of a 10 g scale mechano-fusion machine. The content of conductive fillers was controlled to 3 wt % for CNT and 20 wt % for GNPs. Under the vacuum conditions, the mixtures were mixed for 10 min and the rotation speed was 2,000 rpm for CNT and 5,000 rpm for GNPs. The coated plastic powder was named G-PK, g-PK (depending on the size of GNPs), and C-PK, and they were made into a film with the above procedure at 250 °C. The SFM was cut into 100 x 25 mm² in advance and was embedded into a plastic core layer during the filming process.

Characterization of Electrical Conductive Plastic Core Layer. The morphology and dispersion of conductive fillers in both G-PK and C-PK were observed by scanning electron microscope (SEM, JSM-7800F, JEOL Ltd, JP) under a voltage of 15.0 kV. The electrical conductivity was calculated from the sheet resistance of the film using a four-point probe (JANDEL System, KR) with a resistivity meter (CMT-SR1000N, AIT Co., Ltd, KR) via the following equation:

$$\sigma = (R_S \times t)^{-1}$$

where σ is the electrical conductivity (S cm⁻¹), R_s is the sheet resistance (Ω sq⁻¹) and t is the thickness of the film (m).



Scheme 4-1. Schematic (a) illustration of surface treatment on steel plate, (i) organosilane treatment; APTES aqueous solution, varying time, (ii) bio-inspired coating; TA aqueous solution, 5 min and (b) dimensions of the specimen (iii) PL/plastic composite, (iv) GI/plastic composite.

4.3. Results and Discussion

Process Simplification of Plastic. The process simplification of plastics was conducted in direction of discovering plastic candidates capable of inducing high adhesive properties via molecular adhesion regardless of surface modification. Carbonyl-containing plastics like Nylon 6, which were advantageous for improving cohesion and interface interaction, were selected as listed in Table 4-1, and a comparative evaluation of the adhesion strength of carbonyl-containing plastics was conducted. Among these candidates, PK was singled out as the most suitable plastic since it exhibited high adhesive properties without surface modification.

Aliphatic PK was generally based on alternating polyolefins and carbon monoxide and had a relatively high melting point of 220 °C compared to polyolefin due to regular carbonyl repeating units in the structure. The alternating carbonyl groups in the flexible plastic backbone confer not only cohesive strength but also interfacial physical interaction at the interface. In figure 4-1, the adhesion strength of PL/PK composites significantly increased in 8.3 to 13.4 MPa at 0 d aging and 7.1 to 14.2 MPa at 3 d aging though only the surface treatment of steel plate was performed. Especially for PL-NH₂ and 3 d aging conditions, similar to our previous

study (Chapter 3), the PL steels were fractured during the lap shear test while maintaining the adhesion of PL/PK composites intact.

This increase in adhesion strength was considered as the combined action of thermal crosslinking in the plastic core layer and molecular adhesion at the interface. As shown in Figure 4-2 (a), aliphatic PK was prone to undergoing multifarious inter/intra-chain reactions such as aldol condensation^[13], Wittig^[14], and Baeyer-Villiger^[15] reactions at aerobic conditions during melt processing. Thermal crosslinking and degradation due to these reactions generally limited a melt processing window of PK^[16]. however when adopted as a plastic core layer of SPCs, these phenomena reversely increase the cohesion. Moreover, imine could be formed by a thermal reaction between a ketone and a primary amine at the interface^[17], and electrostatic attraction by hydrogen bonding between carbonyl and amine also formed at the interface^[18] as depicted in Figure 4-2(b). The adhesion mechanisms called molecular adhesion in this work were extremely difficult to detect precisely as mentioned in the previous chapter.

Polymer		T _m (°C)	T _p ^a (°C)	Max. Adhesion ^b (MPa)	Features	
Nylon 6		220	250	13.0 ± 0.4	 High adhesion with modification Lower adhesion by high hygroscopicity 	
PET		260	280	≈ 0	- Collapse of core layer due to crystallization (during cooling process)	
	PC	230	260	9.8 ± 0.3	Modest adhesion without modificationLow chemical resistance	
PU	Soft	150	180	4.1 ± 0.9	- Unsuitable for core layer due to high elongation (Low dimensional stability)	
	Hard	190	220	2.8 ± 0.04		
	PK.	220	250	14.2 ± 0.2 (Fracture of PL)	High adhesion without modificationApplicable to molecular adhesion	
P	'EEK	350	350 / 380 (30 / 50 MPa)	22.6 ± 1.6 (GI/PEEK composites)	 Highest adhesion without modification High thermal resistance 	

 Table 4-1. Properties of carbonyl-containing plastics adopted in this study.

^a Processing temperature for fabrication of SPC

^b Maximum adhesion strength of PL/plastic composites except for PEEK



Figure 4-1. Adhesion strength of PL/PK composites depending on the surface treatment of PL ([†]the fracture of the steel plate while maintaining the adhesion of PL/PK composites).



Figure 4-2. Schematic illustration of (a) thermal crosslinking of aliphatic PK and (b) molecular adhesion at the interface (i) formation of imine and (ii) electrostatic attraction by hydrogen bond.

Process Simplification of Steel. The process simplification of steel was conducted with two different strategies as described in Scheme 4-1 (a). Since it was impossible to accurately validate the molecular-sized level of surface treatment buried in the bulky substrate, the degree of surface treatment was inferred based on the adhesion strength of PL/PK composites which exhibited a distinguishable difference depending on the surface treatment. Firstly, the bio-inspired coating on the steel surface was carried out referring to previous studies^[19-20]. As shown in Figure 4-3, it was visually confirmed that both tannic acid and catechol were coated on the steel surface. However, nearly half of adhesion strength was observed for both bio-inspired coatings compared to the established treatment (Figure 4-4). In the high-temperature condition of the hot-press process (250 °C), tannic acids were decomposed and catechols were boiled which adversely affected the interfacial adhesion. Therefore, the bio-inspired coating method was unsuitable for application in SPC.

Secondly, time reduction of established organosilane-based treatment was performed and detailed time conditions for each step were listed in Table 4-2. In Figure 4-5, the adhesion strength of PL/PK composites decreased, as the processing time decreased. It was determined that UV/O_3 treatment was essential for effectively producing hydroxyl groups on the steel surface because the No. 3 process exhibited a higher adhesion strength compared to the No. 1 and 2 process whereas the ratio of time reduction was quite high, 82.2 %.



Figure 4-3. Image after the bio-inspired coating of steel surface (a) tannic acid and (b) catechol (red and blue arrow indicate the coated part of steel plate, respectively).



Figure 4-4. Adhesion strength of PL/PK composites depending on the surface treatment method of PL.

Ne	Pro	cessing Time (1	nin)	Total	Adhesion	
NO. 1	UV/Ozone	KOH aq.	APTES aq.	(min / % ratio ^a)	Ratio ^b (%)	
1	-	5	10	15 / 10.7	81.1	
2	-	10	30	40 / 28.5	88.2	
3	10	5	10	25 / 17.8	94.3	
4	60	10	30	140 / 100	100.0	

Table 4-2. Processing time of steel surface treatment with organosilane for process simplification.

^a Ratio of total processing time of each No. to a total processing time of No. 4

^b Ratio of adhesion strength of each No. to adhesion strength of No.4



Figure 4-5. Adhesion strength of PL/PK composites depending on the processing time.

Development of SPCs with High Thermal Resistance and Adhesive Properties. For developing the high-performance SPCs via molecular adhesion, GI steel which had excellent mechanical properties compared to PL steel and optimal plastic PK was employed. When applying the GI steel as skin material for SPCs, the contact area of adhesion was adjusted as shown in Scheme 4-1 (b). The plastic deformation and fracture of GI steel in place of the adhesion area were observed when maintaining the previous contact area, resulting in inaccurate evaluation (Figure 4-6). In Figure 4-7, the adhesion strength of GI/PK composites was remarkably high at ca. 18 MPa which was judged to be an effect of molecular adhesion.

Focusing on the chemical structural characteristics of PK, PEEK was adopted for preparing high-performance SPCs. PEEK, also known as super engineering plastic (SUPLA), was characterized by high mechanical properties and thermal resistance^[21]. For fabricating GI/PEEK composites, PI film was applied instead of PTFE film because of the high melting temperature of PEEK (ca. 350 °C), and relatively high-pressure conditions (30 and 50 MPa) were applied considering the high mechanical properties of PEEK. GI/PEEK composites exhibited the highest adhesion strength of above 22 MPa as shown in Figure 4-8. The application of molecular adhesion similar to PK at the steel/plastic interface as well as the strong cohesion of the core layer led to the highest adhesive properties among various candidates. The obtained results were comparable to the application of resin type (acrylate/epoxy) adhesives (ca. 15 ~ 25 MPa) mainly used for manufacturing SPC, and therefore had sufficient potential for industrial application considering the narrow range of application because of the low thermal resistance (ca. 66 ~ 93 °C) of the resin type adhesives^[22].



Figure 4-6. Image showing the occurrence of plastic deformation and fracture of GI steel in place of adhesion area (red circle indicates the fracture of GI steel).



Figure 4-7. Adhesion strength of GI/PK composites depending on the contact area ([†]the occurrence of plastic deformation of GI plate).



Figure 4-8. Adhesion strength of GI/PEEK composites depending on the surface treatment and processing conditions.

Weldable SPC via the Development of an Electrical Conductive

Plastic Core Layer. Both mechanical properties and homogeneous dispersion of fillers within the plastic matrix were required to develop a weldable core layer for SPCs. The mechano-chemstry assisted adsorption of fillers to plastic was adopted in place of directly dispersing fillers into the robust plastic matrix. As shown in Figure 4-9, conductive fillers such as CNT and GNPs were absorbed on the surface of PK powder, which had guaranteed mechanical properties and adhesive properties, using mechanofusion. Adsorbed fillers then facilitated to create percolation pathway by filming process with hot-press. CNT was intrinsically unsuitable for adsorption because of its cylindrical shape, and the steric bulkiness of CNT limited the content up to 3 wt % for mechanofusion. Furthermore, since the structure was prone to collapse under strong shear/compressive forces, the rotation speed was reduced to 2,000 rpm. On the other hand, platelet-shaped GNPs were relatively facile to adsorb resulting in high rotation speed (5,000 rpm) and content of filler (20 wt %). Especially, g-PK with a smaller lateral size (50 \sim 100 nm) exhibited the highest electrical conductivity as listed in Table 4-3. In Figure 4-10, non-conductive PK could be observed by SEM without any pretreatment, indicating that GNPs were well adsorbed onto the PK surface.

Unfortunately, the spot-weldability could be confirmed indirectly through only the actual tests with a spot welder because quantitatively required electrical conductivity was not revealed. Spot welding was unable to proceed even though g-PK was applied as a conductive core layer, and therefore SFM was employed in company with g-PK. As depicted in Figure 4-11, the SFM was successfully embedded in the plastic core layer via the hot-press process, and the surface treatment of SFM with organosilane was carried out in advance to enhance the interaction with the plastic matrix. Consequently, spot welding could be conducted not in the case of neat PK but g-PK embedded with SFM. The embedded SFM was also expected to help suppress the release of the plastic core layer out from the SPC structure by the large heat generated during the spot welding process.



Figure 4-9. Schematic illustration of the preparation of G-PK, g-PK, and C-PK with mechano-chemistry.

Specimens	Conductive Filler	Content (wt %)	Electrical Conductivity (S/cm)
Black Masterbatch	Carbon Black	30	5.4
C-PK	MWCNT	3	2.4
G-PK	GNPs (L.S ^a : 25 μm)	20	92.0
g-PK	GNPs (L.S: 50 ~ 100 nm)	20	207.5

Table 4-3. Electrical conductivity of conductive core layer and content of filler.

^a L.S: average lateral size



Figure 4-10. (a) Image showing conductive core layer with g-PK and SEM images of g-PK (b) 1,500x mag, scale bar: 50 μ m and (c) 5,000x mag, scale bar: 20 μ m.



Figure 4-11. Image showing SFM-embedded core layer (a) Neat PK/SFM and (b) g-PK/SFM.

4.4. Conclusion

In this study, process simplification and development of weldable SPC were conducted for improving the industrial applicability of SPCs. In the course of process simplification, PK was discovered which could be applied to molecular adhesion without surface modification, and presumed adhesion mechanisms were suggested. The processing time of the steel surface was also effectively reduced while maintaining adhesive properties. Moreover, SPC with remarkably high adhesive properties and thermal resistance was developed using PEEK as the plastic core layer. The conductive fillers were adsorbed in the plastic surface via mechanochemistry, and the SFM was also employed for enhancing spot-weldability. At last, the spot welding could be conducted with g-PK embedded with SFM as a conductive core layer. In summary, SPC using molecular adhesion has sufficient potential to be applied in various industrial fields requiring weight reduction.

4.5. References

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국문 요약

강판/플라스틱 복합 재료는 복합재의 무게를 효과적으로 줄임과 동시에 고강성, 내피로성, 내충격성 등의 다양한 장점뿐 아니라 열과 진동 및 소음 차폐와 같은 다기능적 특성을 나타내어 오랜 기간 주목 받아왔다. 이러한 특색들은 강판/플라스틱 복합 재료에 대한 수요를 증가시키고 있으며, 에너지 위기 기간 동안 경량화가 시급히 대두되고 있는 자동차 산업에서 특히 수요가 증가하고 있다. 그러나 상용화된 강판/플라스틱 복합 재료는 미국의 MSC 사에서 개발된 Smartsteel[®] 제품이 유일하며, 개발 필요성에 비하여 관련 연구는 매우 미흡한 실정이다.

강판/플라스틱 복합 재료 개발에 있어 가장 도전적인 핵심 요소는 강판과 플라스틱간 계면 접합이다. 구조재 목적으로 활용하기 위해서는 견고하고 지속 가능한 계면 접합 특성이 요구된다. 기판의 표면 요철에 흡착되는 기존의 물리적 접합 방식은 온도, 습도 혹은 응력과 같은 외부 조건에 의한 계면 접합력 저하와 계면에서 발생하는 박리 현상으로 인하여 내구성 및 활용성이 낮은 결함이 존재한다. 강판과 플라스틱의 높은 접합 특성 유도를 위하여 레이저 용접 및 사출 성형을 통한 직접 결합과 같은 새로운 기술들이 최근 개발되고 있으나, 높은 비용과 다양한 재료에 대한 적용 가능성이 낮다는 한계로 인하여 여전히 널리 활용되지 못하고 있다.

계면 접합 특성을 향상시키기 위해서는 강판/플라스틱 계면에 대한 충분한 이해가 필수적이다. 계면 접합 특성에 영향을 미치는 요인은 일반적으로 플라스틱의 점도 (젖음성), 기판의 표면 조도, 물리적 및 화학적 상호 작용의 네 가지 유형으로 분류된다. 이러한 요인들 중, 플라스틱의 젖음성과 기판의 표면 조도에 의한 영향은 복합 재료의 제작 방식 선정을 통하여 용이하게 조절 가능하다. 본 연구에서는 열 압착 공정을 통하여 플라스틱을 강판 표면 요철 내 완전히 흡착시켜 계면 접합력을 향상시켰으며, 강판 및 플라스틱의 표면 처리 혹은 개질을 통하여 계면간 물리적, 화학적 상호 작용을 증진하였다. 본 연구의 2단원에서는 계면 접합 특성 향상을 위하여 플라스틱 표면의 물리적, 화학적 개질을 진행하였다. 플라스틱 표면 화학의 조절을 위한 자외선/오존 처리 혹은 주 사슬 내 극성 작용기가 도입된

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공중합체 층의 도입 전략을 채택하였다. 두 전략 모두에서 접합 특성이 크게 증가하였으며, 이러한 전략을 기반으로 후속 연구를 진행하였다.

3단원에서는 열 압착 공정간 화학적 공유 결합 형성이 가능한 반응성 작용기를 강판과 플라스틱 표면에 각각 도입하여 접합 특성 향상을 유도하였다. 반응성 작용기로는 1차 아민과, 말레산 무수물을 적용하였으며, 선정한 모든 플라스틱 후보군에서 접합 특성이 크게 향상됨을 확인하였다. 접합 특성 향상의 원인으로 추정되는 세 가지 유형의 메커니즘을 제안하였으며 본 연구에서는 이를 분자 접합이라고 명명하였다.

4단원에서는 강판/플라스틱 복합 재료의 산업적 응용 가능성을 향상시키고자, 공정 단순화와 용접이 가능한 복합 재료 개발을 동시에 진행하였다. 연구 진행 과정에서 높은 접합 특성과 응집력을 나타낸 카보닐 작용기 함유 플라스틱 후보군들의 비교 평가를 통하여, 표면 개질 없이도 분자 접합을 통한 높은 접합 특성 발현이 가능한 폴리케톤이 최적 플라스틱으로 선별되었다. 강판의 경우, 90 % 이상의 접합 특성을 유지하면서 80 % 이상

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표면 처리 시간을 단축하였다. 또한, 슈퍼엔지니어링 플라스틱인 PEEK를 플라스틱 코어층으로 활용하여 고 접합특성 및 내열성을 가지는 복합 재료를 개발하였다. 최종적으로, 기계화학을 통하여 전도성 필러를 플라스틱 표면에 흡착시켰으며, 이와 강섬유 메쉬의 복합 활용을 통하여 용접이 가능한 복합 재료를 개발하였다. 본 연구에서 개발된 분자 접합을 기반으로 한 고 접합 특성의 강판/플라스틱 복합 재료는 경량화를 요하는 다양한 산업 분야에 응용 가능한 충분한 잠재력을 보유하고 있다고 판단된다.

주요어 : 금속/플라스틱 하이브리드 재료, 강판/플라스틱 복합 재료, 샌드위치 라미네이트, 계면 접합, 직접 접합, 표면 처리/개질, 경량화 재료

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