

Surface Characterization of Low-Temperature Cascade Arc Plasma-Treated Low-Density Polyethylene Using Contact Angle Measurements

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ABSTRACT: Low-density polyethylene (LDPE) was treated with a low-temperature cascade arc plasma torch (LTCAT) of argon with or without adding a reactive gas of oxygen or water vapor. The static sessile droplet method and the dynamic Wilhelmy balance method were employed to perform surface contact angle measurement in order to investigate and characterize the effects of LTCAT treatment on LDPE surfaces. These treatment effects included changes in surface wettability and surface stability and possible surface damage that would create low-molecular-weight oligomers on the treated surface. Experimental results indicated that the combination of static and dynamic surface contact angle measurements enabled a comprehensive investigation of these effects of plasma treatment on a polymer surface. Without the addition of a reactive gas, a 2-s argon

LTCAT treatment of LDPE resulted in a stable hydrophilic surface (with a water contact angle of 40°) and little surface damage. The addition of oxygen into argon LTCAT produced a less stable LDPE surface and showed more surface damage. Adding H₂O vapor into argon LTCAT produced an extremely hydrophilic surface (with a water contact angle < 20°) of LDPE but with pronounced surface damage. When compared with conventional radio frequency (13.56 MHz) plasmas, LTCAT treatment provides a much more rapid, effective, and efficient method of surface modification of LDPE. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2528–2541, 2006

Key words: polyethylene (PE); surfaces; modification; cascade arc torch; contact angle; cold plasma

INTRODUCTION

Polymeric materials cannot be selected for a given application only on the basis of their bulk properties. Surface characteristics usually play a critical role in their successful use. Many methods have been developed and used for modifying polymer surfaces to improve adhesion and for other related surface characteristics. These methods include mechanical treatments such as abrasion, wet chemical treatment with strong acids or bases, and exposure to flames or corona discharge. However, these treatment techniques all have considerable drawbacks. For example, wet chemical treatment involves many additional processing steps such as washing, rinsing, and drying, and it has the problems of cost and of disposing of a large amount of toxic waste. In contrast, low-temperature plasma treatment provides a versatile, reproducible, and environmentally benign method of modifying

polymer surfaces while maintaining their desirable bulk properties.¹

Low-temperature plasma that can be simply created by electrical glow discharge contains many reactive species including ions, high-energy electrons, free radicals, and electronically excited molecular and atomic species. Once a polymeric material is subjected to a plasma environment, these highly reactive plasma species can react with the polymer surface, change the surface chemistry, and thus modify surface characteristics. Low-temperature plasma has been widely used to treat polymeric materials in order to improve their surface energy, barrier properties, optical reflection, biocompatibility, and adhesion to other materials. One of the most important features of plasma treatments is that they can modify the outermost surface of polymers without changing their desirable bulk properties.^{2,3} In addition, because plasma processes are “dry” and “clean,” plasma treatment of polymers is becoming more favorable and popular in industrial applications because they avoid the environmental restrictions of wet chemical processes.

Although plasma treatment is one favorable method for modifying polymer surfaces, its large-scale use in industrial applications has not been very successful to date. One of the main reasons for this is the difficulty

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in achieving controllable plasma treatment of a polymer surface with conventional plasma sources, in which polymer surfaces are exposed to many reactive species simultaneously and the processes involved cannot be optimized separately. Ample data indicate that this "uncontrollable" plasma treatment can bring about many undesirable changes in and damage to the surface of polymers, such as degradation of polymer chains and etching of the surface materials.^{4,5} These undesirable changes and damage of polymer surfaces have many detrimental effects on their applications, such as loss of wettability, adhesion failure from weak-boundary-layer (WBL) formation, and loss of tensile strength of polyethylene fibers resulting from plasma etching.^{6,7} If a desirable surface modification is accomplished at the expense of degradation of the substrate, the value of such a modification is questionable. Ultimate success depends on the extent of the substrate damage. Therefore, a plasma system with lower production costs and easily optimized and controlled treatment processes could lead to rapid growth in the utilization of plasma technologies on an industrial scale.

LTCAT offers an alternative plasma method for polymeric surface modification by providing a high flux of excited species of a noble gas, usually argon, directed to the polymer surface. In the LTCAT plasma process, discharge of argon is created in an arc generator and emanates from the generator as a stable luminous plasma torch. The luminous plasma torch can be used to directly treat a surface or to activate a second reactive gas added into the plasma torch. When the LTCAT plasma torch is injected into a vacuum chamber, the torch temperature decreases rapidly after expansion and can be used as a low-temperature plasma source for plasma polymerization and surface modification of polymeric materials.^{8,9} In this process most charged plasma species including ions and electrons are confined inside the arc generator. Plasma diagnostic data have verified that the luminous plasma torch emanating from the arc generator mainly consists of electronically excited argon metastable atoms, which distinguish LTCAT from the rest of conventional plasma processes in which ions and electrons play dominant roles.^{10,11} Because a high flux of electronically excited argon atoms whose energy is well determined is directed to the surface, it is anticipated that with LTCAT treatment there would be rapid surface treatment and less surface damage of polymeric materials by LTCAT treatment than would occur with conventional plasma treatment processes.

In this study LTCAT plasma treatment was used to modify the polymer surface of LDPE in order to improve its surface wettability, which is directly related to characteristics associated with successful applications, such as adhesion, paintability, and printability. Plasma treatment effects, including surface wettability

changes, surface stability, and possible surface damage, were investigated by measuring both static and dynamic surface contact angles, that is, by the sessile droplet and Wilhelmy balance methods, respectively. Dynamic analysis using the Wilhelmy balance method on LTCAT-treated LDPE provided much important information, including about possible surface damage that was created on some treated polymer surfaces in the form of low-molecular-weight oligomer formation on the treated surfaces and surface stability of hydrophilic moieties to undergo surface configuration changes.

EXPERIMENTAL

Materials

The polymeric substrates used for the LTCAT treatments were 1-mm-thick low-density polyethylene (LDPE) sheets, purchased from Goodfellow Cambridge Limited (Cambridge, UK). The LDPE sheets were cut into pieces 1 × 2 cm in size, which were used as the substrates for plasma treatments. To eliminate the effects of various contaminants possibly present on the surface, all the LDPE samples were cleaned for 30 min in an ultrasonic bath solution consisting of 5% detergent in deionized water. The samples were then thoroughly rinsed in deionized water, dried in ambient air for 1 day, and then stored in a dry desiccator. The Ar and O₂ gases, with purities of 99.997% and 99.5%, respectively, were obtained from Praxair (St. Louis, MO). The water vapor consisted of deionized water obtained from a Culligan (Columbia, MO) deionizing system attached to in-house distilled water.

RF plasma reactor

Radio frequency (RF) plasma treatments were performed in a bell jar reactor (80 L) containing a pair of parallel electrodes made of titanium plates (18 × 18 × 0.1 cm) with spacing of 8.5 cm. The vacuum system consisted of a rotary pump (E2M-12; Edwards High Vacuum, Grand Island, NY) and a mechanical booster pump (MB-100F; Shimadzu Corporation, Kyoto, Japan) that evacuated the reactor to a base pressure of 1.4 mTorr. Plasma gases were introduced into the reactor to reach a preset system pressure of 50 mTorr. RF power was supplied to the electrodes using a power-controlled RF power supply with a matching network (RFX-600; Advanced Energy Industries, Inc., Fort Collins, CO). Both electrodes were powered, and the base of the reactor was grounded. The gas flow rate, input power, and exposure time varied for each trial. The polymer samples were placed in the plasma glow on an aluminum disk centered between the electrodes that rotated at a speed of 15 RPM.

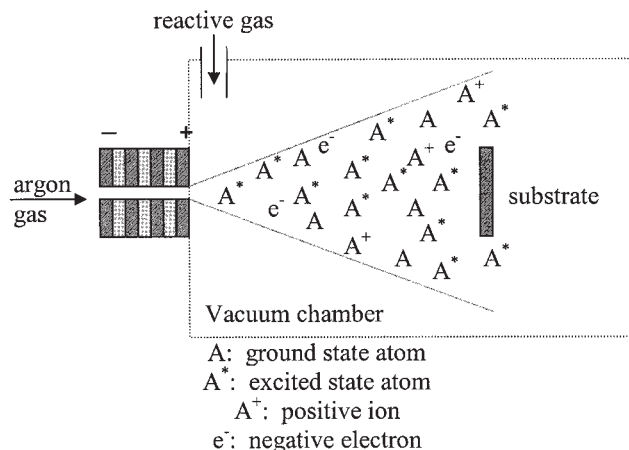


Figure 1 Illustration of the creation of plasma species in the LTCAT process.

LTCAT reactor

A detailed description and the operation procedures of the LTCAT reactor were reported previously.^{9–11} The major components of the LTCAT reactor included an arc generator, a Pyrex glass cross vacuum chamber, and an Edward High-Vacuum EH500A/E2M80 combination pump. The arc generator was mounted onto one part of the Pyrex glass cross. The arc generator consisted of a narrow channel (3 mm) formed by a series of copper disks that were separated by silicone rubber insulators. Before starting each experiment, the arc generator was cooled to 10°C using an ethylene glycol–water mixture that flowed inside the copper disks. Ar flowed through the narrow channel of the arc generator at a rate of 500–3000 standard cubic centimeters per minute (scm). An MDX-5K Direct current magnetron power supply was used to ignite and sustain the argon discharge inside the arc generator. Because of the high speed of argon passing through the generator, the argon discharge was then blown out of the arc generator in order to form a luminous plasma torch into the glass chamber. As shown in Figure 1, the electric field confined most of the charged species inside the arc generator, and as a result, the plasma torch leaving the generator mainly consisted of electronically excited argon neutral species.^{10,11}

LDPE was treated with LTCAT by the Ar plasma torch with or without the addition of a reactive gas. When used, the reactive gas was introduced to the reactor chamber through an inlet next to the torch inlet into the chamber. A LDPE sheet was placed on the substrate clip at the end of a sliding bar that could be moved into and out of the torch through another port of the glass cross chamber. The position of the polymer substrate was 22 cm from the torch inlet. The reactor was pumped down to the base pressure of 10 mTorr before each experiment. When the torch was

steady, the sample was immersed inside the torch for the preset exposure time. Gas flow rate, input current, and exposure time were the variables studied.

Surface contact angle measurements

The wettability of the polymeric surfaces was determined with static and dynamic contact angle measurements. Using the sessile droplet method with a surface contact angle measurement system (VCA 2500XE; Advanced Surface Technologies, Inc., Billerica, MA) to measure the static contact angle, 0.3 μ L of deionized water droplets was placed on the surface of the polymer, and computer software supplied with the equipment was used to obtain a photograph of the image. With the aid of the software, the computer users were able to manually trace the droplet arc, and the computer program calculated the two angles of contact at the water/air/solid interface.

Dynamic measurements were obtained by use of the Wilhelmy balance method, in which a tensiometer (Sigma 70, KSV Instruments, Ltd., Helsinki, Finland) measured the total force exerted on the polymer sample plate while immersed in water. Previously published¹² illustrations of hydrophobic and hydrophilic sample plates being immersed in and emerging from the water showed changes in the meniscus during the advancing and receding cycles. The immersion and emergence speed of the samples was fixed at 5 mm/min, low enough to minimize the dependence of dynamic contact angles on immersion velocity.

The forces exerted on the sample included gravitational force, buoyancy force, and interfacial force between the sample and the water. Before the sample touched the water surface, the computer user zeroed the balance so that the gravitational force could be neglected. The following equation describes the actual sum of the forces measured by the tensiometer:

$$F = L\gamma_L \cos\theta - \rho g t H d \quad (1)$$

where F is the total force measured, L is the perimeter of the plate, γ_L is the surface tension of the water, θ is the contact angle at the solid/liquid/air line, ρ is the mass density of water, g is the acceleration of gravity, t is the plate thickness, H is the plate width, and d is the depth of immersion in the water. The surface tension of water was obtained using the Wilhelmy plate method. The measured force, F , was divided by the plate perimeter, L , to obtain the Wilhelmy balance loops, which plot F/L at the depths of immersion. The results were extrapolated to 0 immersion depth in order to obtain the advancing and receding contact angles for each immersion cycle.

Wettability analysis was performed immediately after each treatment. Some samples were used to examine the effects of aging on the treatments. These sam-

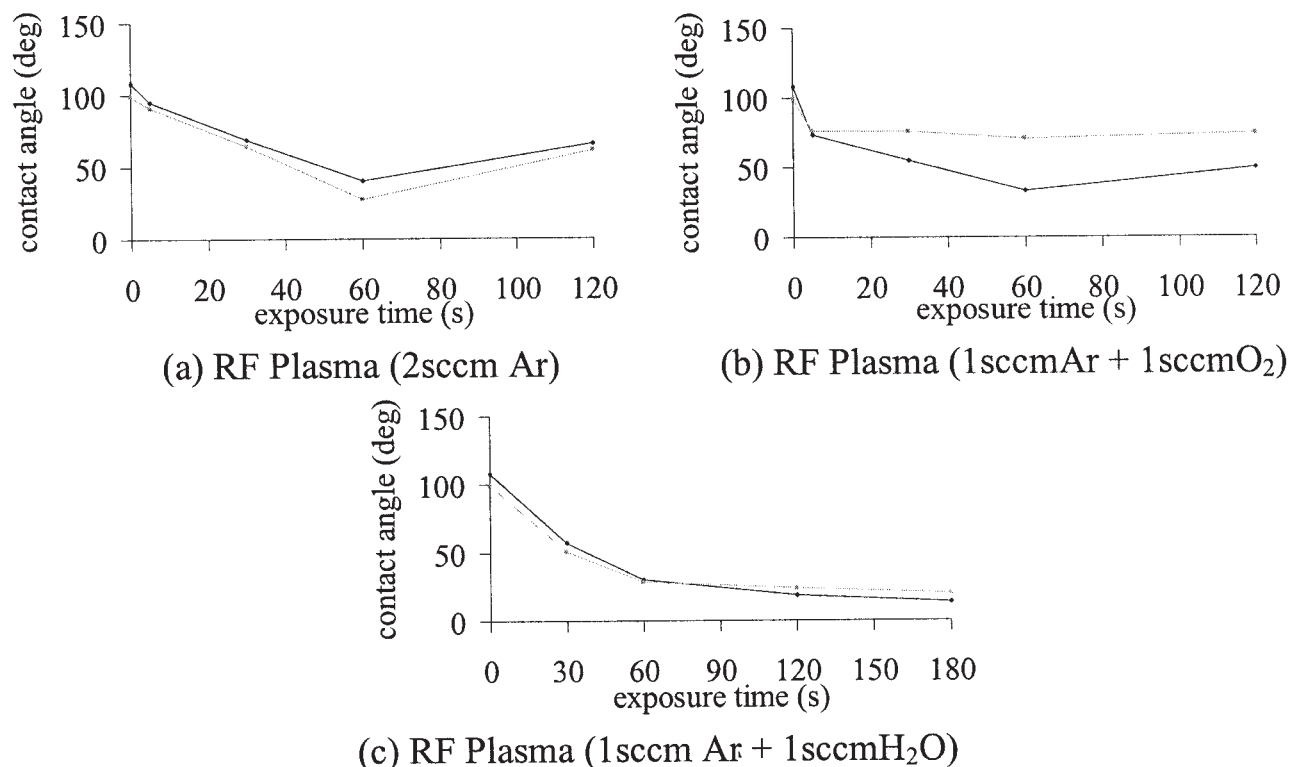


Figure 2 Change in the static surface contact angle of LDPE with plasma exposure time in (a) Ar, (b) Ar + O₂, and (c) Ar + H₂O RF plasmas. The dark lines show water contact angles of freshly treated samples without washing, and the gray lines show water contact angles of treated samples after washing. The plasma conditions were: 8 W of RF power and system pressure of 50 mTorr.

ples were then submerged in deionized water and placed in an ultrasonic bath for 10 min in order to wash away any possible surface oligomers that would have been created during the treatments. The samples were then allowed to dry in ambient air, and subsequent analyses were performed at various stages of aging.

RESULTS AND DISCUSSION

In this study, plasma treatment of LDPE was performed using LTCAT of argon only, argon LTCAT with added O₂, and argon LTCAT with added H₂O vapor. The effects of LTCAT treatment including surface wettability changes, surface stability, and possible surface damage were investigated and compared to the effects of conventional RF plasma treatments.

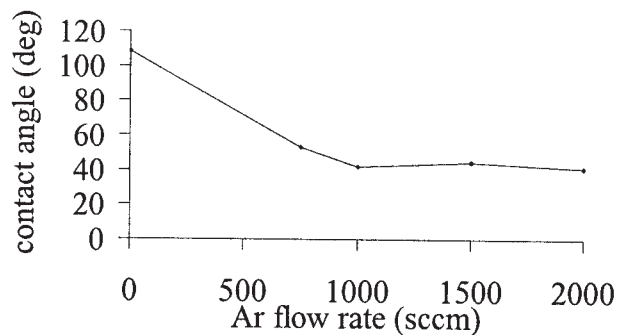
RF plasma treatment

Many studies of the surface modification of polymers using conventional RF plasma techniques have shown a certain degree of surface damage because of the continuous bombardment of high-energy species.^{4,5,13} Weikart and Yasuda¹³ reported that plasma-induced surface damage of polymers resulted in the formation

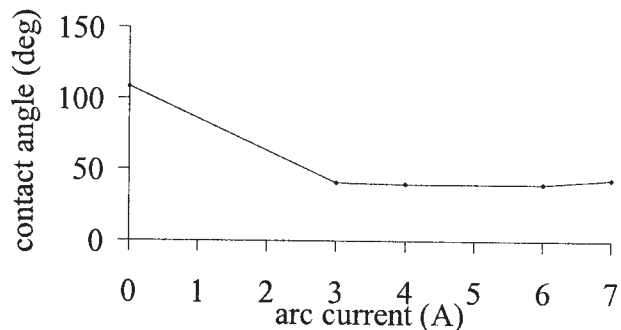
of a certain amount of low-molecular-weight oligomers which were washed away after immersion in water. To compare the effects of LTCAT treatments, in this study RF plasma treatments of LDPE were investigated by varying plasma exposure time, while keeping RF power, system pressure, and flow rate fixed.

Figure 2 shows the surface contact angle change of LDPE measured by the static sessile drop method with different exposure times in RF plasmas of Ar, Ar + O₂, and Ar + H₂O vapor. The black lines indicate the static contact angle measurements immediately after treatment, whereas the gray lines indicate the contact angles of the samples washed in an ultrasonic bath of deionized water for 10 min, then blotting dried with Kimwipes® (Kimberly Clark, United States) and left in the air for 2 min.

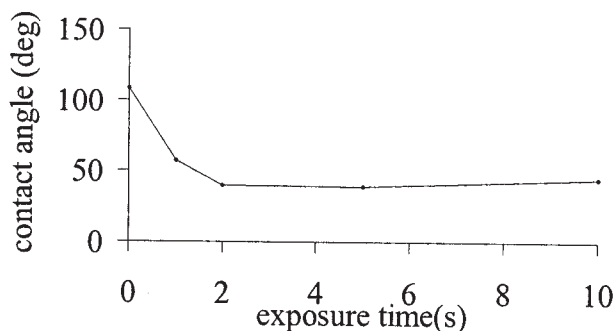
As seen from Figure 2, the untreated LDPE samples (exposure time of 0 s) showed an approximately 8° decrease in the contact angle after washing. It should be noted that after being kept in a dry desiccator for 5 min, the washed samples showed the same contact angle as the unwashed samples. A decrease in the surface contact angle after exposure to water could be an indication of a surface configuration change or of water adsorption or penetration. Untreated LDPE, however, has been shown to possess high surface



(a) Effect of Ar Flow Rate



(b) Effect of Arc Current



(c) Effect of Exposure Time

Figure 3 Surface contact angle changes in Ar LTCAT-treated LDPE with (a) Ar flow rate, (b) arc current, and (c) exposure time. The LTCAT conditions, if not specified in the plots, were: 1500 sccm of Ar, an arc current of 4.0 A, and an exposure time of 2.0 s.

stability and not to undergo surface configuration changes on exposure to water.¹² Therefore, the decrease in the static contact angle after washing is likely to have been a result of water adsorption on the surface. It was assumed that the treated samples also would experience some water adsorption during the time of the washing and drying processes. For the Ar RF plasma-treated samples, as shown in Figure 2(a), the contact angles decreased slightly after washing, and the extent of the effects of surface configuration change and water adsorption could not be distinguished by static contact angle measurement. The treatments required an exposure time of 60 s in order to reduce the surface water contact angle to 40°, and further increases in exposure time resulted in higher contact angles.

The results of the Ar + O₂ RF plasma treatments, shown in Figure 2(b), however, showed a significant increase, from 3° to 38° in static contact angle after washing. Hydrophobicity recovery after washing samples is a clear indication of the washing away of surface oligomers that were formed as result of cleavage of surface polymer chains during the plasma treatment and thus exposing a more hydrophobic layer underneath. The results of the Ar + H₂O vapor RF

plasma treatments shown in Figure 2(c) also showed slight increases (5–6°) in static contact angle measurements after washing with exposure times greater than 60 s, but much less than did the Ar + O₂ RF plasma treatments.

From Figure 2 it can be seen that, in general, RF plasma treatments require about a 1-min treatment time to improve the surface wettability of LDPE. The lowest surface contact angles after water washing achieved by RF plasma treatments were 41° by Ar plasma, 71° by Ar + O₂ plasma, and 17° by Ar + H₂O plasma. The RF plasma-treated samples also exhibited hydrophobic recovery after aging in ambient air. These results are described, discussed and compared with LTCAT-treated samples later in this article.

LTCAT plasma treatments

In the LTCAT process, electric power input into the system can be well expressed by an arc current because of there is very little variation in voltage when argon is used as the carrier gas through the arc generator. In addition, the argon flow rate passing through the arc generator is an indication of the amount of energy that is carried by the luminous

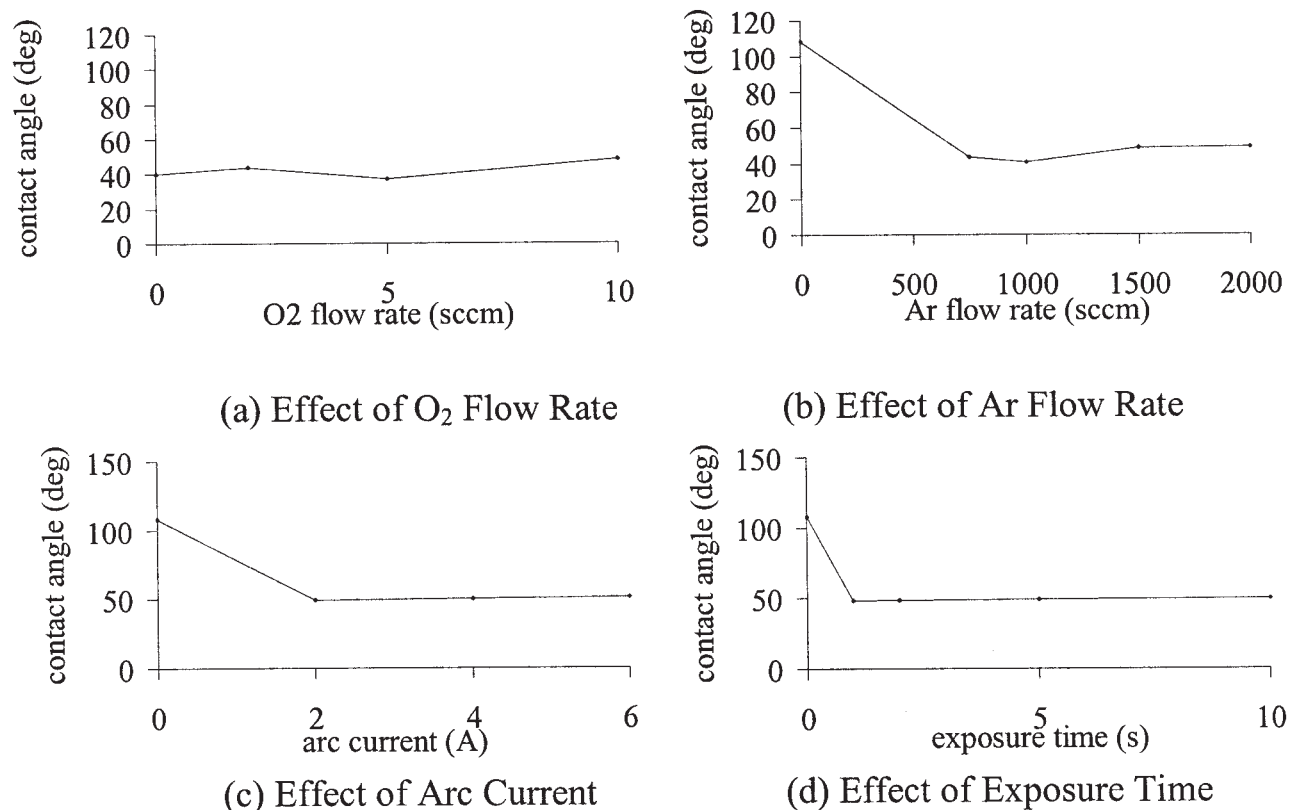


Figure 4 Surface contact angle changes in Ar+O₂ LTCAT-treated LDPE with (a) O₂ flow rate, (b) Ar flow rate, (c) arc current, and (d) exposure time. The other LTCAT conditions, if not specified in the plots, were: 1500 sccm of Ar, an arc current of 4.0 A, an exposure time of 2.0 s, and 10 sccm of O₂.

plasma torch.¹⁴ In this study, therefore, arc current, argon flow rate, and plasma exposure time were the three major operating variables examined in the LTCAT treatment of LDPE.

When a reactive gas was added to an argon LTCAT plasma torch, collisions between excited argon metastable species with the reactive gas molecules occurred, resulting in an energy transfer to the reactive gas molecules. The direct outcome of such an energy transfer was the production of new reactive plasma species from the added reactive gases. These plasma species thus formed also could react with the polymer surface, achieving surface modification of organic materials. In the present study, argon LTCAT without any additional reactive gases as well as that with the addition of oxygen and water vapor were used to modify the LDPE surfaces, and the resulting effects of plasma treatments were investigated.

Sessile droplet method

Figure 3 shows the surface contact angle changes of argon LTCAT-treated LDPE with Ar flow rate, arc current, and exposure time. It should be noted that the surface contact angles of LTCAT-treated LDPE were measured with and without water washing, but no

significant difference was found from the data, as was true with the RF plasma treatments shown in Figure 2. Therefore, Figure 3 does not show the contact angles after washing the LTCAT-treated samples. The data showed that good wettability was achieved with a very short treatment time of only 2.0 s, as compared to the 60 s necessary with RF plasma. Other operating conditions for achieving good surface wettability (with a water contact angle of ~40°) included 1000 sccm of Ar flow rate and a current of 3 A. It should be noted that within the ranges examined, additional increases in argon flow rate and arc current did not contribute much to improving surface wettability.

Figure 4 shows the effects on LDPE surfaces of plasma treatment of argon LTCAT with the addition of O₂. The LTCAT conditions that produced the lowest contact angle (49°) included 1000 sccm of Ar, an arc current of 4.0 A, and an exposure time of 2.0 s. It should be noted that, as is shown in Figure 4(a), the addition of oxygen to argon LTCAT did not provide any advantages in improving the surface wettability of LDPE as compared with the argon LTCAT treatment.

Figure 5 shows the effects on LDPE surfaces of plasma treatment of argon LTCAT with the addition of water vapor. On the basis of the static contact angle

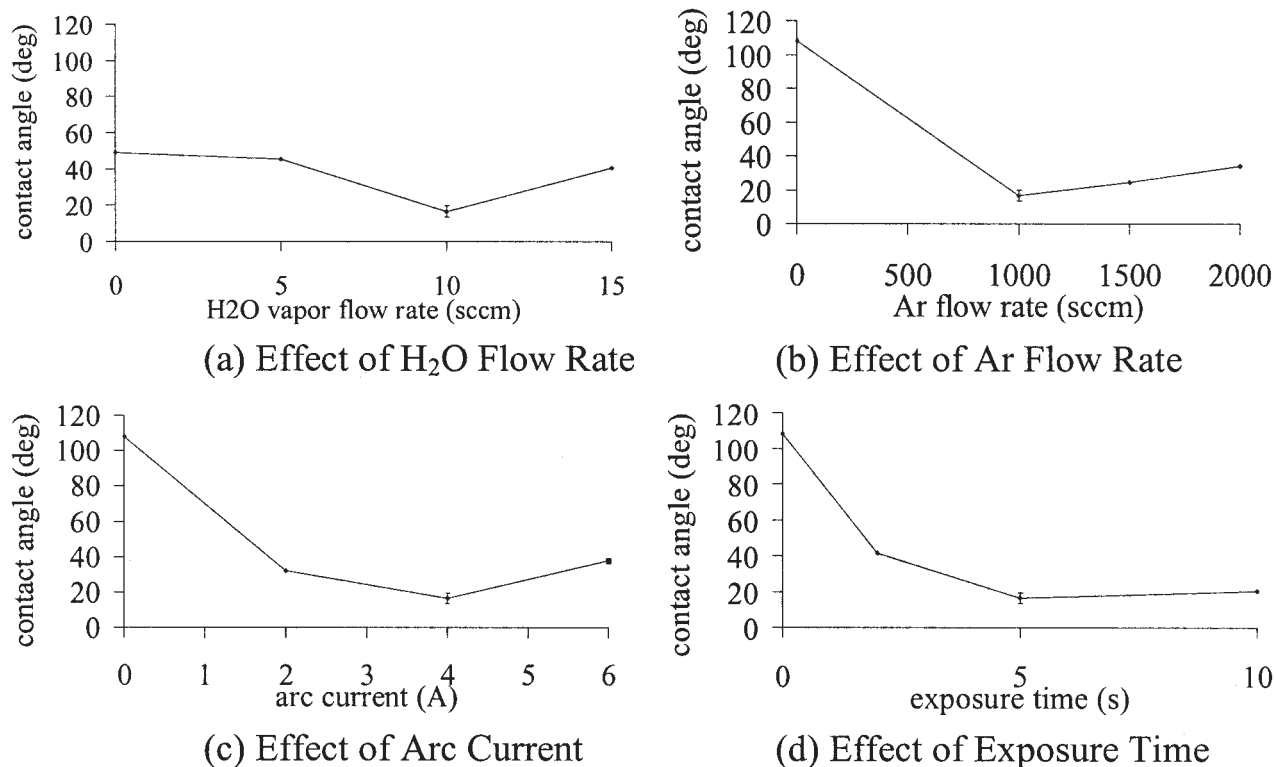


Figure 5 Surface contact angle changes in Ar+H₂O LTCAT-treated LDPE with (a) H₂O flow rate, (b) Ar flow rate, (c) arc current, and (d) exposure time. The other LTCAT conditions, if not specified in the plots, were: 1500 sccm of Ar, an arc current of 4.0 A, an exposure time of 5.0 s, and 10 sccm of H₂O.

data, the conditions that produced the best wettability were found to be 10 sccm of H₂O, 1000 sccm of Ar, a current of 4 A, and an exposure time of 5 s, which resulted in a static contact angle of 17°. At such low contact angles, spreading of the water droplets was significant.

Wilhelmy balance method

Wilhelmy force loops were obtained using the Wilhelmy balance method for LDPE samples treated with LTCAT in order to examine dynamic wettability, surface damage in the form of overshooting,¹³ and surface configuration changes in the form of intrinsic hysteresis.^{12,15} The dynamic contact angles were determined for the advancing (immersion) and receding (emergence) phases of the cycles by using eq. (1) and extrapolating each force trend to the intercept (0 depth), where the buoyancy term is zero. A force trend that has an intercept of 0 mN/m corresponds to a contact angle of 90°. An increase in the force trend corresponds to an increase in hydrophilicity, whereas a decrease in the force trend corresponds to an increase in hydrophobicity.

The stability of a surface can be examined by observing the overshooting and intrinsic hysteresis between two Wilhelmy cycles. Overshooting in Wil-

helmy cycles occurs when the advancing force trend in a second Wilhelmy immersion cycle shows a more hydrophobic surface than the first advancing immersion cycle. It is believed that overshooting results from the presence of surface oligomers, which are formed from polymer degradation or bond cleavage of surface macromolecules during treatment and are washed away during the Wilhelmy cycle, exposing a more hydrophobic layer underneath. Surface configuration changes, on the other hand, are shown by an increase in the force trend from the first immersion cycle to the next, which is called intrinsic hysteresis. These configuration changes involve hydrophilic groups reorienting toward the surface while the sample is immersed in water, thus making the surface more hydrophilic. After longer exposure in air, the hydrophilic surface groups may re-orient toward the bulk sample, making the sample surface more hydrophobic.

During the first cycle the sample was immersed 10 mm into water and then emerged from the water back to a depth of zero and was allowed to dry for 5 min in ambient air. The purpose of drying in air was to allow the reversal of possible surface configuration changes that would have occurred during the first wetting. The second cycle involved immersing the sample in water to a depth of 15 mm, in which overshooting could be observed at 0–10 mm and where the section of the

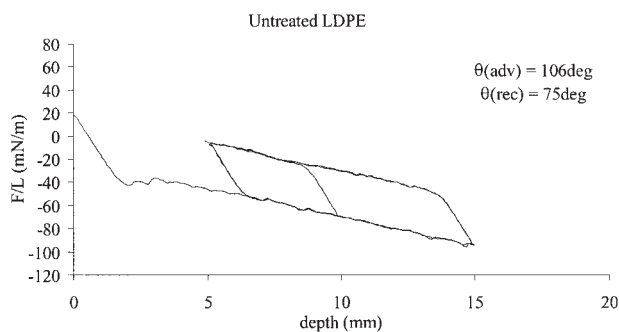


Figure 6 The Wilhelmy force loop of untreated LDPE shows a stable, hydrophobic surface with no intrinsic hysteresis (the second and third immersion lines trace the first immersion line).

sample immersed at a depth between 10 to 15 mm would undergo its first wetting. After the immersion of the sample was reduced back to a depth of 5 mm in the second cycle, the third cycle began immediately. In this cycle the sample was immersed from a depth of 5 mm to a depth of 15 mm and then emerged completely from the water, to a depth of 0 mm. During the third cycle both overshooting from surface damages and intrinsic hysteresis from surface configuration changes could affect the outcome of the Wilhelmy

force loop because the sample was not allowed to dry in ambient air. Therefore, the changes observed at 10–15 mm between the immersion phases of cycle 2 and cycle 3 could be a result of both overshooting and intrinsic hysteresis. When overshooting occurs, the difference in the degree of overshooting in the immersion phase from 0 to 10 mm with that in the immersion phase from 10 to 15 mm can provide some indication of surface configuration changes.

Figure 6 shows the Wilhelmy force loop for a pre-cleaned, untreated LDPE sample with a hydrophobic surface, as exhibited by the dynamic contact angles. The sample exhibited no intrinsic hysteresis from the first to the second immersions and from the second to the third immersions, indicating the sample surface was very stable.

Figure 7 shows the Wilhelmy force loops Ar LTCAT-treated LDPE samples with different exposure times. It can be seen that all treated samples exhibited some degree of overshooting. The overshooting was minimized with a short exposure time of 2.0 s, as shown by the difference in force trends of 2 mN/m at 0–10 mm immersion. The overshooting in the immersion from 10 to 15 mm was reduced to 0 mN/m, which was less than the overshooting of 2 mN/m in the immersion from 0 to 10 mm. These data indicate that

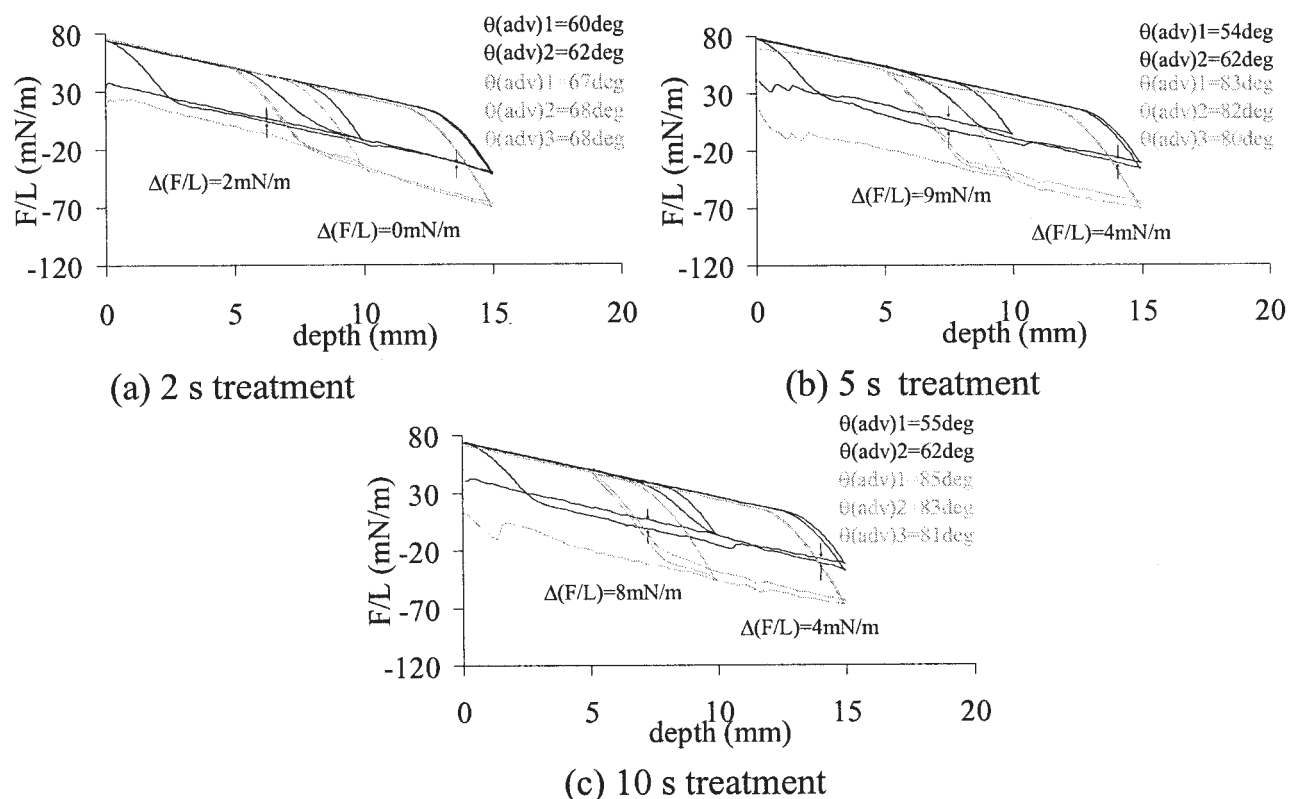


Figure 7 The Wilhelmy force loops of Ar LTCAT-treated LDPE samples with different treatment times. The black lines show the force loops obtained immediately after treatment, and the gray lines show the force loops obtained after 2 weeks of aging in air. The other LTCAT conditions included 1000 scfm of Ar and an arc current of 4.0 A.

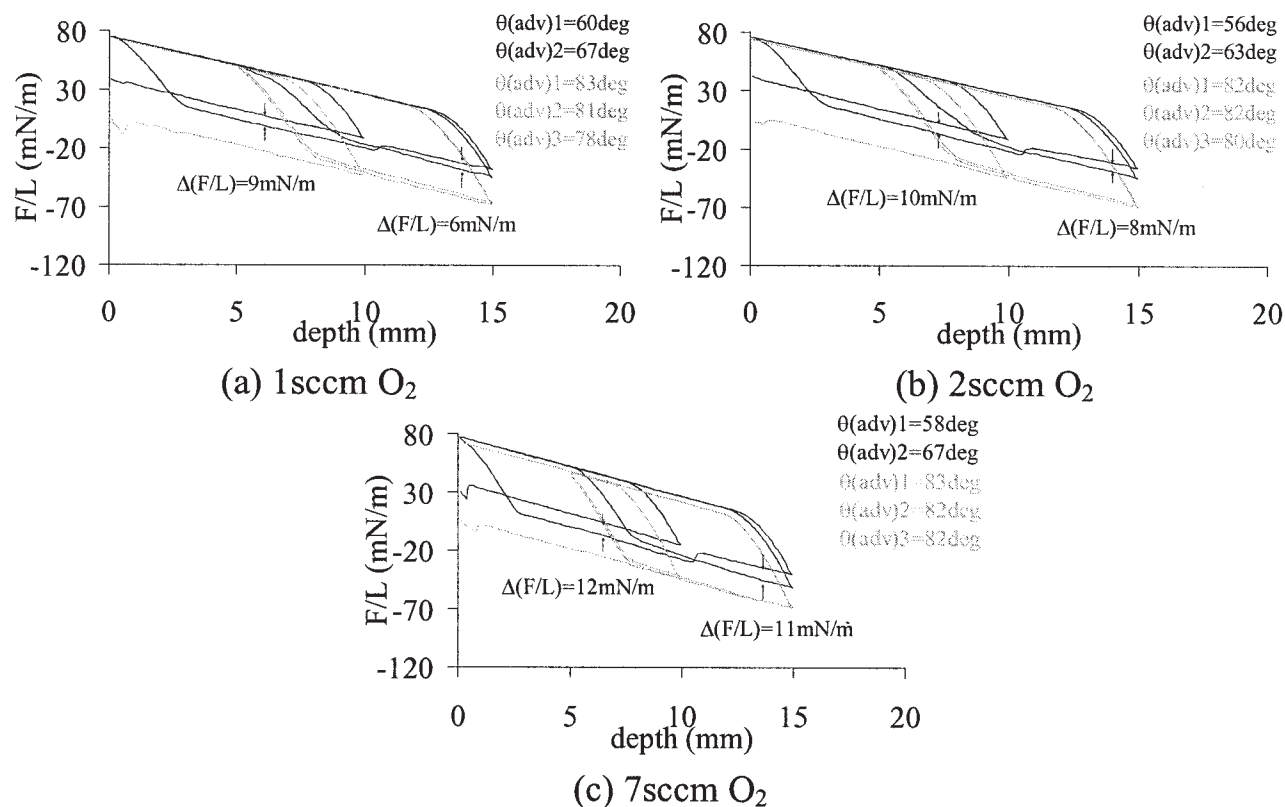


Figure 8 The Wilhelmy force loops of Ar+O₂ LTCAT-treated LDPE samples with different O₂ flow rates. The black lines show the force loops obtained immediately after treatment, and the gray lines show the force loops obtained after 2 weeks of aging in air. The other LTCAT were 1000 sccm of Ar, an arc current of 4.0 A, and an exposure time of 2.0 s.

the sample also underwent some degree of surface configuration change when shifting the contacting medium from air to water. Wilhelmy loops were obtained after aging the samples in air for 2 weeks, shown in Figure 7 by the gray loops. The aged samples showed no overshooting, which indicates that the surface oligomers were washed away after obtaining the first Wilhelmy force loop and washing in deionized water. At the same time, all the aged samples in Figure 7 showed some degree of intrinsic hysteresis, further confirming surface configuration changes for argon LTCAT-treated LDPE. It should be noted that after 2 weeks of aging, the sample treated with a shorter exposure time of 2.0 s showed the greatest surface stability, as shown by both the least amount of hydrophobic recovery and the minimal intrinsic hysteresis.

Figure 8 shows the Wilhelmy force loops obtained with LDPE samples treated by argon LTCAT plasma torch with the addition of different amounts of oxygen at 1, 2, and 7 sccm. As can be seen in Figure 8, all the treatments resulted in overshooting, which was significantly higher than that with the Ar LTCAT treatments. It should be noted that for each condition, the overshooting with immersion from 10 to 15 mm was less than the overshooting with immersion from 0 to 10 mm. This indicates that all the treated samples also

exhibited some degree of change in surface configuration.

The conditions involving 1 sccm O₂, which resulted in the lowest overshooting, were used to examine the effects of exposure time on LDPE using Wilhelmy force loops. As shown in Figure 9, the loops showed that overshooting decreased with increasing exposure time, up to 15 s, when the overshooting was 3 mN/m for immersions of both 0–10 mm and 10–15 mm. Further increasing the treatment time to 20 s increased the degree of overshooting, indicating that more surface damage occurred. For all of the treatments, the loops showed intrinsic hysteresis after aging in ambient air for 2 weeks, indicating significant mobility of hydrophilic moieties on Ar + O₂ LTCAT-treated LDPE surfaces.

Figure 10 shows the Wilhelmy force loops obtained with LDPE samples treated by an argon LTCAT plasma torch with the addition of different amounts of water at 1, 2, and 10 sccm. All the treatments resulted in a high degree of overshooting, in the range of 13–20 mN/m, which was even greater than with the treatments involving Ar LTCAT with the addition of O₂. These data clearly indicated that LTCAT treatment with the addition of water vapor resulted in more damage on LDPE surfaces. From Figure 10 it also can

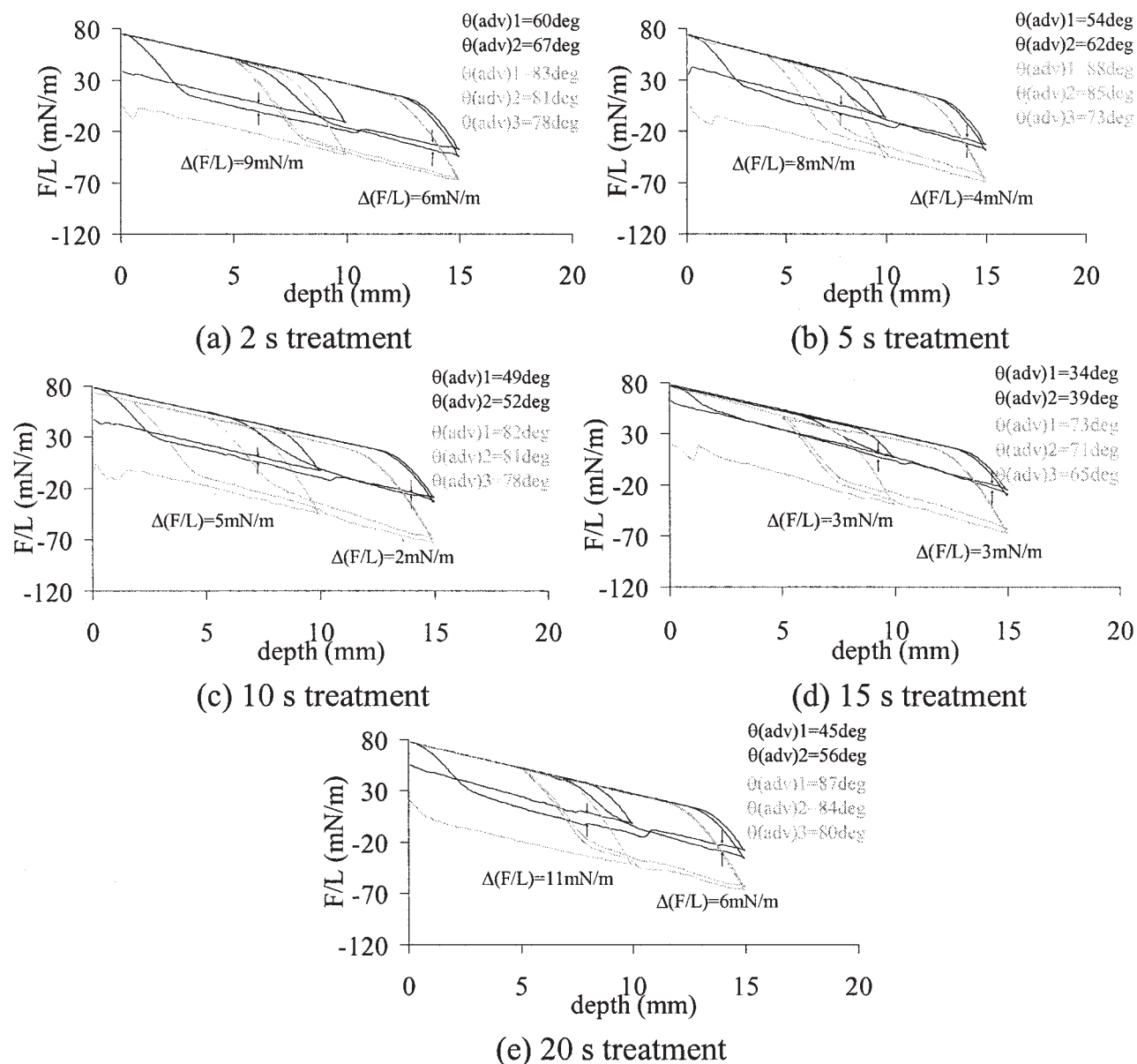


Figure 9 The Wilhelmy force loops of Ar+O₂ LTCAT-treated LDPE samples with different treatment times. The black lines show the force loops obtained immediately after treatment, and the gray lines show the force loops obtained after 2 weeks of aging in air. The constant conditions included: 1000 sccm of Ar, 1 sccm of O₂, and an arc current of 4.0 A.

be seen that the addition of more water vapor resulted in a higher degree of overshooting. When H₂O vapor was added, the LTCAT torch became fainter than was the case with the addition of O₂, which indicated the H₂O molecules had greater consumption of the argon torch than did the O₂ molecules. In other words, the energy carriers (excited Ar atoms in this case) in the LTCAT torch were more favorably disposed to transfer their energy to the H₂O molecules than to the O₂ molecules. It is well known that argon plasma treatment of polymers usually causes a surface CASING (crosslinking via activated species of inert gases) effect,¹⁶ which helps to stabilize the hydrophilic moieties and minimize the formation of low-molecular-

weight oligomers on the surface. Therefore, a possible reason for the high degree of surface damage on LDPE from LTCAT treatment with the addition of water could be the reduction of argon plasma species in the LTCAT because of their energy being transferred to the added water molecules. As a result, the CASING effects from argon plasma species diminished.

The Ar LTCAT treatments that had 2 sccm of H₂O vapor showed the greatest wettability, the least overshooting, and the minimum surface configuration changes, as shown by the smallest differences in overshooting between 0 and 10 mm and between 10 and 15 mm. This condition was used to investigate the effects of LTCAT exposure time on the LDPE surface, as

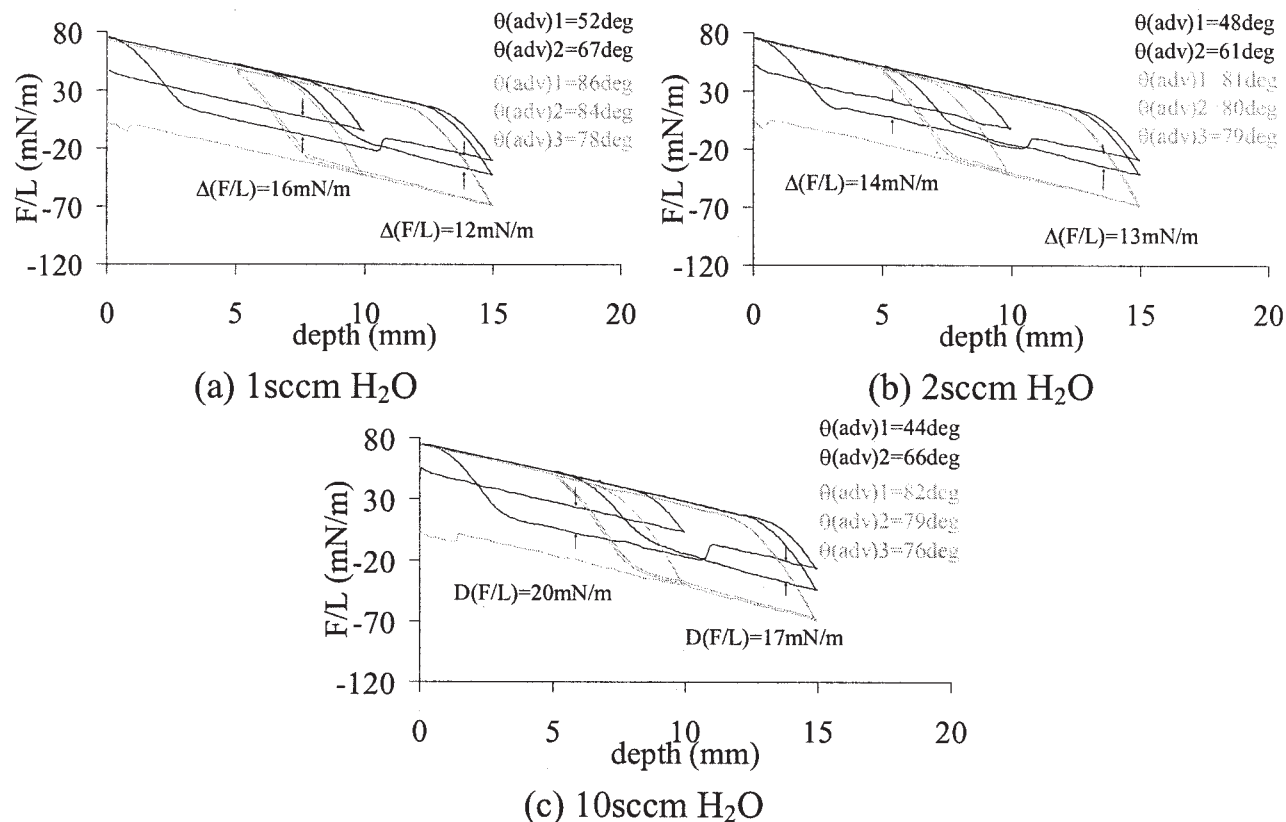


Figure 10 The Wilhelmy force loops of Ar+H₂O LTCAT-treated LDPE samples with different H₂O flow rates. The black lines show the force loops obtained immediately after treatment, and the gray lines show the force loops obtained after 2 weeks of aging in air. Other LTCAT conditions included: 1000 sccm of Ar, an arc current of 4.0 A, and an exposure time of 3.0 s.

shown in Figure 11. The data showed that with a treatment time of 3.0 s, the least amount of overshooting occurred, but no clear trends developed with increased exposure time. The Wilhelmy force loops of the aged samples showed that most LTCAT treatments of LDPE with added water vapor resulted in relatively stable surfaces after aging in ambient air, as shown by the very small degree of intrinsic hysteresis.

Surface stability of the treated surface on aging

The effects of aging on LTCAT- and RF plasma-treated LDPE samples were investigated by storing the samples in ambient air for more than 2 weeks. Figure 12 shows the static contact angle changes of these samples after aging. After a 2-week aging, the sample treated by Ar LTCAT with added H₂O vapor showed the best wettability, whereas the samples treated by Ar + O₂ RF plasma showed the most hydrophobic recovery. Overall, the LTCAT treatments for each gas combination resulted in better wettability on LDPE surfaces than did their RF plasma counterparts.

As a comparison, Figure 13 shows the Wilhelmy force loops measured from LTCAT- and RF plasma-

treated LDPE samples, which were prepared under the conditions that gave the best wettability for each gas combination. Most LTCAT and RF plasma treatments resulted in certain surface damage, shown as overshooting on the Wilhelmy force loops. One exception was the Ar RF plasma-treated sample [Fig. 13(a)], which did not show overshooting but had significant mobility of the surface moieties as shown by the high degree of intrinsic hysteresis. The Ar LTCAT treatment that did not have added reactive gas [Fig. 13(b)] produced the best wettability after a 2-week aging, the least hydrophobic recovery, and the most slight intrinsic hysteresis, indicating the most stable surface. In addition, the treatment time of 2.0 s was the shortest and thus the most rapid and efficient treatment process. It was expected that the Ar LTCAT without added reactive gas would result in a stable surface because of the CASING effect. Slight overshooting (2 mN/m) was observed, however, immediately after treatment, which pointed to a small degree of surface damage. The damage induced during treatment possibly was the result of UV irradiation of the LTCAT.

The Ar LTCAT treatments containing the addition of O₂ produced more wettable surfaces with less damage than did the Ar + O₂ RF plasma treatments, as

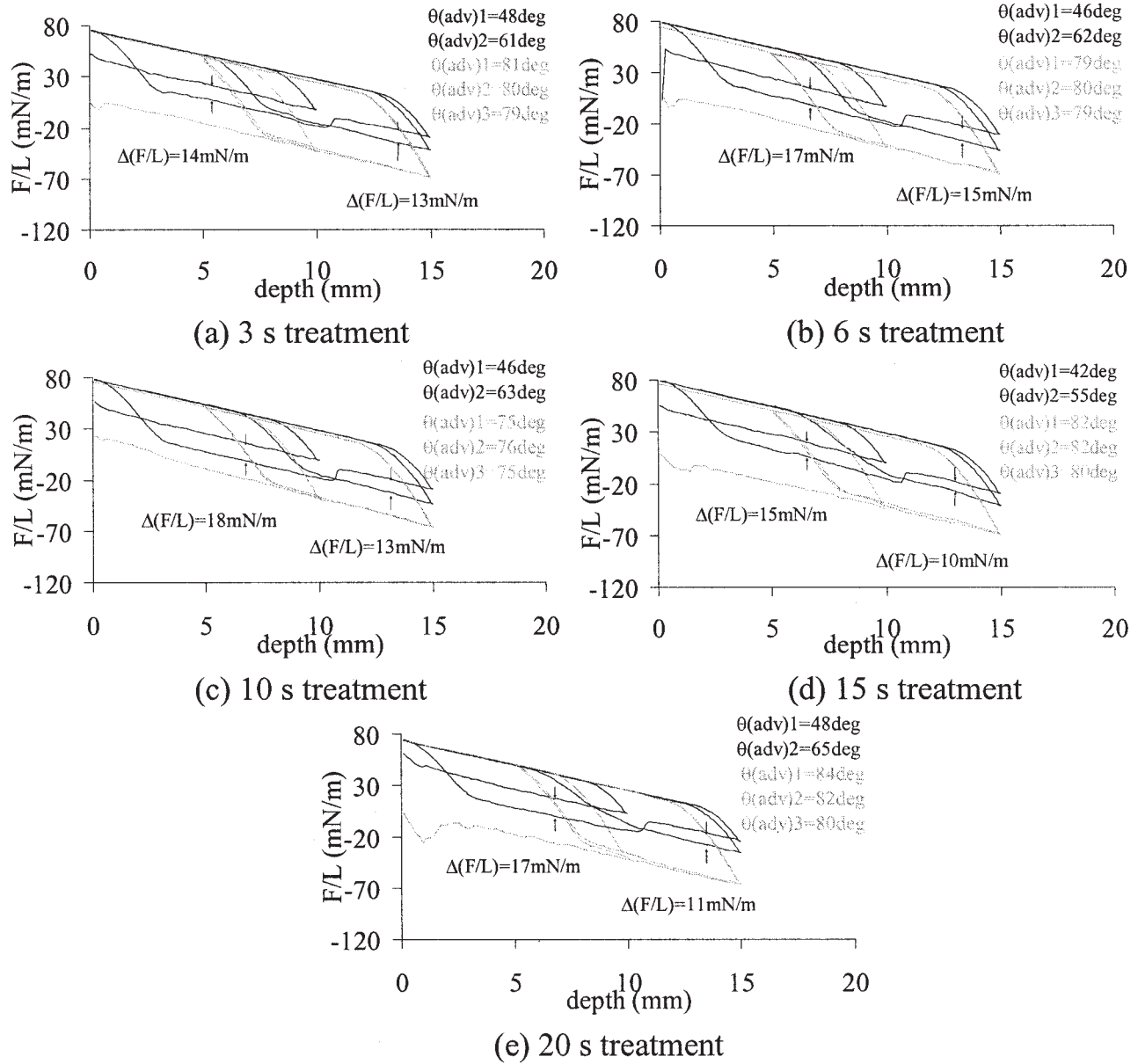


Figure 11 The Wilhelmy force loops of Ar+H₂O LTCAT-treated LDPE samples with different treatment times. The black lines show the force loops obtained immediately after treatment, and the gray lines show the force loops obtained after 2 weeks of aging in air. Constant conditions included 1000 sccm of Ar; 2 sccm of H₂O, and an arc current of 4.0 A.

indicated by significantly less overshooting. In addition, with LTCAT the treatment time was much shorter—15 s—compared to with RF plasma, which required 60 s. After aging in air for 2 weeks, the immersion force trended and the intrinsic hysteresis showed that LTCAT-treated sample exhibited greater wettability, but also higher mobility of surface functionalities than did the RF plasma-treated sample.

The LDPE samples treated by LTCAT involving H₂O vapor showed lower wettability and greater overshooting than did the Ar + H₂O vapor RF plasma-treated samples immediately after treatment. This trend is the opposite in the case of oxy-

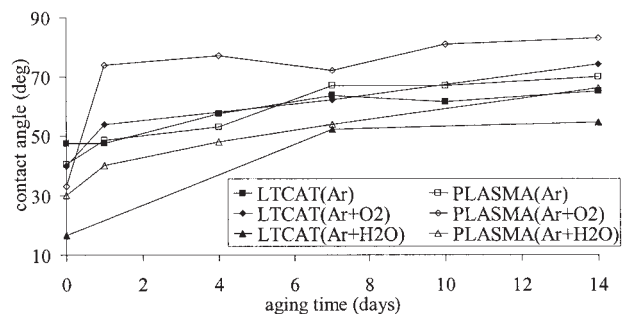


Figure 12 Aging effects on the static surface contact angles of LTCAT- and RF plasma-treated LDPE samples that were prepared under plasma conditions that produced the lowest static surface contact angles.

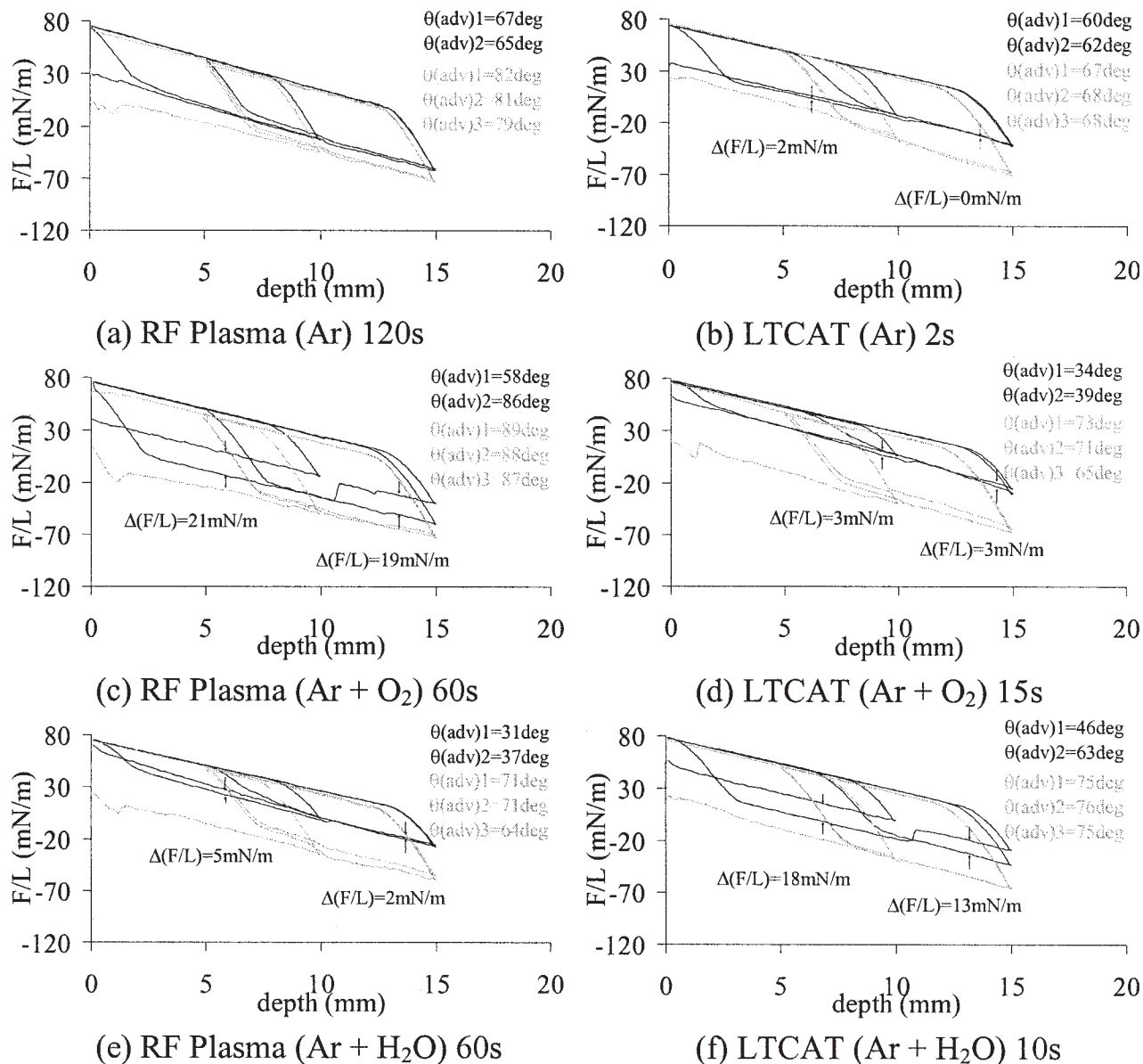


Figure 13 Wilhelmy force loops measured from LTCAT- and RF plasma-treated LDPE samples that were prepared under conditions that provided the best wettability for each gas combination.

gen addition. In RF plasma the energy was carried both by the Ar and the reactive gas, whereas in LTCAT the energy was carried by the excited Ar atoms and transferred to the reactive gas. A previous study of surface modification of polymers using RF plasma treatments indicated there was a high degree of surface damage in H₂O vapor plasma using a low-frequency input.¹³ It is possible that the Ar plasma species in Ar + H₂O RF plasma could remedy some of the damage induced by H₂O plasma species. In the LTCAT process, however, the addition of H₂O vapor consumed the excited Ar atoms to a greater extent than did the addition of O₂ and caused greater surface damage of LDPE.

Continuing studies are now examining the energy transfer processes involved in Ar LTCAT with reactive

gas added, the plasma constituents created in the LTCAT and RF plasmas, and the reactions induced on polymeric surfaces during the LTCAT and RF plasma treatments. The results of these investigations are expected to provide deep insight into the plasma surface modification process of polymers in order to elucidate how damage is induced on polymeric surfaces and how surface stability is created by LTCAT and RF plasma treatments.

CONCLUSIONS

The application of LTCAT to the surface modification of LDPE polymer sheets was studied by various methods of surface contact angle measurement including

the static sessile droplet method and the dynamic Wilhelmy balance method. The combination of static and dynamic surface contact angle measurements enabled a comprehensive investigation of the plasma treatment effects, including surface wettability change, surface stability, and possible surface damage induced by the LTCAT plasma. The experimental results clearly indicated that LTCAT treatment is a very rapid, effective, and efficient technique for surface modification of LDPE polymers.

Without adding reactive gases, plasma treatment using LTCAT of only Ar significantly improved the LDPE surface wettability to 40° within a very short treatment time of 2.0 s. Dynamic analysis of Wilhelmy force loops of the treated LDPE samples indicated that such a short Ar LTCAT treatment produced a stable hydrophilic surface with slight surface damage, as shown by very low initial overshooting (2 mN/m) and little intrinsic hysteresis and low hydrophobic recovery after 2 weeks of aging. The excellent surface stability was attributed to CASING effects on the LDPE surface resulting from argon plasma species in the Ar LTCAT plasma torch.

The experimental data showed that the addition of reactive gases of oxygen or water vapor into the Ar LTCAT resulted in greater damage of the LDPE surface, as shown by the increased overshooting in the Wilhelmy force loops measured with the treated samples. Surface treatment of LDPE by Ar LTCAT with the addition of oxygen did not cause additional improvement in surface wettability. In contrast, it yielded a less stable surface, as shown by the significant intrinsic hysteresis in the Wilhelmy force loops measured with the treated samples after 2 weeks of aging in air. Plasma treatment of LDPE by Ar LTCAT with added H₂O vapor produced an extremely wettable surface with a water contact angle of 17°. However, it caused greater damage on the LDPE surface, as observed by the pronounced overshooting in the Wilhelmy force loops.

Compared with the RF plasma treatments, the LTCAT treatments were much more rapid and efficient in modifying the LDPE surface. LTCAT treatment usually required a few seconds to achieve a significant improvement in surface wettability of LDPE, whereas the RF plasma treatment took several minutes. The

Wilhelmy analysis showed that greater wettability was obtained with LDPE samples treated with Ar LTCAT alone and Ar LTCAT with added O₂ than with samples treated with the corresponding RF plasmas. Despite the small degree of surface damage initially, the Ar LTCAT-treated surface was more wettable and stable than was the Ar RF plasma-treated surface for both the freshly treated samples and the samples aged for 2 weeks in air. The Ar + O₂ RF plasma treatment resulted in much more damage on the LDPE surface than did the Ar LTCAT treatment containing the addition of O₂.

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