Atmospheric pressure plasma treatment of polypropylene to improve the bonding strength of polypropylene/aluminum composites


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1. Introduction

Polypropylene (PP) is a useful thermoplastic polymer with a wide range of applications such as in packaging, automobile, and aerospace industries. PP has outstanding properties such as low density, good abrasion resistance, and excellent mechanical and electrical properties [1]. For this reason, many studies have been made on the material properties of PP matrix composites [2–8]. In recent years, the use of polypropylene (PP) as an indoor panel material is increasing in the automobile industry since it can be recycled. PP is adhesively bonded to metal material or other plastic material as an indoor panel part. Thus, the technology to join PP with other materials is important in order for PP to be applied broadly as a component of indoor panels. It is well-known that the mechanical behavior of an adhesively bonded structure is affected by the adherend, adhesive, and surface preparation of the adherends. In particular, the strength characteristics of the joints are highly dependent on the surface treatment of the adherends [9–11]. As a consequence, many attempts have been made to improve the adhesive strength between PP and other materials (metal, plastic, and composites) [12–23].

Carrado et al. [24] investigated the effect of corona treatment of a PP sheet to increase its surface energy and adhesion to austenitic steel. They reported that the peel strength was improved by increasing corona exposure time from 20 s to 120 s. Guild et al. [25] investigated the effect of forced air-plasma pre-treatment on PP using X-ray photoelectron spectroscopy (XPS), angle-resolved XPS (AR–XPS), and atomic force microscopy (AFM). They showed that pre-treatment induced both surface chemistry changes and topographical changes. Mirabedini et al. [26] studied the microwave irradiation of a PP surface, and reported that the surface became hydrophilic upon exposure to microwave irradiation for 120 s. They also reported a slightly pitted structure on the PP surface and chemical changes evident from the presence of a carbonyl group, as well as the formation of carbon double bonds due to the microwave irradiation. The above-mentioned surface treatments of PP are effectively employed for bonding PP to metal; however, further studies are still needed to devise better surface treatments for the PP and metal.

In a previous study we reported that the hydrophilic property of carbon fiber-reinforced plastic was significantly improved by plasma modification with oxygen gas [27]. In this study we treated PP with atmospheric pressure plasma and investigated the effect of the plasma treatment on the bonding strength between PP and aluminum plates. The variation in the contact angle on the surface of the PP was measured as a function of the number of plasma treatments. Scotch tape peel tests and paint adhesion tests were also performed as functions of treatment number. AFM and FTIR analyses were conducted on the surfaces of the PP before and after
plasma treatment to determine the physical and chemical changes on the surface due to the atmospheric pressure plasma treatment.

2. Experimental

The materials used were PP and aluminum plates with thicknesses of 3 mm and 2 mm, respectively. The surfaces of both plates were ultrasonically cleaned in acetone for 5 min. The plasma treatment was performed using atmospheric pressure plasma equipment. The processing parameters in the atmospheric pressure plasma treatment are power and the number of treatment. In this study, the power was fixed at 600 W and the optimal number of treatment was determined. Contact angle tests, paint adhesion tests, and Scotch tape peel strength tests [28] were used to determine the optimal number of plasma treatments for PP. The contact angle was measured with a contact angle meter using distilled water. Measurements were taken at room temperature, and the relative humidity was 52%. The water droplets comprised of 0.025 ml of distilled water were dropped at three different sites on each panel, and the measured values of the contact angle were averaged. The chemical and physical changes on the PP surface due to the atmospheric pressure plasma treatment were determined by FTIR and AFM analysis, respectively.

Peel and shear strength tests between PP and aluminum were performed using untreated and plasma-treated PP to quantify the improvement of adhesion strength due to the plasma treatment. Both SLS (single lap shear) and T-peel specimens were fabricated using a conventional secondary bonding procedure in which the PP plate was bonded to the aluminum plate using the adhesive in a hot press. The adhesive used was an epoxy cured at room temperature, and it was made by mixing 80% diglycidyl ether of bisphenol A, YD-115 (Kukdo Chemical, Korea) with 20% curing agent dianiline, and D-230 (Kukdo Chemical, Korea). Here
crosslinking polymerization type interactions happened between epoxy and plasma treated PP. The PP/aluminum composites were fabricated in a hot press under a pressure of 5 kg/cm² at room temperature for 24 h. For the T-peel specimens, the right-angled tabs were adhesively bonded to the ends of the PP and aluminum plates to produce the loading grips. Fig. 1 shows schematic diagrams of the SLS and T-peel specimens used in this study. SLS and T-peel tests were performed with a universal testing machine at room temperature by applying displacement-controlled loading at a rate of 1 mm/min and 0.5 mm/min, respectively.

3. Results and discussion

Fig. 2 shows the changes in the contact angle on the surface of PP as a function of treatment number. As shown in the figure, the contact angle was affected by the atmospheric pressure plasma treatment. The figure also shows that the contact angle decreased as the number of treatment increased (up to six treatments), and remained almost constant thereafter. The contact angle of the untreated PP was about 91°, and that of the PP plasma-treated eight times was about 53°.

The optimal number of atmospheric pressure plasma treatments was also determined from the Scotch tape T-peel tests by measuring the variation in T-peel strength as a function of the number of treatments. Fig. 3 shows the variation of the Scotch tape peel strength as a function of the number of treatments. As shown in the figure, the Scotch tape peel strength was also affected by the number of plasma treatments. The Scotch tape peel strength of the untreated case was 1.4 N. The T-peel strength increased to a maximum value (4.3 N) at eight treatments. However, there was no significant difference in the values of peel strength for eight and ten treatments.

Paint adhesion tests were also performed to determine the optimal number of treatments. A paint adhesion test is used to assess the adhesion of paint to a metallic or plastic substrate by applying and removing pressure-sensitive tape over cuts made in the paint. In this study, untreated and plasma-treated PP plates were coated with enamel paint, and the surfaces of the painted layers were divided into small squares (1 x 1 mm²) with a sharp knife. Fig. 4 shows the results of paint adhesion tests for various numbers of plasma treatments; the bright lattices indicate the areas where the paint detached from the PP plate. As shown in the figure, the adhesion strength between the paint and the PP was highest for eight treatments. Therefore, based on the contact angle measurement, Scotch tape T-peel tests, and paint adhesion tests, eight
treatments was determined to be the optimal number for the PP plate.

SLS tests were performed using plasma-treated and untreated PP/aluminum joints to investigate the effect of atmospheric pressure plasma treatment on the shear strength of a PP/aluminum composite. Fig. 5 shows typical shear load versus displacement curves obtained in SLS tests of plasma-treated and untreated PP/aluminum composites. The figure shows that for both specimens, the shear load increased linearly with displacement up to the maximum load, and then fracture occurred. Fig. 6 shows the average shear strength of both specimens. The average shear strength of each specimen was determined by averaging the maximum loads in the corresponding shear load–displacement curves. As shown in the figure, the average shear strength of the plasma-treated PP/aluminum specimen was \( \approx 44\% \) higher than that of the untreated PP/aluminum specimen. Specifically, the average shear strengths were 3550 N and 2450 N for the plasma-treated and untreated PP/aluminum specimens, respectively.

Fig. 7 shows typical load versus displacement curves obtained in the T-peel tests on plasma-treated and untreated PP/aluminum specimens. As shown in the figure, the load increased linearly with displacement at the early stage for both specimens. The load increased nonlinearly with displacement up to the maximum load, decreased, and then remained almost constant. Fig. 8 shows the peel strength for both specimens, where the peel strength in each case was determined as the maximum load in the corresponding load–displacement curve. As shown in the figure, the peel strength is significantly improved by the surface treatment of PP by atmospheric pressure plasma. The average peel strength of the plasma-treated PP/aluminum specimen was almost 42% higher than that of the untreated PP/aluminum specimen.

The increase in the peel and shear strengths of the atmospheric plasma-treated PP/aluminum composites was attributed to two main factors. One is the physical change and the other is the chemical change on the surface of the PP due to the atmospheric pressure plasma treatment. The surface roughness of the PP before and after plasma treatment was examined by AFM to investigate physical changes according to the atmospheric pressure plasma treatment. Fig. 9 shows AFM images of the surface roughness of the PP before and after plasma treatment. As shown in the figure, the surface roughness of PP changed noticeably after plasma treatment. The surface roughness RMS\( _{xy} (R_q) \) of the atmospheric pressure plasma-treated PP increased more than 20% compared to that of the untreated PP. Specifically, \( R_q \) was 22.99 nm before plasma treatment and 27.86 nm after treatment. In general, the bonding area between the substrate and adhesive increases as
the surface roughness of the substrate increases, which increases the peel and shear strengths. It is noted that oxidation layer generated by plasma treatment on the surface of aluminum plate gives better performance for the bonding strength between PP and Al plate.

FTIR analysis was performed on the untreated PP and atmospheric pressure plasma-treated PP in order to investigate plasma-induced chemical changes on the surface. Fig. 10 shows the FTIR spectra of the untreated PP and plasma-treated PP. The FTIR spectrum of the untreated surface contained the CH$_3$ asymmetric and symmetric stretching vibration peaks at 2950 cm$^{-1}$ and 2868 cm$^{-1}$, respectively, while the peaks at 2917 cm$^{-1}$ and 2838 cm$^{-1}$ were due to CH$_2$ asymmetric and symmetric stretching vibrations, respectively. The peak at 1460 cm$^{-1}$ was caused by either CH$_3$ asymmetric deformation vibrations or CH$_2$ scissor vibrations, while the peak at 1378 cm$^{-1}$ was due to CH$_3$ symmetric deformation vibrations. The FTIR spectra of the untreated PP and plasma-treated PP also exhibited numerous small peaks in the wave number range of 1200–700 cm$^{-1}$. The peak at 1167 cm$^{-1}$ was attributed to CH$_3$ asymmetric rocking, C–H wagging vibrations, and C–C asymmetric stretching, while the CH$_3$ asymmetric rocking vibration peak was at 998 cm$^{-1}$. The peak at 973 cm$^{-1}$ was attributed to C–C asymmetric stretching vibrations and CH$_3$ asymmetric rocking, while the peak at 901 cm$^{-1}$ was due to CH$_3$ asymmetric rocking and C–C asymmetric and symmetric stretching vibrations. The peaks at 841 cm$^{-1}$ and 810 cm$^{-1}$ were due to CH$_2$ rocking vibrations. After atmospheric plasma treatment, the most pronounced changes observed in the spectra occurred in the ranges of 3250–3750 cm$^{-1}$ and 1625–1800 cm$^{-1}$. The new absorption bands were assigned as follows. A very broad absorption band between 3750 cm$^{-1}$ and 3250 cm$^{-1}$ was assigned to OH stretching vibrations. The transmittance band arising around 1720 cm$^{-1}$ appeared due to the presence of carbonyl (C=O) groups in ketones, aldehydes, and carboxylic acids. We noted that the C=O group content increased significantly after plasma treatment. With the increase in plasma treatment time, a continuous increase in the band intensity was observed. These results also suggest that the C–C/C–H groups underwent local oxidation on the surface of the PP due to atmospheric plasma treatment to form oxygen-containing polar functional groups, which improved the hydrophilicity of the PP surfaces.

The failure surfaces of PP and aluminum panels were examined with an optical microscope after the T-peel tests in order to determine the bonding characteristics due to atmospheric pressure plasma treatment of the PP panel. Fig. 11 shows photographs of the failure surfaces of PP and aluminum panels for untreated and plasma-treated PP/aluminum specimens. For the untreated specimen shown in Fig. 11a, most of the epoxy adhesive was on the aluminum panel, which indicates that failure occurred at the interface between the adhesive and the PP panel. On the contrary, the
plasma-treated specimen shown in Fig. 11b indicates that the epoxy adhesive was cracked and adhered on the aluminum and PP panels, which indicates that failure occurred within the adhesive. This occurred because the bonding strength between PP and adhesive increased due to an increase in hydrophilicity on the PP surface. That is, adhesive failure was a dominant fracture mechanism for the untreated PP/aluminum specimen, but cohesive failure was a dominant fracture mechanism for the plasma-treated PP/aluminum specimen.

4. Conclusion

Polypropylene (PP) was surface-treated with atmospheric pressure plasma and its effects on the peel and shear strengths of adhesively bonded PP/aluminum composites were investigated. The conclusions obtained in this study are as follows:

1. The optimal number of plasma treatments for the PP by the atmospheric pressure plasma treatment was eight, and the contact angle was reduced from ~91° to ~53°.
2. The peel and shear strengths of adhesively bonded PP/aluminum composites were significantly improved by the atmospheric pressure plasma treatment of PP. The peel strength and the shear strength improved by ~42% and ~44%, respectively, after eight treatments.
3. The improvement in bonding strength was attributed to the increased surface roughness and newly created hydrophilic functional group (C=O) on the PP surface by the atmospheric pressure plasma treatment.

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References