

Low-Temperature Cascade Arc Torch Treatments for Enhanced Adhesion of Primer to Thermoplastic Olefins

Y.-S. LIN, H. K. YASUDA

Department of Chemical Engineering and Center for Surface Science and Plasma Technology, University of Missouri–Columbia, Columbia, Missouri 65211

Received 12 December 1996; accepted 27 July 1997

ABSTRACT: Improvement of primer adhesion to thermoplastic olefins (TPOs) by a low-temperature cascade arc torch treatment was investigated. A cascade arc was created with argon, and a treatment gas (air or methane) was added in the reaction chamber. It was found that the argon torch as well as the air/argon torch and the methane/argon torch can improve the primer adhesion to TPOs. Tape adhesion tests (ASTM method 3359-92a) demonstrated this improvement; a rating of “0” for untreated TPOs and “5” for air, methane, and argon torch-treated TPOs under certain operating conditions. Wettability of primer and of deionized water to TPOs were evaluated by contact angle measurements. TPO surface morphology was evaluated using scanning electron microscopy (SEM). The surface composition was characterized by using electron spectroscopy for chemical analysis (ESCA). The mechanism of improvement of primer adhesion to TPOs is discussed in this article. Primer adhesion was easily enhanced by the treatments for the soft and flexible TPOs (ETA-3041c and ETA-3101). Primer adhesion to hard and brittle TPOs (ETA-3183) was more difficult. Adhesion performance of primer to air, methane, and argon torch-treated TPOs was shown to have different mechanisms. For air plasma-treated surfaces, polar oxygen and nitrogen-containing groups were produced in the nonpolar surface layers, forming chemical bonds to TPOs; and plasma-etched pits spread all over the surface of TPOs into which the primer penetrated to form a mechanical interlock between TPOs and primer. For argon plasma-treated surfaces, the weak boundary layers (WBLs) of TPO surfaces were converted to a stronger layer by argon plasma, which resulted in enhancing primer adhesion to the surfaces of TPOs. The methane/argon torch allowed the deposition of a plasma polymer layer which replaces the weak boundary layer on untreated TPOs with a tightly crosslinked plasma polymer layer, and provides polar groups on the surface (by postplasma reaction of the residual free radicals with air). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 855–863, 1998

Key words: cascade arc plasma; plasma surface modification; thermoplastic olefins; adhesion

INTRODUCTION

Automotive applications of thermoplastic olefins (TPO) have been growing because of their re-

cyclability, low cost, good mechanical properties, and ease of molding. Typical applications include bumper end caps, bumper guards, filler panels, and air dams. However, these substrates are difficult to paint due to their nonpolar, low surface free energy characteristics.^{1,2} While TPOs possess the mechanical properties desired for automotive applications, they cannot be successfully painted without surface modification.

Correspondence to: H. K. Yasuda.

Contract grant sponsor: National Science Foundation; contract grant number: NSF-CTS-9400725.

Journal of Applied Polymer Science, Vol. 67, 855–863 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/050855-09

The gas plasma treatment is an advanced technology that is dry, clean, cost-effective, and environmentally safe.³ Plasma treatment increases the surface energy of the substrate and provides reactive groups, resulting in increased chemical bonding strength between the substrate and coating.³ This technology is replacing more traditional methods to improve primer adhesion to TPOs, or to enhance paintability of TPOs. These traditional methods include wet chemical or flame abrasion, corona discharge, acid etching, and application of adhesion promotion primers and coatings.³ In this study, the low-temperature cascade arc torches were used to create paintable surfaces of TPOs. The low-temperature cascade arc torch technology is an extension of conventional plasma methods (such as glow discharge) to a larger scale operation. The advantages of this technology are that (1) the process has a high deposition rate (fast treatment), (2) the process is capable of coating a large surface area without scaling-up problems, (3) the method can be applied regardless of nature and shape of the substrate, (4) the process eliminates pollution-prone wet chemical processes and reduces volatile organic content in the final products, and (5) the process does not create nonrecyclable materials and maintain high recyclability of final products.

Yasuda⁴ classified the low-temperature plasmas which can be used in the surface modification of polymers to the following three major groups: (1) chemically nonreactive plasma (such as inert gas plasma), (2) chemically reactive plasma (such as O₂, N₂, and CF₄), and (3) polymer-forming plasma (such as trimethylsilane and methane). The terms chemically reactive and nonreactive are based strictly on whether the gas used in a plasma is consumed in chemical processes in the plasma, yielding products in the gas phase, or being incorporated into the solid phase by chemical bonds. In this study, argon (group 1), oxygen (group 2), and methane (group 3) were used for enhancing primer adhesion to TPOs.

Baglin^{5,6} summarized the factors which affect adhesion of a thin film coating to a substrate as follows: interface chemistry, contaminated layers, added reactive layer, interface polarization, differential thermal expansion, interface toughness, stress in the film, and film thickness. In this work, the effects of interface chemistry, contaminated layers (weak boundary layers), added reactive layer, and interface morphology on the adhesion of primer to TPOs were investigated. The interface polarization effects did not influence primer

adhesion to TPOs because no electrostatic attraction was observed in the interface. The differential thermal expansion effects were not addressed in this study. To eliminate stress and film thickness as variables in the present study, consistent primer coating procedures were used for all sample preparations.

The chemistry of interface can play a key role in adhesion performance.^{7,8} The atomic composition and functional groups of plasma polymers which can be determined by using electron spectroscopy for chemical analysis (ESCA), are helpful in characterizing the interfacial chemistry between primer and plasma-treated TPOs. The mechanical interlocking between primer coating and TPOs was also considered to affect the adhesion performance of primer to TPOs. Scanning electron microscopy (SEM) was used to characterize surface morphology of the plasma-treated TPOs.

Ryntz¹ pointed out that the paintability of TPOs can be improved by plasma treatment to enhance paint adhesion due to the increase in the polar surface energy component without significantly changing the dispersion component. Wetting and spreading of liquid on a solid is required for good adhesion at a liquid/solid interface.⁹ In this study, the surface properties of plasma-treated TPOs were evaluated by determining the polarity and wettability for deionized water and primer on TPOs, and these parameters were related to adhesion performance.

EXPERIMENTAL

Materials and Sample Preparation

Three kinds of TPO were used in this study: Hifax ETA-3041c, ETA-3101, and ETA-3183. Hifax is a trademark of Montell North America, Inc. Physical characteristics of TPO samples used in this study are shown in Table I. ETA-3041c is soft and flexible; ETA-3183 is hard and brittle. ETA-3101 has characteristics between ETA-3041c and ETA-3183. ESCA analysis of surfaces of TPOs showed that carbon and oxygen atomic compositions were 95–99% and 1–5%. These TPOs have almost the same surface compositions, although they have different physical and mechanical properties.

Methane (CH₄) with purity more than 99.5%, was purchased from Matheson Inc. Argon and air were at least 99.9% pure. The primer was Primer (764-189) from E. I. Du Pont de Nemours and Company. Primer coatings were sprayed onto

Table I Physical Properties of TPOs

| Physical Properties | Units | ASTM Method | ETA-3041c | ETA-3101 | ETA-3183 |
|---------------------------------|--------------------------------------|-----------------------|-------------|-------------|--------------------|
| Melt flow rate | g/10 min | D1238 | 4.5 | 8.8 ± 1.5 | 6.5 |
| Specific gravity | | D792 | 0.91 | 0.92 ± 0.02 | 0.99 |
| Hardness, shore D | | D2240 | 52 | 59 ± 5 | 68 |
| Mold shrinkage | | Montell | | | |
| Tool | mils/in. | (Himont for ETA-3101) | 6 | 13 ± 1 | 10 |
| Afterbake, 1 h at 250°F | mils/in. | | 11 | 16 ± 1 | 13 |
| Mechanical properties | Units | ASTM Method | ETA-3041c | ETA-3101 | ETA-3183 |
| Tensile strength at yield | psi (MPa) | D638 | 1600 (11) | n.a. | 3000 (20.7) |
| Elongation at yield | % | D638 | 600 | n.a. | 13 |
| Tensile strength at break | psi (MPa) | D638 | 2400 (16.6) | 2200 (15.2) | 2100 (14.5) |
| Elongation at break | % | D638 | 650 | 500 | 250 |
| Tear strength | lb/in. (kN/m) | D624 | 500 (88) | 600 (108) | 600 (105) |
| Flexural modulus | | | | | |
| Tangent at 0.5 in./min at 23°C | psi (MPa) | D790 | 45000 (310) | 80000 (552) | 175000 (1207) |
| Tangent at 0.05 in./min at 23°C | psi (MPa) | D790 | 40000 (275) | | 155000 (1070) |
| Gardner falling dart impact | | | | | |
| at 73°F (23°C) | in. lb (J) | D3029 | n.a. | >320 (36.2) | 250 (28) |
| at -20°F (-30°C) | in. lb (J) | D3029 | n.a. | >320 (36.2) | 200 (23) |
| Heat deflection temperature | | | | | |
| at 66 psi (0.46 MPa) | °F (°C) | D648 | n.a. | n.a. | 180 (82) |
| at 264 psi (1.82 MPa) | °F (°C) | D648 | n.a. | n.a. | 120 (49) |
| Notched Izod impact | | | | | |
| at 23°C | ft lb in. ⁻¹ (J/m) | D256 | n.a. | n.a. | 6 (320) |
| at -30°C | ft lb in. ⁻¹ (J/m) | D256 | n.a. | n.a. | 1.5 (80) |
| CLTE, -30°C to 30°C | °F ⁻¹ (°C ⁻¹) | D696 | n.a. | n.a. | 0.000039 (0.00007) |

n.a., data are not available.

TPOs surfaces with an air brush. The coated TPOs were oven cured at 250°F for 30 min. The measured thickness of primer coatings after baking was ~ 2.5 μm.

Equipment

The plasma treatment was carried out in a low-temperature cascade arc torch chamber (shown schematically in Fig. 1). Three cascade arcs and monomer inlets were located on the top of the reactor (30 cm radius, 62.5 cm high). Each cascade arc had a MDX-10k DC (Advanced Energy Company) power supply to provide arc current. The cascade arc consisted of an anode, a stack of electrically isolated copper plates, and one cathode. The cathode tips were made from pure tungsten welding rods, 1.59 mm ($\frac{1}{4}$ in.) diameter. All copper plates were fabricated to allow coolant flow through the interior. The last copper plate was

used as the anode (grounded) by using the 6.4 mm ($\frac{1}{4}$ in.) o.d. copper coolant outlet tube as the lead conductor. Coolant was a 4% ethylene glycol aqueous solution. Coolant temperature was controlled between 12.2 and 13.3°C.

TPOs were precleaned by wiping the surface 3–4 times with a Kimwipe paper that was moistened with 2-propanol. The TPOs were put into the plasma chamber for plasma treatment. The plasma settings were adjusted at #2 and #3 torches: arc current at 2 A and argon flow rate at 1000 sccm (standard cubic centimeter per minute) for each cascade arc, methane or air flow rate at 10 sccm for each gas monomer inlet, chamber pressure at 270 mtorr, substrate rotation rate at 15 rpm, substrate axial position at 22.86 cm (9 in.) from the top of the chamber, and power supply operation times from 44 to 360 s. The reactor chamber was pumped down to a chamber pressure < 5 mtorr and the pressure leak rate < 2

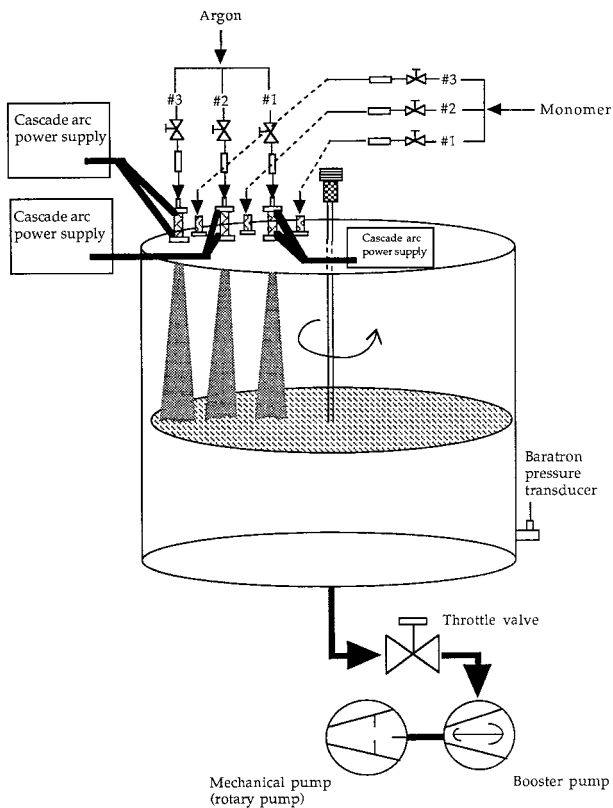


Figure 1 Schematic of the low-temperature cascade arc discharge plasma reactor.

mtorr/min; that is, leak flow rate of air into the chamber is $< 1\%$ of the monomer flow rate. Monomer and argon gas were then fed through needle valves. Argon was admitted to the cascade arc at the cathode. The treatment gas (air) or the monomer (methane) was introduced into the reaction/deposition chamber. As the chamber pressure stabilized, the DC current was applied to create the plasma torch. After plasma treatment, DC power was turned off. Gases were pumped out and system pressure returned to background pressure (~ 5 mtorr). Vacuum was broken by opening a valve to admit air into the chamber. Once the chamber pressure reached atmospheric pressure (typically within 5 min), the plasma-treated TPOs were taken out for further treatment and testing.

Measurements and Testing

The plasma-treated TPO samples were further treated by primer coating with an air brush for adhesion tests or analyzed by ESCA, SEM, polarity, and wettability measurements. Samples for

ESCA, SEM, polarity, and wettability measurements were made immediately after removal from plasma chamber. TPOs (1-cm o.d.) were used for ESCA, SEM, polarity, and wettability measurements. The tape adhesion test was performed after primer coating onto plasma treated TPOs. TPO samples (10.2×10.2 cm) were used in adhesion tests.

ESCA Analysis

ESCA has high resolution for carbon, oxygen, and nitrogen. This analysis was performed at the Analytical Service Laboratory of Micron Inc (3815 Lancaster Pike, Wilmington, DE 19805-1599). ESCA data were collected in both survey and high-resolution mode on a Phi LS-5600 and system equipped with a Mg anode (X-ray source). Data were recorded at 30° and 90° collecting angles resulting in analysis depths of ~ 5 and ~ 10 nm. The element-specific detection limit was on the order of 0.5 atom %.

SEM Observation

SEM was performed at the Department of Geology, University of Missouri–Columbia. An Amray model 1600T SEM apparatus was used. Gold coatings of 20 nm thickness were coated onto the non-conducting TPO samples (1-cm diameter) to make them conductive. A tungsten filament was used as the electron source. A 10 KeV accelerator voltage was used for scanning the sample surfaces. The samples were imaged on a 640×480 pixel array. Magnification of 1000 was sufficient to observe the surface morphology of TPOs.

Contact Angle Measurements

The static contact angles of deionized water and of primer on TPO surfaces were measured by the sessile drop method. The static contact angles were measured 20 s after the deionized water and primer drops contacted the surface of TPOs. The decrease of contact angles of deionized water and primer to TPOs indicates the increase of polarity and wettability characteristics of TPOs.

Tape Adhesion Test

The adhesion performance of primer to TPOs was evaluated using the ASTM 3359-92a tape adhesion test. Primer-coated TPO samples were cut six crosscuts with a knife. The six parallel cuts were made ~ 2 cm long. Pressure-sensitive tape (Permacel #99) was applied to the surface over

of the crosscut area and then removed, and the amount of removed primer served as the measurement of adhesion. Ratings range from "0" to "5," depending upon the number of squares left. The classification of adhesion test results is "0" when > 65% flaking of the surface of the crosscut area has occurred, "5" for no flaking observed, and "1" to "4" are flaking areas in between. Only rating "5" is considered a "pass" for the adhesion test, otherwise it is considered a "fail."

"Dry" adhesion tests refer to those tests performed on primer-coated TPOs immediately after removal from the oven. "Wet" adhesion tests refer to those tests which were performed on dry adhesion test samples which had been exposed to air at 60°C and 80% relative humidity for 5 days. The tape adhesion test was used to interpret the adhesion performance of primer to TPOs. The wet adhesion test is a measure of the weatherability of the primer coating on plasma-treated TPOs.

Calculation of Total Resident Time of Plasmas on TPOs

For a rotating substrate, the power supply operation time was not equal to actual treatment time of the substrate exposure to the plasmas. The total resident time of the plasmas on the substrate was defined as the actual treatment time of plasmas on substrate. Total resident times of plasmas on the TPO samples were calculated by taking the arithmetic average of resident time for each radial position at 15 to 25 cm.

Total resident time was equal to resident time of one revolution multiplied by the number of rotations at each radial position. Residence time for one revolution at a certain radial position was calculated based on the area of TPOs covered by the plasma torches during the rotation. The area of TPOs covered by the plasma torches was measured with a ruler by determining the size of the plasma torch on TPOs from the window of the plasma chamber. The size of the plasma torch was dependent on the nature of monomer and plasma variables: arc current, argon flow rate, monomer flow rate, chamber pressure, and substrate axial position.

The total number of revolutions of TPOs treated by plasma torches was calculated from power supply operation time multiplied by the rotation rate of the substrate.

In this study, the typical resident times of plasmas on the substrate were 0.7–5.7 s for methane plasma and 4.5–36.8 s for air and argon plasmas.

RESULTS AND DISCUSSION

Depending on the experimental parameters, the nature of the substrate, and monomers, the following effects can be obtained by cascade arc torch treatments: (1) plasma cleaning to remove low molecular weight contamination, (2) plasma etching to degrade and ablate the outermost surface of the substrate, (3) crosslinking by recombination of free radicals generated at the surface via plasma-induced polymer chain scission, (4) introduction of functional groups either by direct reaction with species in the plasma or by post-treatment exposure of active surface sites to reactive molecules, and (5) polymerization or grafting onto a substrate surface by posttreatment exposure to polymerizable or graftable species. All of the above can influence adhesion performance of the surface, with one or more of the following effects: removal of a low surface energy layer or a weak boundary layer, strengthening of the top layer, formation of reactive groups at the surface, and formation of a coating tightly bonded to the substrate.^{4,5} These effects are considered for influencing adhesion performance of primer to cascade arc air/argon, methane/argon, and argon plasma-treated TPOs.

In this study, the air and methane plasmas refer to the argon plasma jet with air and methane, while argon plasma refers to the argon plasma jet (torch). Upon addition of air or methane to the plasma jet, the gas molecules are excited by the argon excited species which exist in the cascade arc torch.^{10,11} The excited species of argon, which constitute luminous cascade arc torch, do not contain excited species which have high enough energy to ionize the added gases. The low-temperature cascade arc torch treatment can be considered to be a milder treatment than the conventional low-temperature plasma treatments because of the absence of impinging ions. Although the term "plasma" is used, no ionization occurs in the cascade arc torch (of argon) as used in this article.

Adhesion Enhancement by Air Plasma

The untreated TPOs failed the wet adhesion test. The wet adhesion test results of untreated TPOs showed flaking had occurred on 100% of the tested area. Figure 2 shows the adhesion of primer to TPOs is enhanced by using air plasma. The air plasma-treated ETA-3041c and ETA-3101 passed the wet adhesion test for resident times of 4.5–

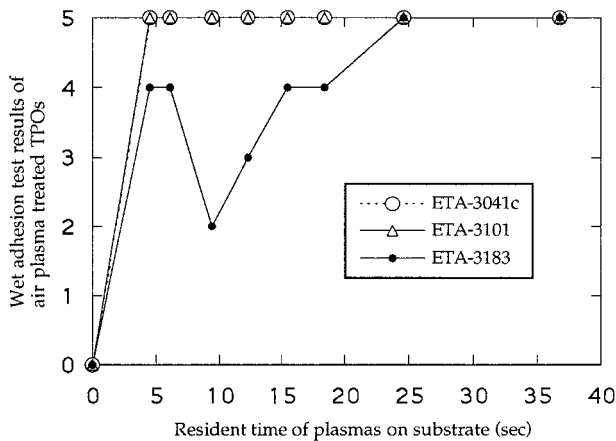


Figure 2 Wet adhesion test results for air plasma-treated ETA-3041c, ETA-3101, and ETA-3183 at various resident times. Other settings: #2 and #3 torches, 2A, Ar 1000 sccm, air 10 sccm, 270 mtorr, 15 rpm, and 22.86 cm.

36.8 s. The air plasma-treated ETA-3183 passed the wet adhesion test for resident times of 24.6–36.8 s. Figure 3 indicates ETA-3183 is the most difficult TPO for adhesion enhancing by air plasma.

Surface Characteristics of Air Plasma-Treated TPOs

In an earlier article,¹¹ it was found that the reactive species such as excited oxygen atom, excited N_2 species, and neutral argon excited species were found in the air/argon cascade arc torch. The oxy-

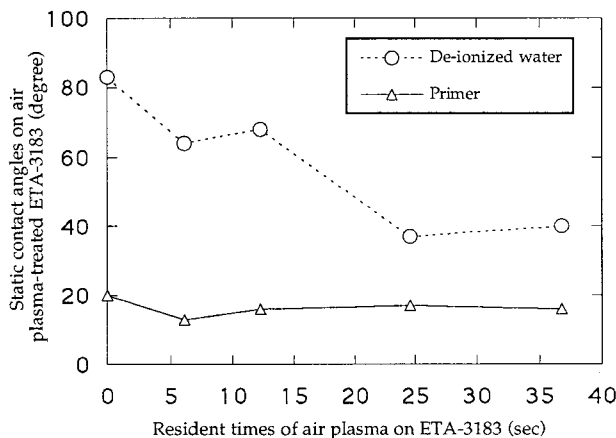


Figure 3 Static contact angles of deionized water and primer on air plasma-treated ETA-3183 at various resident times. Other settings: #2 and #3 torches, 2 A, Ar 1000 sccm, air 10 sccm, 270 mtorr, 15 rpm, and 22.86 cm.

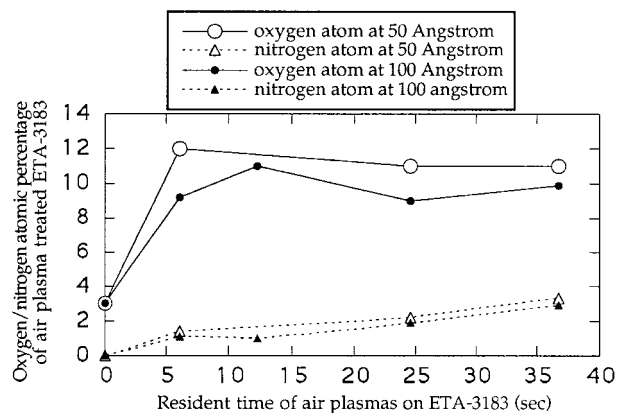


Figure 4 Oxygen and nitrogen atomic composition for air plasma-treated ETA-3183 at various resident times analyzed by ESCA at the depth of 50 and 100 Å from surfaces. Other settings: #2 and #3 torches, 2 A, Ar 1000 sccm, air 10 sccm, 270 mtorr, 15 rpm, and 22.86 cm.

gen- and nitrogen-containing functional groups were formed on the surface of TPOs.

The contact angles of deionized water and of the primer to untreated ETA-3183 was 83° and 20°, respectively. According to Figure 3, the polarity and wettability (by the primer paint) of ETA-3183 were increased by using air plasma. The polarity of air plasma-treated ETA-3183 increased, i.e., contact angles of deionized water decreased with resident time increased. The wettability of air plasma-treated ETA-3183 was independent of resident time. The surface tension of the paint is low enough that the wetting of the TPO surface by the paint is not a problem.

According to C_{1s} ESCA spectra of air plasma-treated ETA-3183 indicates the polar groups such as C—H/C—C (aliphatic carbon or graphitic), C—O (hydroxylic or ether groups), C=O (carbonylic groups), and C—N are introduced in ETA-3183. The atomic compositions of oxygen and nitrogen at the depth of 100 Å increased from 3% and 0% of untreated ETA-3183 to 9.2% and 1.1% of air plasma-treated ETA-3183 at resident time of 6.1 s, as shown in Figure 4. The atomic compositions of oxygen at the depths of 50 and 100 Å are independent of resident time. The oxygen-containing polar layer of air plasma-treated ETA-3183 seems to reach a “saturated” oxygen atomic composition. However, the atomic compositions of nitrogen increase as resident time increases. The increasing nitrogen composition at the depth of 100 Å indicates that the depth of treatment increases with the treatment time. As ETA-3183 is

treated by air plasma at resident times from 6.1 to 24.6 s, the wet adhesion test results increased from "4" to "5" and the nitrogen atomic compositions at the depth of 100 Å increase from 1.1% to 2.9%.

Venables¹³ studied the detailed morphology of the surfaces of aluminum and titanium which have been treated by plasma for adhesive bonding and demonstrated the effect of etching on the adhesion. The evidence indicates that there is mechanical interlocking of the polymer in the adhesive which gives much stronger bonds than if the surface had been smooth. The chemical etching of TPO surfaces by excited oxygen atom is the main ablation process by air plasma treatment. SEM observation of treated surfaces indicated that the surface of ETA-3183 became significantly rougher than that of untreated sample at the resident time of 36.8 s. Figure 2 shows the wet adhesion test results of air plasma-treated ETA-3183 at resident time of 12.3 s was "3" and at resident time of 36.8 s was "5."

The enhancement of primer adhesion by the air/argon cascade arc torch could be attributed to (1) roughening of the surface by oxygen plasma, and (2) introduction of polar moieties on the surface.

Adhesion and Surface Characteristics of Methane Plasma-Treated TPOs

In low-temperature plasma of an organic compound, two major processes occur in a competitive manner: the competitive ablation and polymerization (CAP) principle.⁴ One is the deposition of a polymeric material which is often referred to as "plasma polymer," and the other is the ablation of material which can be either the substrate material or the once-deposited plasma polymer. The ablation process could occur by the physical sputtering or by the chemical ablation, depending on what kinds of species are involved in a specific operation. The addition of carrier gas such as argon in a low-temperature plasma tends to increase the ablation effect due to the physical sputtering mechanism. The balance between ablation and polymerization on TPO surfaces is dictated by the nature and composition of reactive species.

In the cascade arc torch used in this study, argon is exclusively used as the plasma gas; i.e., argon plasma is created in the cascade arc generator and ejected from a small hole located in the downstream end of the cascade arc generator into the deposition chamber in vacuum. It is important

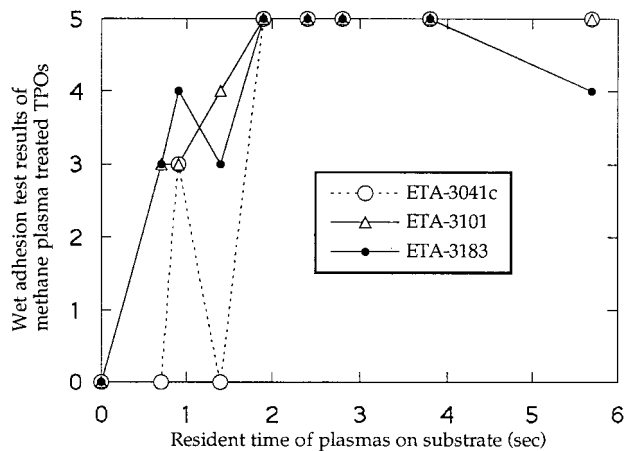


Figure 5 Wet adhesion test results of methane plasma-treated ETA-3041c, ETA-3101, and ETA-3183 at various resident times. Other settings: #2 and #3 torches, 2 A, Ar 1000 sccm, methane 10 sccm, 270 mtorr, 15 rpm, and 22.86 cm.

to note that no ionization other than Penning ionization occurs in the deposition chamber, and consequently the physical sputtering due to the bombardment of ions is minimal to nonexistent.

In a previous study,¹⁰ it was observed that the reactive species such as excited CH species, excited hydrogen atoms, molecular hydrogen, and neutral argon excited species were found in the methane/argon cascade arc torch. Because of this situation, a tight and crosslinked methane plasma polymer was deposited on TPOs without ablation, yielding smooth surfaces of methane plasma polymer-deposited TPOs which were observed in SEM micrographs. Thus, the enhanced primer adhesion to TPOs using methane plasma was independent of the surface roughness of the TPOs.

Figure 5 shows the enhanced primer adhesion to TPOs. The methane plasma-treated ETA-3041c and ETA-3101 passed the wet adhesion test for resident times of 1.9–5.7 s. The methane plasma-treated ETA-3183 passed the wet adhesion test for resident times of 1.9–3.8 s. This indicates ETA-3183, which is the most difficult TPO for adhesion, can be treated successfully by methane plasma.

Figure 6 indicates the polarity of ETA-3183 is slightly affected by methane plasma with various resident times. The polarity decreases, i.e., the contact angle of deionized water increases, from 83° of untreated ETA-3183 to 88° of methane plasma-treated ETA-3183 at resident time of 0.9 s, and the wet adhesion test results increase from "0" to "4." This indicates the polar functional

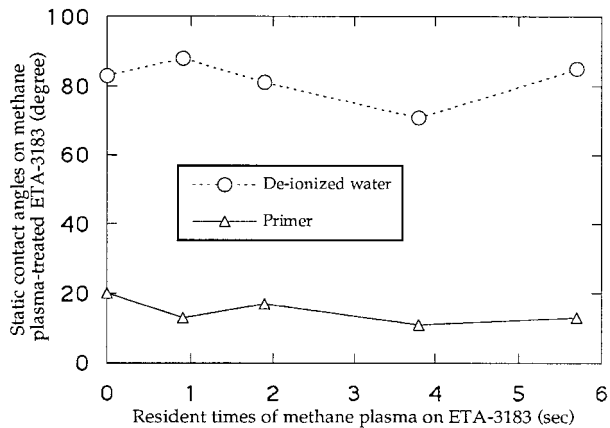


Figure 6 Static contact angles of deionized water and primer on methane plasma-treated ETA-3183 at various resident times. Other settings: #2 and #3 torches, 2 A, Ar 1000 sccm, methane 10 sccm, 270 mtorr, 15 rpm, and 22.86 cm.

groups in methane plasma-treated ETA-3183 do not play a key role for adhesion enhancing by methane plasma, because of the fact that the wetting of surface by the primer is not a major problem, as mentioned earlier.

Adhesion and Surface Characteristics of Argon Plasma-Treated TPOs

As described in the preceding section, the argon plasma in the cascade arc torch is significantly different from most argon plasmas which exist in

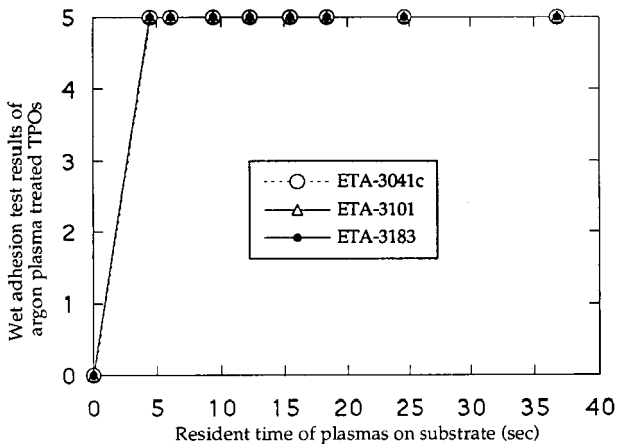


Figure 7 Wet adhesion test results of argon plasma-treated ETA-3041c, ETA-3101, and ETA-3183 at various resident times. Other settings: #2 and #3 torches, 2 A, Ar 1000 sccm, 270 mtorr, 15 rpm, and 22.86 cm.

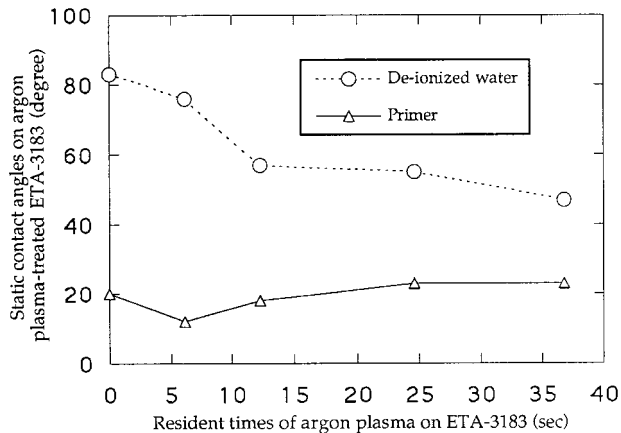


Figure 8 Static contact angles of deionized water and primer on argon plasma-treated ETA-3183 at various resident times. Other settings: #2 and #3 torches, 2 A, Ar 1000 sccm, 270 mtorr, 15 rpm, and 22.86 cm.

the ionizing environment. According to a previous study,¹⁰ the emissions from the argon plasmas correspond to neutral argon excited species, with no argon ion observed. The physical sputtering of TPO surfaces by neutral argon excited species is believed to be the main process in the low-temperature cascade arc torch treatment.

Figure 7 shows that the argon plasma-treated ETA-3041c, ETA-3101, and ETA-3183 at resident times of 4.5–36.8 s passed the wet adhesion test. The adhesion of TPOs with primer was easily enhanced by using argon plasma. Ryntz, Xie, and Ramamurthy¹² proposed the surface morphology of TPO. According to their interpretation, the PP transcristalline region of TPO was considered as a weak boundary layer (WBL), which affected the resultant adhesion of primer (764-189) to TPOs. If such WBLs of TPO surfaces are responsible for the poor adhesion of a paint, it can be postulated that the cascade arc torch treatment without additional gas converts the WBLs of TPO surfaces to a stronger layer, probably by introducing crosslinks. Thus, the primer adhesion to TPOs was enhanced to the extent which passed the wet adhesion test.

The introduction of crosslinks can be explained by the formation of free radicals by the excited species of argon, which also explains the formation of oxygen-containing polar groups on the surface by reaction of oxygen and free radicals when the treated sample is exposed to the atmosphere. As mentioned earlier, the contact angles of deionized water and primer to untreated ETA-3183 were 83° and 20°. Figure 8 indicates the lower

contact angles of deionized water on the cascade arc torch-treated TPOs. The surface of cascade arc torch-treated TPOs was found to be smooth by SEM micrographs, which seems to be in accordance with the above postulation of the mechanism of adhesion enhancement.

CONCLUSIONS

The treatment of surface of TPOs by low-temperature cascade arc was found to be an effective method to improve the adhesion of a primer paint. The relatively short treatment time (2–40 s) yielded an excellent level of adhesion to pass the wet adhesion test. The adhesion of the primer to the soft and flexible TPOs (ETA-3041c and ETA-3101) were easily enhanced. The more brittle TPO (ETA-3183) required more careful optimization of plasma conditions to enhance the primer adhesion to pass the wet adhesion test.

As the air plasma is applied onto ETA-3183, the increased contents of oxygen and nitrogen-containing functional groups, the increased thickness of nitrogen-containing polar layers, and the increased surface roughness caused improvement of primer adhesion to ETA-3183. The air plasma-treated ETA-3183 at resident times of 4.5–36.8 s passed the wet adhesion test. The rougher surface of air plasma-treated ETA-3183 at resident time of 36.8 s results in the stronger adhesion with primer.

For methane plasma-treated ETA-3183, superior primer adhesion to ETA-3183 was obtained by replacing the weak boundary layers with a tightly crosslinked plasma polymer layer. The optimum thickness of the network of methane plasma polymer films formed on ETA-3183 at the optimum resident times from 1.9 to 3.8 s yielded the improvement, which passed the wet adhesion test.

For argon plasma-treated TPOs, an excellent primer adhesion to TPOs were obtained by con-

verting the weak boundary layers of TPO surfaces to a stronger boundary layer. The argon plasma-treated ETA-3041c, ETA-3101, and ETA-3183 at resident times of 4.5–36.8 s passed the wet adhesion test.

The authors are indebted to Dr. T. J. Lin, Dr. J. A. Antonelli, and the E. I. Du Pont de Nemours and Company for assistance in obtaining TPOs, primer, and ESCA spectra. This work was supported by National Science Foundation Grant NSF-CTS-9400725.

REFERENCES

1. R. A. Ryntz, *Polymeric Materials Science and Engineering, Proceedings of ACS Division of Polymeric Materials: Science and Engineering*, **63**, 78 (1990).
2. R. A. Ryntz, K. E. Scarlet, J. A. Henchel, and K. L. Arthur, *Automotive Engineering*, 37–40, May 1993.
3. S. L. Kaplan, P. W. Rose, W. P. Hansen, P. H. Sorlien, and O. Styermo, *Technical Papers Regional Technical Conference—Society of Plastics Engineers*, 1993, p. 84.
4. H. Yasuda, *Plasma Polymerization*, Academic Press, New York, 1985.
5. J. Baglin, *Fundamentals of Adhesion*, Chap. 13, 1991, p. 363.
6. J. Baglin, *Handbook of Ion Beam Processing Technology*, Chap. 14, 1989.
7. F. Garbassi, M. Morra, and E. Occhiello, *Polymer Surfaces from Physics to Technology*, John Wiley and Sons, New York, 1994.
8. F. Gargassi, E. Occhiello, F. Polato, and A. Brown, *J. Mater. Sci.*, **22**, 1450 (1987).
9. K. W. Allen, *The Tenth Annual Meeting of the Adhesion Society*, February 1987, 85.
10. S. P. Fusselman, Ph.D Thesis, University of Missouri at Columbia, December, 1992.
11. Q. Yu, MS Thesis, University of Missouri at Columbia, May, 1995.
12. R. A. Ryntz, Q. Xie, and A. C. Ramamurthy, *21st Annual Waterborne, Higher-Solids, and Powder Coatings Symposium*, April 1995, 45.
13. J. D. Venables, *J. Mater. Sci.*, **19**, 2431 (1984).