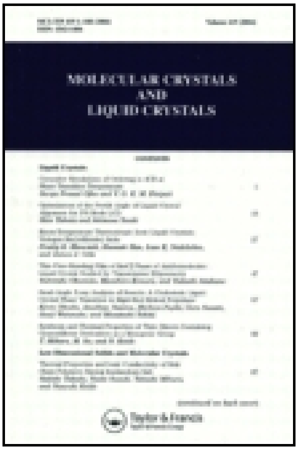

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SURFACE MODIFICATION OF POLYMER-COATED STEEL SHEET BY PLASMA TREATMENT

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In order to control the rate of corrosion, plasma gas discharge was applied to modify the surface of a polymer coated-steel sheet to be hydrophobic. Since the corrosion resistance of steel is strongly related to water permeation, the surface hydrophobicity of materials was introduced by CF_3H plasma exposure. The corrosion property before and after the plasma treatment was investigated in a slat spray tester of 3.5% NaCl fog at 35°C. The results showed that the CF_3H plasma-induced polymer exhibited significant retardation of corrosion.

Keywords: corrosion; hydrophobicity; plasma; retardation; steel

INTRODUCTION

Corrosion is the destructive result of chemical reactions between a metal and its environment. Corrosion impacts many aspects of our lives including economic loss and human safety. The most common way to prevent a metal from corroding or to retard its corrosion is to provide an impervious coating over it [1–3]. If a barrier layer is applied to the surface of a metal exposed to a corrosive environment, then neither oxygen or water can reach its surface and corrosion will be prevented. A similar behavior can be observed in a

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*Corresponding author. E-mail: wonki@pknu.ac.kr hydrolyzable polymer [4]. However, a desired polymer surface sometimes often cannot be obtained from the material itself but through chemical or physical modification. The most common surface modification techniques include blending, copolymerization, chemical surface reactions, flame treatment, and plasma treatment [4,5].

The expose of a polymer to a plasma produce in the surface wettability as a post-treatment changes. Perfluorocarbon plasmas are a potentially attractive means for modifying hydrocarbon polymers because it generates a fluorinated layer at the surface of polymers, causing water proofing polymeric substrates either by fluorination of the surface layer or deposition of plasma polymers, depending on the plasma gas composition on the F/C ratio of the fluorocarbon [5–7].

In this work, organic-coated steel sheet was exposed to CF_3H plasma to improve surface hydrophobicity which retards water permeation into its bulk. Therefore, the effect of plasma treatment on corrosion was investigated. The surface-layer properties of the plasma-treated samples were evaluated by Elemental Spectroscopy for Chemical Analysis (ESCA) and contact angle as well as Scanning Electron Microscopy (SEM) and the slat spread tests of samples were carried out in 3.5% NaCl fog at 35°C. The results are discussed in term of surface wettability.

EXPERIMENTAL

Materials

Water emulsion solution of Modified Polyethylene (MPE) was supplied by Myongkwang Chem. Co. The concentration of the solution with Cymel was adjusted to be 15%. The MPE with 1 μm thickness was coated on the hot-dip coated mild steel with Zn (5 μm thickness) using a conventional roll coater and the coated steel sheet (MPE-SS) was cured at 170°C of metal temperature for 15 sec.

Plasma Treatments

Plasma was generated by the inductively coupled discharge at 200 W power level using an RF generator (SMACO RIE system 10NR, Kyoto, Japan). Plasma treatment was carried out with the discharge of CF_3H. The chamber had a base pressure below 10 mTorr achieved by mechanical and oil diffusion pumps. The sample chamber was purged with modification gas at 200 mTorr using a flow rate of 200 L/min before initiating plasma. The operating pressure of the plasma was 200 ± 10 mTorr. The modification gas was pumped through a ultrahigh vacuum leak valve. The plasma conditions are 0, 10, 25, and 50 sec of plasma exposure times at 200 W power level.

Samples were then stored in Petri dish. To achieve thermodymanically stable states, all measurements were carried out after 1 month of plasma treatment.

Corrosion

The corrosion resistance of samples was measured by a salt spray tester where 3.5% NaCl solution is continuously spread in a chamber at 35°C and the surfaces were compared.

Characterization of Surfaces

Surface atomic mapping image was obtained on a JEOL JSM-6100 Scanning Electron Microscope (SEM). The static contact angle of water onto the surface of samples was measured using a Kyowa contact angle meter. The surface chemical compositions of materials before and after plasma treatment were obtained using Perkin-Elmer Physical Electronics Model 5300 ESCA. ESCA measurements were performed with MgKα X-ray source at 15 kV and 20 mA at takeoff angles of 30° and 90°, which led to the sampling depth of the C1s region of 5 and 10.3 nm, respectively. When exposed to x-ray radiation, fluoropolymers are known to defluorinate [8]. In order to minimize this effect, shorter exposure times (four minutes) was determined from the relationship between exposure time and atomic ratio for poly(vinylidene fluoride) (PVDF) as a standard material. No defluorination of PVDF during this period was detected within 95% confidence level. High-resolution scans of the C1s, O1s, and F1s were acquired.

RESULTS AND DISCUSSION

Many reviews have been devoted exclusively to the introduction of functional groups onto a material's surface for the improvement of adhesion, protein adsorption, and protective coatings. Plasma discharge processes provide a unique and powerful technique for altering the surface properties of materials without changing their bulk properties.

On the other hand, fluorocarbon plasmas generate a fluorinated layer at the surface of nonpolar polymers such as polyethylene and polypropylene, causing the decrease in the surface wettability [5–7]. This fluorination shows poor adhesion between materials but there is strong requirement for modifying the polymer surfaces more hydrophobic and less wettable.

Figure 1 shows the survey spectra of MPE-SS before and after CF_3H plasma exposure of 10 sec, taken at 90°. According to the molecular architecture, a strong signal from C1s at 285 eV is from a neutral carbon of polyethylene. After exposure of CF_3H plasma, however, the appearance of

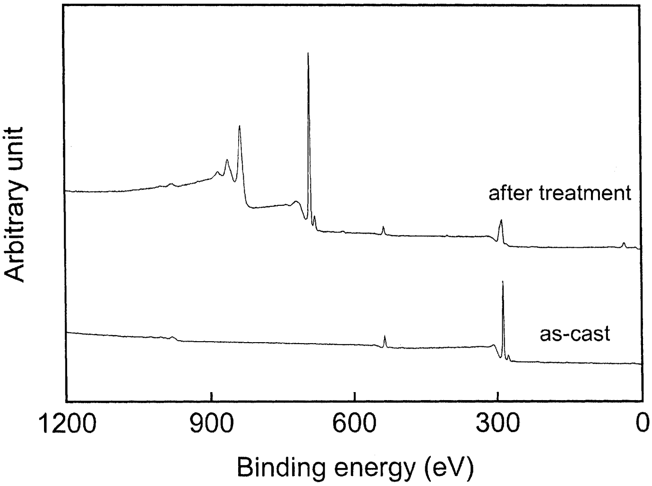

FIGURE 1 ESCA survey spectra of MPE-SS taken at 90° before and after CF_3H plasma treatment of 10 sec.

strong fluorine peak (700 eV) is clearly the evidence of surface fluorination. This will lead to increase the surface hydrophobicity of samples. From the results of the influence of plasma exposure time on the F1s/C1s ratio. The F1s/C1s ratio was little changed, regardless of the exposure time and the take-off angle. The CF_3H plasma treatment quickly increases fluorine content to over 50% of atomic percentage, regardless of the exposure time and the take-off angle.

To investigate the effect of plasma treatments on the surface structure of the coated MPE, the high resolution C1s spectra for pure and plasma-treated samples were recorded at a take-off angle of 90°. Figure 2 shows the high resolution C1s spectra for pure and CF_3H plasma-treated MPE-SS for 50 sec. According to the polymer structure, the curve of C1s peak of pure MPE-SS can be resolved into one component with 285 eV, corresponding to -C-C-. However, the C1s spectrum obtained after the CF_3H plasma exposure was very different. There are new several peaks at higher binding energies. Based on the data of atomic concentration composed of carbon and fluorine, it indicates that the components of C1s are mainly composed with CH_xF_y species, CF, C-CF_n, and CF-CF_n.

When polymers were treated with CF_3H-plasma, the surface generally became hydrophobic due to the surface fluorination. The water contact angle of CF_3H-plasma treated films was increased from 85° to 120°, not much depending on exposure time. Figure 3 shows the fluorine-mapping image of CF_3H plasma-treated MPE steel sheets. The white parts in the image are corresponded to fluorine atoms. This image indicates that the

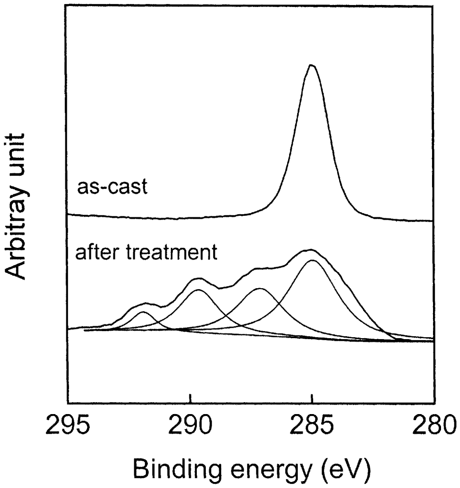

FIGURE 2 High-resolution C1s spectra of MPE-SS at a take-off angle of 90° before and after CF_3H plasma treatment of 50 sec.

CF_3H plasma homogeneously introduced fluorine groups in whole surface area. These behaviors are not surprising if one considers a lower water wettability of surface fluorine groups induced by plasma.

Visual tests have also been performed on pure and CF_3H plasma-treated MPE-SS. Figure 4 shows the salt fog data before and after 10 sec plasma-treated MPE-SS for 72 hrs. Usually, the first stage in steel corrosion consists of white corrosion (white region in the Figure 4) and the second state shows red corrosion (black region in the Figure 4). It is evident that the CF_3H plasma-treated MPE-SS (right) shows significantly lower extent of red

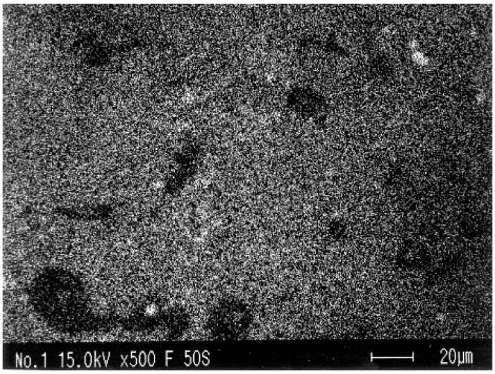

FIGURE 3 F-mapping SEM image of CF_3H plasma treated MPE-SS.

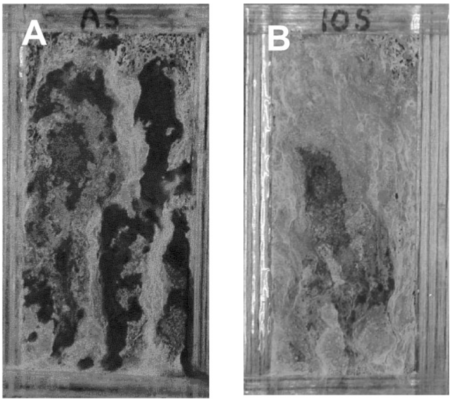

FIGURE 4 Visual test of pure (A) and 10 sec CF_3H plasma-treated (B) MPE-SS (dimension: $3 \times 5\,cm^2$) after 72 hrs in a salt fog chamber.

corrosion. The other samples with different plasma treatment times showed similar morphologies. The distinct corrosion resistance can be explained by slower water permeation into the plasma-treated layers due to their dewettability.

In conclusion, plasma-induced surface modification of polymers is an effective method to delay corrosion, causing hydrophobicity by plasma fluorination. The distinct corrosion resistance can be explained by slower water permeation due to their dewettability. By the proper control of fluorine-containing plasma exposure time, the material life-time in a specific environment can be controlled for further commercial applications.

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