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Abstract
Concrete Formation of Organic Thin Film on Metal via Reduction of Aryl Diazonium Salt

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In this study, surface modification with organic thin layer concretely adhered to commercially available zinc coated steel surfaces was achieved with diazonium induced grafting process. Unlike electrically induced grafting process requiring extremely anhydrous condition, the diazonium induced grafting process works at room temperature, atmospheric pressure, in aqueous medium and without any external energy source. This process relies on the chemical reduction of diazonium salts by reducing agents in absence or presence of a vinylic monomer. Typically, aryl diazonium salts are reduced by reducing agent to give aryl radicals leading (i) to the formation of a grafted polyphenylene-like film on the substrate surface and (ii) to the initiation of the radical polymerization of the vinylic monomer in solution. The resulting radical-terminated oligomer chains formed in solution are then able to react with ortho site of the polyphenylene prime layer. Herein, a number of polymer thin-films, i.e. poly (acrylonitrile) (PAN), poly (methyl methacrylate), PMMA, poly (acrylic acid) (PAA) in addition to polynitrophenylene (PNP) were
successfully grafted on the steel substrates. Accordingly, scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy and contact angle were used to investigate grafted organic layers. Furthermore, lap shear test was conducted to evaluate the grafted organic layer can be used as an adhesion primer to plastic, i.e. polyamide 6 (PA6), and the durability of these joins after exposing to 92°C hot water.

**Keywords:** diazonium salt, spontaneous redox grafting, adhesion primer, interfacial shear strength.

**Student Number:** 2014-22537
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1. Introduction

Altering the surface properties of materials by organic coatings has drawn a huge attention from an industrial point of view since the surface modification of materials is a technique to incorporate bulk properties (e.g. mechanical, electrical) with the suitable surface properties (for instance protection against corrosion, wettability, biocompatibility, adhesion, …). In consequence, a wide range of coating techniques has been developed. Seven methods\(^1\) mentioned in below have been widely known as representatives for their industrial importance, providing submicron scale deposition, which is a highly demanding technique in various industries.

**Spin coating** is the most widely used technique for organic coatings based on polymer solutions, for example, photosensitive resins used in lithography in the microelectronics industry\(^2,3\) antireflection coatings for flat-screen displays and television tubes, and compact discs. The range of obtained thicknesses is generally 1–200 mm, but thinner films can be produced with dilute solutions and high spinning rates. The homogeneity of the spin-coated film strongly depends on the quality of the pristine solution and the chosen combination of solvent, spinning rate, and atmosphere. Spin coating is ideal for temporary organic coatings (as is the case with lithographic resins), since the organic film is only physisorbed on the substrate. Spin coating is also widely used to prepare in-organic coatings from sol–gel solutions

**Electrodeposition** has been known for years for coating conducting surfaces with metals. Electroplating is currently the most widely used method
for coating surfaces in the automotive, petrochemical, and aerospace industries; propulsion, combustion, and microwave applications; printed circuit boards, vias, and copper interconnections for electronics; and many decorative applications. For a long time, organic electrodeposition was limited to the conducting polymer coatings that were developed in the 1980 together with the fundamentals of polymer conductivity. After more than 30 years of basic research, both on mechanisms and processability, conducting polymers are now starting to be used industrially in light-emitting displays

**Self-assembly** is a very attractive technique for forming organic coatings. Indeed, it combines low-cost processes that are music to industrial ears, soft conditions that prevent degradation of the coating molecules, and spontaneous formation of true chemical linkages between the molecules and the substrates. The surfaces of oxides, noble metals, and silicon can be successfully functionalized provided suitable reactive molecules are used (halogenosilanes, alkoxy silanes, organophosphonates, carboxylic acids, thiols, disulfides, selenols, alkenes, alkynes, etc.). Van der Waals interactions between neighboring chemisorbed molecules generally lead to long distance ordering in the first monolayer. Self-assembly from solution or the gaseous state (for smaller molecules) provides very good coverage in short times. Very stable coatings are obtained with silanes on oxides and alkenes on silicon. In contrast, noble metals with sulfur containing molecules give weak bonds that can be easily broken under harsh conditions (high temperature, oxidative or reductive potentials, solvents, etc.). Multilayers can be obtained by sequential steps, but self-assembly is the method of choice for molecular-thickness films
for use under moderate conditions and up to now has been confined to prospective applications such as molecular electronics. It is clearly the method of choice for fundamental studies on the molecule–metal bonds, as shown recently for the chemisorption of thiols on gold.\textsuperscript{1,5,6}

**Plasma deposition** of polymers for producing highly robust polymeric coatings has been known for 50 years.\textsuperscript{7-9} Strong chemical linkages that are assumed to be formed between the reactive species produced within the plasma and the surface of the substrate lead to highly adherent films. Since the glow discharge is a very energetic process, organic gases or vapors that are not regarded as monomers for conventional polymerization can be used. Indeed, free radicals are generated whatever the starting organic species, and the final deposit is very different from a conventional polymer film prepared by a casting technique: the plasma polymer does not contain regular repeat units, but branched and randomly terminated chains with a high degree of cross-linking. In some cases, free radicals remain trapped within the highly cross-linked structure, and their subsequent recombination results in ageing of the coatings. Plasma polymerization has been widely used for corrosion protection, scratch-resistant coatings, and anti-soiling applications, although deposition rates are generally low, and film thicknesses are always higher than 1μm.

**Vapor deposition** is generally used for inorganic coatings (ceramics, silicon carbide, nitrides, metals), but can also be applied to small organic molecules, for example, in the fabrication of organic thin-film transistors, organic light emitting diodes, and organic photovoltaic cells. Soft conditions
(low pressure, flash heating) are generally chosen to prevent thermal degradation of the organics during vaporization and retain the molecular properties in the final film. Hence, only weak interactions can be created between the molecular film and the substrate. This technique is thus limited to organic coatings that are not subject to mechanical or thermal constraints. Vapor-deposited films can be locally highly crystalline, but are often prone to defects such as grain boundaries, cracks, and disclinations.\textsuperscript{10,11}

**Electrografting** allows the deposition of very thin organic films via very strong substrate–polymer links. Contrary to electrodeposition of conducting polymers, electrografting is an electro-initiated process which requires a charged electrode only for the grafting step, but not for thickening\textsuperscript{12}. The resulting organic films are generally insulating\textsuperscript{13}, highly adherent.\textsuperscript{14} Electrografting is mainly (but not only) a cathodic process.

**Redox grafting** is a recently developed technique forming also concrete metal-carbon bond through non-electrochemical route. This processes work at room temperature, atmospheric pressure, in aqueous medium and without any external energy source. The grafted layer formed by aryl radical can act as either primer itself or immobilized initiator for additional polymerization such as surface initiated atom transfer radical polymerization\textsuperscript{15}, surface electro initiated emersion polymerization\textsuperscript{15,16}, diazonium induced anchoring process (DIAP).\textsuperscript{17,18} Indeed, aryl diazonium salts are able to be spontaneously grafted on many surfaces or molecular objects such as carbonaceous materials such as graphite, glassy carbon, CNTs\textsuperscript{19}, noble\textsuperscript{20} or industrial materials\textsuperscript{21-23} and semiconductors\textsuperscript{24,25}
Among such polymer coating methods, last two grafting processes have been known as formation of covalent bond at the interface. With such advantage of grafting processes, we have concerned that the grafted thin polymer film can be utilized as insulating film for electronic devices as well as adhesion primer at plastic-metal interface. In this context, we have investigated a relatively new approach, i.e. a grafting process based on diazonium salts, for the chemical grafting of aryl layers but more important the surface modification by polymers of commercial metal substrates. Herein, we confirmed that 4-nitrobenzenediazonium can be grafted on steel surface via spontaneously and redox activation, resulting in formation of polynitrophenylene (PNP) prime layer. We will also show that PAA, PAN and PMMA layer were grafted only when reducing agent is presence in the solution. Hence, the objective of the present work was to understand the diazonium involved grafting mechanism and to explore potential usage of the film obtained by grafting as insulative thin film in electrical devices and adhesion primer at metal-plastic interfaces.
2. Experimental Section

2.1. Materials

All reagents N, N-dimethylformamide (DMF, 99.5%, Daejung), Ethanol (98%, Dae-jung), and acetone (97%, Daejung) were used without further purification. 4-nitrobenzenediazonium tetrafluoroborate (NBD, 97%) and L- (+)-Ascorbic acid also called Vitamin C (VC, >99%) were used as received from Alfa Aesar. Acrylic acid (AA, 99%), acrylonitrile (AN, 99%) and methyl methacrylate (MMA, 99%) were purchased from Sigma Aldrich. These monomers were passed through aluminum column to remove monomethyl ether hydroquinone (MEHQ, inhibitor). Electrogalvanized (EG) and Galvannealed (GA) steels were received from POSCO, Koera and Galvanized (GI) steel was purchased from DONGBU. They were first washed with commercial detergent solution to remove the surface oil before they used in reaction. For reliable measurement of thickness of grafted organic layer, 5 nm thick nickel sputtered Si wafer was used in the grafting process.

2.2. General mechanism for grafting process

The experiments were carried out in ambient air, at room temperature, atmospheric pressure with magnetic stirring. Deionized water was used as solvent for all agent used in diazonium induced grafting process. L-ascorbic acid was chosen as reducing agent in this study for its ability to reduce 4-nitrobenzenediazonium tetrafluoroborate (NBD).\textsuperscript{26,27} In addition, unlike iron
powder, VC acts as a reducer in homogeneous phase, which is essential for a quantitative study. VC is also unable to reduce protons from the solvent which will ease our interpretations by avoiding any potential hydrogen radical formation from the reactive mixture. Ascorbic acid has already been used as a reducer, for instance, in Sandmeyer reaction or for the reduction of metal ions in solution, particularly in the case of gold or silver nano-object formation.

In this context two types of diazonium associated grafting process were studied; (i) spontaneous grafting, (ii) redox activation diazonium assisted grafting process.

2.2.1. Spontaneous Grafting of Diazonium salt.

Scheme 1 shows the NBD grafting via electron transfer from metal substrates which readily donate electron. Once NBD reduces, deamination occurs to produce aryl radical and dinitrogen gas. In addition to electron transfer directly from reducing metal, photochemical decomposition of diazonium salts in water was reported in the literature to lead to aryl cations. Therefore, we assumed that a cationic mechanism possibly occurs (Scheme 2).
Scheme 1. Spontaneous NBD grafting on reducing metal

Scheme 2. Cationic grafting mechanism on reducing metal
2.2.2. Redox Grafting

Aforementioned dediazoniatiion is very important because this step must be preceded by the grafting process in order to produce an nitrophenyl radical which is essential for grafting process. Scheme 3 shows dediazoniatiion of NBD involving a dissociative electron transfer via reducing agent (VC) that gives dinitrogen and aryl radicals.

Scheme 3. Dediazoniatiion of NBD via redox pathway

Scheme 4 illustrates that nitrophenyl radicals formed by reducing agent graft on the surface. Once monolayer deposited, the attack of the nitrophenyl radical is represented in ortho of the nitro group resulting in poly (nitrophenylene) (PNP) layer since some previous work from Combellas et al.\textsuperscript{34,35} on the influence of steric effects of the aromatic ring on the growth of the films showed that those nitrophenyl radicals mainly linked on the α-position of the NO\textsubscript{2}.
In the case of monomer introduced in grafting bath, mechanism of DIAP was proposed by Mévellec et al.\textsuperscript{17} as follows (Scheme 5): (1) initiation of radical polymerization by nitrophenyl radical after redox activation, (2) propagation via radical pathway and (3) grafting of synthesized radical end polymer either directly onto metal substrate or ortho-site of polynitrophenylene layer.

\textbf{Scheme 4.} Radical grafting mechanism via redox pathway to give mono- or multilayers resulting in polynitrophenylene (PNP) layer
2.2.3. Overall procedure of grafting

In the case of the grafting of the NBD via redox pathway, 0.02 M NBD salt was dissolved in DI water. Then, substrates and 0.002 M L-ascorbic acid (1/10 equiv. vs NBD) were introduced in the NBD solution and, in order to start the reaction. Instantaneously, the pale yellow solution turned into a lemon yellow mixture and a few small bubbles were observed, corresponding to dinitrogen evolution from the reduction of NBD by VC.\textsuperscript{26}

In the case of vinylic monomer involved in grafting, 0.3 M vinylic monomer (AN, MMA, AA, 15 equiv. vs NBD) was added in the 0.02 M NBD solution prior to the substrate and the reducing agent introduced. Note that the experimental parameters in this experiment were followed parameter optimization study by Alice et al. After the reaction, substrates were thoroughly rinsed with DI water, ethanol, and acetone. In the case of samples prepared for XPS analysis, substrates were additionally sonicated for 3 minutes in DMF to remove any species attached in the form of physisorption.
2.3. Characterization

2.3.1. Electrochemical analysis

Electrochemical data were recorded on PGSTAT 302 (AUTOLAB) electrochemical workstation. All glass wares were oven-dried before each experiment. A standard 3-electrode electrochemical setup was employed, with steel strips employed as the working electrode, platinum wire as a counter electrode, and Ag/AgCl as a pseudo reference electrode. In the case of exploring reduction potential of NBD, copper wire of 800 μm diameter was used as it was covered with nail varnish. At the end of each experiment the standard potential was referenced against the standard hydrogen electrode.

2.3.2. Scanning Electron Microscopy (SEM)

The modifications on the steel surface morphology were observed using a scanning electron microscope JEM-7100 at an accelerating voltage, a pressure, a beam current, and a working distance of 3.0 kV, 3.8 mbar, 40 nA, and 8 mm, respectively. These parameters were specifically optimized for these types of samples.

2.3.3. Spectroscopic Analysis

Infrared spectra were obtained on a Bruker TENSOR27 spectrometer equipped with ATR Pike-Miracle device. The detector was high sensitivity DLATGS detector. The spectra were obtained after 150 scans at 0.4 cm⁻¹ resolution, and contributions from H₂O and CO₂ (gas) were subtracted.
X-ray photoemission spectroscopy (XPS) analyses were performed with an AXIS-HSi (KRATOS) using a high-resolution monochromatic Al-KR line X-ray source at 1486.6 eV. A survey spectrum and core-level spectra of C1s (280-290 eV), and N1s (396-410 eV) regions were systematically recorded. The C1s peak component C-C/C-H set at 284.8 eV was used as the reference for charge correction.

The thickness of the modified films was measured using a variable angle spectroscopic ellipsometer (V-Vase, J.A. Woollam). The test was conducted at 60° and 75° angle of incidence respectively. The ellipsometric parameters of the bare (Δs, Ψs) and the grafted (Δg, Ψg) substrates were measured in air at ambient temperature, where Δ is the phase shift and tan Ψ is the amplitude ratio upon reflection. The complex refractive index of the bare substrate was calculated from the measured Δ and Ψ values. The grafted layer characterized by its refractive index and thickness, and the surrounding medium (air) was used to calculate the overall reflection coefficients for in-plane (Rp) and out-of-plane (Rs) polarized lights. The real and the imaginary parts of the refractive index of the substrates was obtained by measuring the clean substrate before grafting modification. Ellipsometric measurements were performed on the two regions (grafted/non-grafted) of the sample plates after partial modification. Because measurements are carried out on dried and collapsed polymeric films, the refractive index of PAN was extracted from literature (1.52) and PNP layer was set as 1.45 according to typical values usually employed for organic films.
2.3.4. Atomic Force Microscopy (AFM)

AFM analyses were carried out using a NANOStation II (SIS) operated in noncontact tapping mode with a resonant frequency of 146 to 236 kHz. The spring constant of the cantilever was 21 to 98 Nm\(^{-1}\). The instrument was calibrated using a standard sample with known step height. The images were recorded at a resolution of 256 pixels per line, and analyzed using the Gwyddion 2.40 software.

2.3.5 Single Lap Shear Test

The interfacial shear strength (IFSS) between metal and polyamide6 (PA6) was measured in accordance with ASTM 1002 (Scheme 6). The interfacial ultimate failure strength was determined using Galdabini tensile machine (Max 5kN). The specimens were prepared with PA6 film of 25 x 12.5 mm\(^2\) intercalated in two GI steel thin plate (100 x 25 x 0.8 mm\(^3\)). The joints were prepared at 260°C for 5 min preheating followed by 10 min preheating under mild pressing. To control thickness of PA6, specimens were shimmed using 0.1 mm Teflon film. After preparing joint, specimens were tested under dry condition at room temperature and after exposing to 92°C tap water for 12 to 72 h.
Scheme 6. Single lap shear test samples

Figure 1. Mechanical test of shear strength with universal testing machine
3. Results and Discussion

3.1. Redox Grafting of NBD

3.1.1. SEM analysis

The pristine GI steel surface shows the typical spangle free galvanized steel (Figure 2a). The NBD grafted GI surface showed an apparent change in the surface morphology (Figure 2b). In addition to the morphology, change in the dark intensity of the SEM image indicates surface conductivity has changed due to deposited insulating PNP layer.

As the magnified SEM images reveal, on the microscale, the film grows in a rather heterogeneous way. This was as expected for the multilayer growth of films using radical poly addition pathway.

![Figure 2](image)

**Figure 2.** Scanning electron microscopy images of GI steel surfaces (a) before and (b) after NBD grafting
3.1.2. IR-ATR analysis

The polynitrophenylene (PNP) film obtained by dipping in NBD solution with reducing agent (VC) for 5 minutes was analyzed by IR-ATR. The subsequent film (Figure 3b) after rinsing procedure was compared to pristine GI steel (Figure 3a). The spectrum of PNP grafted GI steel exhibits the major absorption bands of the expected PNP: 1525 and 1350 cm$^{-1}$ were attributed to the NO$_2$ group while the one at 1600 cm$^{-1}$ signals are the presence of phenyl groups. These nitrophenyl moieties were identical meaning that PNP film was actually grafted on the substrate.

![Figure 3. IR-ATR spectra of (a) a bare GI steel (b) and the NBD grafted GI steel obtained after the rinsing procedure followed by 5 min immersion in the grafting solution bath](image-url)
3.1.3. AFM analysis

Additional morphology characterization of the PNP film deposited on GI steel was confirmed by topographical images using AFM. The progressive morphological change was observed.

Figure 4. AFM images of (a) bare GI steel and (b) NBD grafted GI steel after the extensive rinsing procedure

From the Figure 4a, we assessed that the roughness of the surface of bare GI steel. The root mean square (RMS), implying the surface roughness, of bare GI steel was 7.4 nm which indicates the relatively low protruded
morphology. In contrast, the roughness (RMS) of PNP grafted GI steel surface was measured as 18.9 nm which corresponded to the large degree of lumpy surface shown in figure 4b.

3.1.4 XPS analysis

The major XPS spectra corresponding to bare and PNP grafted GI steel substrates obtained by DIAP for 15 min are shown in Figure 5. It was confirmed that GI steel substrates are contaminated by organic material containing COO and C−O/C−N groups (Figure 5b). Nevertheless, a component centered at 283.5 eV appears after grafting of PNP. This peak can be attributed according to the literature to a metal carbide bond. Likewise, the metal−carbon bonds already reported, the corresponding peak in our experiment is very weak. However, we can undoubtedly attribute it to a bond with the diazonium salt, as it was absent in the pristine substrate taken as reference (Figure 5b, 5b'). For PNP grafted GI steel, two N1s main peaks near 400 and 406 eV were detected whereas the surface of bare GI steel reveled no detectable peak (Figure 5c, 5c'). The former is assigned to azo groups derived from the diazonium chemistry occurring during multilayer formation and the latter to the nitro group of the grafting agent. In addition, X-ray irradiation-induced degradation of the nitro group to amine may to a minor extent contribute to the peak at 400 eV.

[3,41,42]
**Figure 5.** X-ray photoelectron spectroscopy for GI steel plates. Non and Single upper strophe stand for bare and PNP grafted GI steels respectively. Wide scan (a, a'). High resolution scan in the C1s region (b, b') and N1s region (c, c').
3.2. The role of reducing agent in the grafting process

One of the good things in this grafting method, the electron transfer at the origin of diazonium salt is achieved by a chemical oxidation-reduction reaction via the addition of reducing agent in solution otherwise external electrical potential would be needed. Accordingly, we have estimated how reducing agent plays an important role in grafting process. In that respect, we chose L-ascorbic acid (VC) as the reducing agent because its standard oxidation potential is known as lower than the reduction potential of diazonium salt which enables redox reaction between NBD and VC thereby generating homogeneous nitrophenyl radical. Moreover, VC is also unable to reduce protons from the solvent which will ease our interpretations by avoiding any potential hydrogen radical formation from the reactive mixture. Figure 6. indicates that the reduction of NBD which induces dediazoniation starts near 0.23 V/SHE, then the passivation of the electrode was observed in following sweeps. As we also have measured the open circuit potential (OCP) of three types of steel (Table 1). Since the $E_{OCP}$ of the steels are lower than the reduction potential of NBD, the possibility of occurrence of the spontaneous grafting without reducing agent is provided.
Figure 6. Linear sweep voltammogram of 5mM NBD (0.02V/s scan rate, copper electrode) in DI water + 10mM NaCl. aPotential range was corrected against S.H.E

Table 1 Open circuit potentials of metal studied in a 2 mM diazonium salt in DI water + 2mM VC. aThese potentials were measured immediately after dipping the steels in solution.

<table>
<thead>
<tr>
<th>Steel</th>
<th>GI</th>
<th>GA</th>
<th>EG</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_{OCP} (V/S.H.E)</td>
<td>-0.59</td>
<td>-0.27</td>
<td>-0.56</td>
</tr>
</tbody>
</table>

To investigate whether we additionally need reducing agents or not, pH variation with time was measured because we have hypothesized that VC had been regenerated during the reaction thereby increasing the acidity of the
solution. As scheme 7 shows that hydrogen radicals produced from poly addition of nitrophenyl radical react with ascorbate radical to regenerate L-ascorbic acid. To confirm the regeneration of L-ascorbic acid in addition to obtaining the coarse information about the occurrence and efficiency of grafting process, pH change during the reaction was monitored (Figure 7, 8). At first glance of Figure 7, the black square line exhibits the pH change when 2mM VC (1/10 equiv. vs NBD) was added in NBD solution and the red upper triangle line showed pH change of same solution without NBD. Though the fact that VC increases acidity of the solution as it dissolves, the black line decreased more rapidly than red line during the first 10 minutes indicating regeneration of VC occurred by vigorous poly addition process. From Figure 8, pH of solution did not distinctly decrease when GI steel was introduced. Accordingly, GI steel, despite of its capability of reducing NBD, did not seem to work as initiator to produce polynitrophenylene (PNP) because no synthesized PNP powder was precipitated in the solution. Instead, it could be regarded that reduction occurred only at the interface. Figure 8a shows that the role of reducing agent was obvious. After first 5 minutes of reaction, the moieties corresponding to polynitrophenylene were detected only in the GI steel on which VC was added in the solution. However, characteristic bands of PNP were observed after 30 min when VC was not added in solution (Figure 9b). Thus it can be deduced that the addition of the reducing agent not only helps quick NBD reduction but also increases the grafting efficiency
Scheme 7. Regeneration of L-ascorbic acid after reducing NBD. (Ⅰ) An ascorbate radical formed after reduction of NBD reacts with (Ⅱ) hydrogen radical produced from poly addition of aryl radical.
Figure 7. Plot of acidity change in solution for various time. (▲) 2mM VC aqueous solution and (●) 20mM NBD added in 2mM VC aqueous solution.

Figure 8. Plot of acidity changes for various time. (●) is 20 mM NBD dissolved in DI water and (▼) GI steel was immersed in the NBD solution.
Figure 9. Influence of reducing agent on ATR-IR spectra of GI steel surface. (a) the spectra were obtained by dipping in 0.02M NBD solution for 5 min with and without VC. (b) evolution of characteristic band of PNP varied with reaction time when VC was absent.
3.3. Grafting of various polymers on steel substrate

It was known that diazonium induced grafting process is able to functionalize the surface with not only polynitrophenylene (PNP) layer but also all polymer layers that can be synthetized via a radical pathway. With such respect, we have introduced three different vinylic monomers in the solution: acrylonitrile (AN), methyl methacrylate (MMA), acrylic acid (AA). Accordingly, a signature absorbance band of target polymer film were observed after modification the surfaces obtained by DIAP. Figure 10 reveals the major peak of each grafted polymer. IR-ATR absorbance pertaining ester C=O stretch band at 1729 and 1702 cm\(^{-1}\) detected in PMMA and PAA grafted films and C≡N for PAN grafted film near 2243 cm\(^{-1}\) confirms the existence of the vinylic polymer film. As also shown in Figure 10 and table 2, all grafted polymer film exhibits the characteristic bands of PNP layer indicating that inhomogeneous grafted polymer layers were deposited.

Figure 11 shows a water drop deposited on untreated and PAA grafted GI steel respectively. Among grafted various polymers, PAA grafted substrate have showed distinct change in contact angle of water drop since PAA contains hydrophilic functional group (COO⁻). The average value of contact angle reached around 94.6° before PAA grafting. This value dwindled to near 48.3° after 30 min reaction time. Thus, it seems that the contact angle of water drop decreased with grafting reaction time indicating that the longer reaction time, the denser grafting occurred. In particular, the rate of change
in contact angle during first 30 min reaction was rapidly decreased (Figure 12). This implies that surface chemistry of steels can be tailored.

![IR spectra of (a) PMMA, (b) PAN, (c) PAA grafted GI steel, and (d) bare GI steel respectively](image)

**Figure 10.** IR spectra of (a) PMMA, (b) PAN, (c) PAA grafted GI steel, and (d) bare GI steel respectively

**Table 2.** Major IR absorption bands of grafted polymers on GI steel

<table>
<thead>
<tr>
<th>entry</th>
<th>target polymer</th>
<th>reaction time (min)</th>
<th>IR absorbance band (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>PMMA</td>
<td>15</td>
<td>(v\text{NO}_2) (1346, 1521), (v\text{C} = \text{C}) (1595) (v\text{C} = \text{O}) (1729)</td>
</tr>
<tr>
<td>(b)</td>
<td>PAN</td>
<td>15</td>
<td>(v\text{NO}_2) (1346, 1520), (v\text{C} = \text{C}) (1597) (v\text{C} - \text{H}) (1456) (v\text{C} = \text{N}) (2243)</td>
</tr>
<tr>
<td>(c)</td>
<td>PAA</td>
<td>15</td>
<td>(v\text{NO}_2) (1346, 1518), (v\text{C} = \text{C}) (1595) (v\text{COO}-) (1407), (v\text{C} - \text{H}) (1452) (v\text{C} = \text{O}) (1701)</td>
</tr>
</tbody>
</table>
Figure 11. Contact angle measurements. DI water drop on GI steel for various grafting time.
3.4. Thickness control

In regards to the thickness control of the grafted polymer layer, the initial study on the Graftfast\textsuperscript{TM} process conducted by Mévellec et al.\textsuperscript{5} has demonstrated that the intensity of the IR band characteristic of the grafted polymer increased with the reaction time. Beside, ellipsometry is good tool for thin film measurement. Note that the roughness of the steel substrates in the case of measurements as well as the lack of adequate models of organic layers on steel substrates were the main obstacles measuring reliable thickness with ellipsometer. Instead, using 5 nm nickel sputtered Si wafer as substrate, thickness change varied reaction time was evaluated. As Figure 13 indicates that the thickness of the film can roughly be controlled within 15 min reaction. Interestingly, chain growth rate showed quite similar behavior.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{contact_angle_graph.png}
\caption{Plot of contact angle varied with reaction time}
\end{figure}
with contact angle change, indicating that both chain length and contact angle variation were likely to be reached the saturation value within 30 min reaction time. Figure 14 and Table 3 show that an increase in reaction time led larger IR (ν\text{C=O}) intensity, thereby higher thickness was recorded in the case PMMA film except 30 min sample. Additionally, AFM images of PAN grafted GI steel with various reaction time not only indicate the similar tendency but also give information on the morphology of the grafted film (Figure 15). Calculated roughness of bare (7.4 nm) and grafted PAN (18.6 ± 0.9 nm) surfaces on GI steel and spiky morphology together demonstrated the grafted film to the steel was not uniform. Uneven organic layer obtained by DIAP is probably because anchoring of polymer chains synthesized in solution dominates over the surface growing nature in the grafting process. Therefore, we confirmed that by controlling the reaction time, the thickness of the grafted films can be tailored. Nevertheless, the morphology of the film is not homogeneous.
Figure 13. Thickness of PMMA film on variation with reaction time

Figure 14. Evolution of intensity of $\nu_{\text{C=O}}$ IR band in PMMA film on with reaction time
Table 3.
IR intensity and Thickness of PMMA layer on Si wafer. Thickness was measured by Ellipsometer

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>30</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>I νC=O (%)</td>
<td>3.5</td>
<td>3.9</td>
<td>4.6</td>
<td>5.8</td>
<td>7.6</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>29±1.5</td>
<td>42±2.1</td>
<td>49±2.7</td>
<td>47±3.8</td>
<td>51±2.4</td>
</tr>
</tbody>
</table>

Figure 15. AFM images PMMA grafted on GI with various reaction time

3.5. Lap shear strength

Under harsh environment the polymer/metal interface tends to delaminate or experience a significant diminishing in load bearing capacity and thus potential in-service failures\(^{36}\). Increasing temperature generally increases the water transport to the interface, and may lead to chemical degradation of the
polymer or oxidation of the metal and thus loss of adhesion\textsuperscript{37}. In this context, the use of carefully designed primers, as an alternative to the more environmentally harmful etching treatment, is important for improving the adhesion strength and durability further\textsuperscript{38}. Thus, we have concerned that the grafted film covalently linked to the steel substrates (cf. 3.1.4) would provide excellent protection against corrosion for some metals\textsuperscript{39,40} and therefore contributes to the development of adhesion and coating applications. Moreover, PA6 was used because it shows admirable thermal stability and relatively low price together let us consider PA6 is good candidate for plastic-metal composite. Figure 16 provides an overview of lap shear strength of PA6 to three types of commercial steels with and without of PNP primer present. It was observed that the PNP primer layer deposited on EG, GA, and GI steel played as actual adhesion improving primer.
Figure 16. Lap shear strength of before (■) and after primer grafted (●) on various samples. The primer layers were obtained by DIAP for 30 min reaction time.

Among three types of steel, GI steel was used in the following experiments because it displays the most notable change in interfacial shear strength before and after surface modification. However, it should not be ignored that the reason of enhanced IFSS might have resulted from an increase in surface roughness by acidic etching. Thus, we have confirmed that 2mM of VC dissolved 2 mM NBD dissolved in DI water exhibits acidic condition around pH 2. Accordingly, we found that 25 mM VC aqueous solution exhibits similar pH value to the reaction condition. Consequently, measurement IFSS was followed to evaluate the influence of acidic solution on GI steel surface.
As Figure 17 indicates that the IFSS of PA6 to GI immersed in 25mM VC (pH=2) aqueous solution has slightly increased (11.6±0.5 MPa) compared to PA6 with pristine GI (8.4±0.9 MPa).

Figure 17. Influence of acidic solution to IFSS. (■) 25mM VC aqueous solution and (□) 2mM VC added in 0.02M NBD solution for 5 and 60 min

Nevertheless, the IFSS of PA6 with PNP primer grafted GI (16.5±0.2 MPa) showed still much higher than the others.
Moreover, PNP primer grafted GI sample showed the highest adhesion strength to PA6 among other polymer primers grafted in this study (Figure 18). Figure 19 shows a plot of the lap shear strength of PA6-GI and PA6-PNP-GI after having been immersed in 92°C hot tap water for various time (0-72h). The IFSS of both PA6-GI and PA6-PNP-GI decreased with submerging time. However, the IFSS of PA6-GI approached to 0 MPa after 24 h immersion in hot water, whereas PA6-PNP-GI samples still exhibited higher strength (9.8 MPa) than the pristine sample (8.3 MPa). Furthermore, cohesive failures were observed in PA6-PNP-GI sample of whole experimental condition. This demonstrates such reduction of IFSS in PA6-PNP-GI was more likely resulted

**Figure 18.** Lap shear strength of various sample under dry condition. Each adhesion primers were obtained after 30 min reaction time.
from degradation of PA6 by an extensive exposure of hot water rather than water was transported through either PA6/PNP or PNP/GI interface. Note that debonding prior to the test was first observed from one out of five samples in identical condition after 48 h of PA6-GI sample. Nevertheless, the bonding joint of PA6-GI samples exposed to hot water for 12h showed that interfacial failure was dominating over the failure area (Figure 20). This is probably because lack of primer layer which protects the steel surface from corrosion, thereby formation oxide/hydroxide complex\textsuperscript{41} which is detrimental to adhesion property. Beside such interfacial failure supports that adhesion between the PA6 and steel without modification consists of mainly Van der Waals dispersion force.

**Figure 19.** IFSS of PA6-GI (■) and PA6-PNP-GI (□) after exposing to 92°C hot water for various periods
<table>
<thead>
<tr>
<th>Time (h)</th>
<th>PA6-GI</th>
<th>PA6-PNP-GI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td><img src="image" alt="Cohesive failure" /></td>
<td><img src="image" alt="Cohesive failure" /></td>
</tr>
<tr>
<td>12</td>
<td><img src="image" alt="Interfacial failure" /></td>
<td><img src="image" alt="Cohesive failure" /></td>
</tr>
<tr>
<td>24</td>
<td><img src="image" alt="Interfacial failure" /></td>
<td><img src="image" alt="Cohesive failure" /></td>
</tr>
<tr>
<td>72</td>
<td><img src="image" alt="Interfacial failure" /></td>
<td><img src="image" alt="Cohesive failure" /></td>
</tr>
</tbody>
</table>

**Figure 20.** Fracture surfaces (25 × 12 mm$^2$) after lap shear test under hot water treatment
To sum up, the IFSS of both bare and modified with PNP samples were weaken by immersion into hot water. Such reduction of IFSS was more likely resulted from degradation of PA6 by extensive exposure of hot water rather than the scope of interfacial interaction between PA6 and the substrate. In spite of the degradation of PA6 in hot-wet environment, the PA6-PNP-GI sample showed far retarded diminishing in the lap shear strength.
4. Conclusion

In this report, the grafting of 4-para-nitrobenezenediazonium (NBD) salt and polymers on steel substrates was achieved by nitrophenyl radicals via redox activation. This NBD involved redox activation grafting process enabled vinylic polymers such as PAA, PAN and PMMA to graft on steel substrates. Unlike general organic thin film coating methods such as vapor deposition and spin coating, the organic layer obtained by NBD involved grafting process was not homogeneous and uniform confirmed by SEM, AFM and IR analysis. Thus, the thin film layers containing defects or pinhole is not appropriate for insulative usage in electrical device. Nevertheless, the thickness of the grafted layer can be controlled with reaction time. In the case of PMMA grafted film reached maximum thickness of around 56 nm after 30 min reaction. Taking into account of the role of VC used as reducing agent, VC altered grafting nature from “grafting from\textsuperscript{42-44}” technique to “grafting to\textsuperscript{45-47}” technique since polymer synthesized in solution was not observed when VC was not added. It was also found that VC is necessary when vinylic polymer grafting. In particular, organic layers obtained by both electrografting and diazonium involved grafting revealed metal-carbide boding confirmed by XPS analysis. This let us consider that such organic film concretely deposited on steels by covalent bond is able to prevent steel surface from corrosion and increase adhesion property to plastic materials. Hence, the lap shear test was used to evaluate both initial adhesion of plastic-metal joints and the durability of these joints after
exposure to hot water. Among modified steel surfaces, PNP grafted GI steel showed higher IFSS to PA6 than PAN and PMMA grafted GI steels including bare GI samples. In regards to durability of these joints, IFSS of PA6-bare GI sample dropped from 8.4 MPa to 2.9 MPa after 12 h exposure to hot water, whereas PNP grafted GI steel exhibited 11.2 MPa which is still a higher value than initial strength of PA6-GI samples. For all PA6-GI samples immersed in hot water have shown interfacial failure since after 12 h immersion while PA6-PNP-GI sample revealed cohesive failure throughout the experiment. Therefore, PNP primer has actually increased the adhesion property of plastic-metal joints and its durability. In short, this stable coating under harsh condition will provide huge potential in many industrial fields, for instance, development in composite materials by providing adhesion primer layer at the interface, painting in automobile industry for anti-corrosion protection as well as biocompatible coating for medical devices.
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요약

유기박막이 코팅된 재료는 코팅막의 특성과 재료 자체의 특성을 모두 활용할 수 있어 여러 산업 분야에서 응용되고 있다. 용도에 따라 필요한 작용기를 표면에 형성하여 재료의 도장성, 내부식성, 생체적합성 등을 부여함으로써 구조재료와 기능성 재료에 응용할 수 있다. 유기박막코팅을 위해 스피너팅, 화학기상증착법, Langmuir-Blodgett과 같은 균일한 박막이 도포될 수 있는 방법들을 사용하는데, 이 코팅법들은 박막과 기판 간의 물리적 결합을 하고 있어 이중물질인 기판과의 접착이 오래가지 못하고 계면 분리현상이 쉽게 일어난다. 본 논문에서는 이러한 현상을 개선하기 위해 금속표면과 유기박막층 사이에 물리적 결합이 아닌 화학적 공유결합을 갖는 코팅방식인 전기적고분자접합과 다이아조늄을 이용한 고분자 접합법을 연구하였다. 본 연구에서는, diazonium 염을 이용해 poly(acrylic acid) (PAA), poly(acrylonitrile) (PAN)과 poly(methyl methacrylate) (PMMA)고분자를 성장과 동시에 금속표면에 접합하였다. AFM과 SEM을 통해 표면형상을 확인하고 IR을 이용해 접합된 고분자를 확인하였다. 또한, X-ray photoelectron microscopy를 통해 metal-carbide bonding이 관찰됨에 따라 고분자가 스틸 표면 위에 화학적으로 결합한 사실을 증명하였고 이는 유기용매 속에서 sonication 세척에도 제거되지 않을음을 확인하였다. 따라서 금속기판과 공유결합을 이루고 있는 유기층이 스틸-플라스틱 계면에서 접착 프라이머 역할을 함으로써 계면전단강력이 향상됨을 lap shear test를 통해 확인하였다.

주요어: 다이아조늄 염, 공유결합, 접착프라이머, 계면전단강력
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