Hydrophilization of PP Resin and ABS Resin by Applying Electrolyzed Sulfuric Acid

Yasushi Umeda^{1*}, Yuki Nakabayashi², Tatsuo Nagai³
Katsuhiko Tashiro⁴, Hideo Honma² and Yukihiro Sakamoto⁵

1 Materials and Surface Engineering Research Institute, Kanto Gakuin University : 1162 -2 Ogikubo, Odawara, Kanagawa 250-0042, Japan

2 Graduate School of Engineering, Kanto Gakuin University : 1162 -2, Ogikubo, Odawara, Kanagawa 250 -0042, Japan

3 MicroAce Co., Ltd. : 1411 -1 Kyode, Hanagashima-cho, Miyazaki 880 -0036, Japan

4 Kanto Gakuin University Research advancement and management organization : 1162 -2, Ogikubo, Odawara, Kanagawa 250-0042, Japan

5 Graduate School of Engineering, Chiba Institute of Technology : 2 -17-1 Tsudanuma, Narashino, Chiba 275 -8588, Japan

* Corresponding author : umeda@kanto -gakuin.ac.jp

Abstract

Mixture of chromic acid and sulfuric acid has been widely applied for hydrophilization of ABS resin. However, it is difficult to make the hydrophilic surface of PP resin, because chromic acid has poor oxidizing power for PP resin. In addition, due to environmental concerns, alternative technologies that do not use hexavalent chromium are required. The authors have confirmed that PP resin and ABS resin can be hydrophilized with electrolyzed sulfuric acid solution and then be plated to obtain enough adhesion strength in practical use. In this report, focusing on its hydrophilization behavior, we investigated the reason why hydrophilization is created, and assumed that hydrophilization is due to oxygen entering between bonds of carbon and hydrogen to become hydroxyl groups. Key words : PP resin, ABS resin, electrolyzed sulfuric acid, hydrophilization

1. INTRODUCTION

Plastics have replaced metals as structural materials and parts materials, taking advantages of weight saving, cost reduction, shape freedom, and ease of mass production. In general, it is widely used not only for decoration, but also for exterior and interior parts of automobiles, household electric appliances and so on. At that time, in order to improve rigidity, abrasion resistance, weather resistance, heat resistance, metal plating is often applied to the plastic surface.

Since plastics are nonconductive, it is necessary first to form a metallic film as a conductor on the plastics in order to perform plating. The methods are roughly classified into dry methods and wet methods. There are methods such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) as dry methods, and there are techniques such as electroless nickel plating and electroless copper plating as wet methods. The wet techniques have been adopted so far because the dry methods are mostly to form films under vacuum conditions and are not suitable for mass production and/or application to big parts.

Chromic acid etching is used as a hydrophilization treatment of plastics molded products before metal plating. However, it is difficult to make the hydrophilic surface of polypropylene (hereinafter PP) resin, although possible to hydrophilize acrylonitrile-butadiene-styrene (hereinafter ABS) resin. Because chromic acid has poor oxidizing power for PP resin. In addition, due to environmental concerns, alternative technologies that do not use hexavalent chromium are required [1]. Therefore, we have studied the plating method to ABS resin and PP resin

using electrolyzed sulfuric acid (hereinafter ESA) treatment [2,3] for pretreatment of plating process [4,5].

The reason why the hydrophobic surfaces of resins can adsorb the catalyst to enable electroless plating is that functional groups are created on the resin surfaces and the surfaces become hydrophilic. We report the hydrophilization behavior of PP resin and ABS resin surface from the viewpoint of functional groups.

2. EXPERIMENTAL METHODS

2.1 Sample

(1) PP resin

PP resin plates (50 mm × 50 mm) made by Japan Polypropylene Corp. were used. Since PP resin is excellent in chemical resistance, the amorphous surface becomes crystalline by a swelling treatment [6] with an organic solvent and can be etched by acid easily. For this reason, swelling treatment with xylene (80 degree -C., 30 minutes) was carried out and heating was carried out at 80 degree-C for 1 hour in the air for drying and stress relaxation before performing ESA treatment. Thereafter, the PP resin plates were immersed for 60 minutes, 90 minutes, or 120 minutes in ESA solution of 120 degree -C whose sulfuric acid concentration was 92 weight percentage and oxidizer concentration is 10 g/dm³, and they were provided for X-ray Photoelectron Spectrometer (JPS-90SX by JEOL, hereinafter XPS) and Fourier Transform Infrared Spectroscopy (Spectrum One by Perkin Elmer, hereinafter FT-IR) respectively.

(2) ABS resin

ABS resin plates (50 mm × 50 mm) made by Sumitomo Bakelite Co. were immersed for 10 minutes, 20 minutes, and 30 minutes in ESA solution of 50 degreeC whose sulfuric acid concentration was 75 weight percentage and oxidizer concentration is 10 g/dm³ respectively, and they were provided for XPS and FT-IR analysis respectively.

2.2 Analysis

After the ESA treatment, two kinds of analyzes were performed on all samples; XPS analysis and FT-IR analysis.

3. RESULTS AND DISCUSSION

3.1 XPS analysis

(1) PP resin

XPS analysis was carried out for all samples before and after ESA treatment with and without swelling treatment. However since there was no influence of the swelling treatment, we report on samples which are generally subjected to the swelling treatment (XPS spectra was omitted).

Since the same XPS spectra were obtained regardless of the treatment time in ESA treatment, XPS spectra both untreated before ESA treatment and treated for 120 minutes were shown in Fig.1. By ESA treatment, a large change occurs in the peaks around O1s (533 eV) and C1s (285 eV).

Fig.1 XPS spectra of untreated PP resin and PP resin surface treated for 120 minutes by ESA

First, C1s spectrum was investigated carefully. It is possible to know the presence of carboxyl group (-COOH), carbonyl group (-C=O), and so on [7,8]. An example of the analysis is shown in Fig.2. In the presence of -C=O or -C-O, the base of the C1s spectrum spreads in the direction of high binding energy.

Here, C1s spectrum before treatment and C1s spectrum treated with ESA for 120 minutes are shown in Fig.3. Additionally separated spectra on before treatment are shown in Fig.4, and those on after treatment are shown in Fig.5. Comparing both spectra of Fig.4 and Fig.5, -C-O bond increases slightly and -C=O bond occurs slightly, too. As they are almost the same as the peak position and charge-up amount, -COOH and -C=O contain little. From the result, it can be said that carbon (C) is not combined with oxygen (O), that is, it is not oxidized. In

addition, the C1s peak height is decreased by ESA treatment, that is, the carbon (C) concentration is lowered. It is thought that organic matter adhering to the surface was decomposed and removed by ESA treatment.

Fig.2 Example of C1s XPS spectra after oxidizing by Zenglin Wang et al.[7]

Fig.3 C1s XPS spectra of untreated PP resin and PP resin surface treated for 120 minutes by ESA

Fig.4 Separated C1s XPS spectra of untreated PP resin

Fig.5 Separated C1s XPS spectra of PP resin surfaces treated for 120 minutes by ESA

Next O1s spectrum was investigated, too. Fig. 6 shows O1s spectra before and after ESA treatment for 120 minutes. Additionally separated spectra on before treatment are shown in Fig. 7, and those on after treatment are shown in Fig. 8.

Although oxygen is not originally contained in PP resin, when it is left in the atmosphere for a short period of time, it will inevitably adsorb water and organic matter as impurities and oxygen will be present along with it. Therefore, slight oxygen is detected on the surface before treatment. Comparing both spectra of Fig.7 and Fig.8, it can be said that oxygen atoms (O) increased due to the fact that the peak was about 6 times higher by ESA treatment. In addition, most of the O peak of ESA treatment is a hydroxyl group (-OH).

Fig.6 O1s XPS spectra of untreated PP resin and PP resin surface treated for 120 minutes by ESA

Fig.7 Separated O1s XPS spectra of untreated PP resin

Fig.8 Separated O1s XPS spectra of PP resin surfaces treated for 120 minutes by ESA

(2) ABS resin

Since the same XPS spectra were obtained regardless of treatment time in ESA treatment, XPS spectra both untreated before ESA treatment and treated for 30 minutes were shown in Fig.9. As the result of ESA treatment, large changes are generated in the peaks around O1s (533 eV) and C1s (285 eV) as PP resin.

Fig.9 XPS spectra of untreated ABS resin and ABS resin surface treated for 30 minutes by ESA

On investigating the C1s spectra, it is almost the same as the peak position, the width at half maximum, and amount of charge -up as PP resin, and there exist no other peaks such as carboxyl group (-COOH) and carbonyl group (-C=O) as shown in Fig.2. Thus carbon (C) is not oxidized. And C1s peak height is decreased by ESA treatment. It is thought that organic matter adhering to the surface was also decomposed and removed by ESA treatment. From the O1s spectra, the oxygen (O) is increased by ESA treatment as PP resin.

3.2 FT-IR analysis

Fig.10 and Fig.11 show the results of FT-IR analysis of PP resin and ABS resin surface under the same processing conditions as those used for XPS analysis.

Fig.10 FT-IR spectra of untreated PP resin and PP resin surface treated for 120 minutes by ESA

Fig.11 FT-IR spectra of untreated ABS resin and ABS resin surface treated for 30 minutes by ESA

It was confirmed that -OH group in the range of 3100 to 3600 cm^{-1} was greatly increased in FT-IR spectra about both of PP and ABS resin. In particular, the OH group on the PP resin showed a remarkable change. This is consistent with the result of XPS analysis. On PP resin, C=O peak near 1650 cm^{-1} is increased by ESA treatment. It can be said that -COOH is slightly created as the distortion in C1s spectrum in XPS analysis.

3.3 Oxidation reaction on the surface of PP resin and ABS resin

(1) PP resin

The structure of PP resin is showing Fig.12 and has a tertiary carbon in the main chain. Since tertiary carbon has lower binding energy than primary and secondary carbon, it is susceptible to be oxidized, and the main chain is cut to decrease the molecular weight [9,10].

Fig.12 PP resin structure

As the sulfuric acid concentration was as high as 92 wt%, the presence and quantitative determination of 2-propanol could not be done. However, as understood from XPS and FT-IR analyses, hydroxyl group (-OH) occurs on the surface of PP resin, and PP resin is dissolved in ESA solution and roughened at the actual ESA treatment [5]. Therefore we suppose that the tertiary carbon is cleaved and is oxidized as follows Fig.13.

Fig.13 shows a model in which 2-propanol is liberated, but the concentration of sulfuric acid is as high as 92 wt%, and the presence and quantitative determination of 2-propanol cannot be done. Alcohol having a carbon

number larger than that of 2-propanol may be liberated.

Fig.13 PP resin structure

(2) ABS resin

ABS resin is a terpolymer of acrylonitrile, butadiene, and styrene, and the structure is generally written as showing in Fig.14. However, polybutadiene particles disperse in acrylonitrile-styrene copolymer as the matrix phase actually. Therefore, when it is etched with chromic acid, the butadiene parts are preferentially dissolved [11].

Fig.14 ABS resin structure

Since acrylonitrile-styrene resin contains tertiary carbons as PP resin, it is considered that hydroxyl group (-OH) occurs at the carbon site.

4. CONCLUSION

It is possible for ESA treatment to enable PP resin and ABS resin to be plated with adhesion which can withstand practical use, although PP resin cannot be plated up to now and ABS resin is conventionally pretreated with chromic acid. That is because the surface of the resin can be changed hydrophilic by ESA treatment. We investigated the hydrophilization behavior from the viewpoint of functional group and found that the appearance of hydroxyl group (-OH) must be created hydrophilic mainly.

In order to create strong adhesion between the resin surface and the plating film, it is necessary to have irregularities on the surface of the resin and to make the hydrophilization as discussed in this paper. We intend to discuss the importance of linking these two phenomena occurred simultaneously in ESA treatment and the application to other resins in the future.

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