The Mesh Disturbance Effects in a Low-Temperature Cascade Arc Torch for Surface Modification of Low Density Polyethylene

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ABSTRACT: A stainless steel mesh was placed in a low-temperature cascade arc torch (LTCAT) to study its disturbance effects on the plasmas and on the surface modification of low density polyethylene (LDPE). It was found that the photoemitting species were deflected by the screen and only faint glow was observed after the mesh. Optical emission spectroscopy examination indicated that the amount of electronically excited species in the plasma was greatly reduced after passing through the mesh. Grounding the mesh altered the nature of the discharge and a greater intensity of O emission was observed in Ar LTCAT + O_2 discharge, which indicated greater energy transfer to the oxygen. Although a decrease in surface damage was observed on the treated LDPE samples by placement of the mesh in the Ar LTCAT discharges, the wettability achieved was also greatly reduced. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 805–817, 2010

Key words: polyethylene; cascade arc torch; plasma treatment; mesh disturbance; surface modification; contact angle

INTRODUCTION

Surface modification treatments are often applied to polymeric surfaces for the enhancement of adhesion, wettability, biocompatibility, printability, barrier properties, susceptibility to harsh agents, and other interfacial characteristics.[1–6] Surface modification treatments can involve deposition of thin films or chemical changes in the top molecular layers. Among the surface modification treatments applied to polymers, plasma processes, including low-pressure plasma, present advantages over other treatments, such as wet chemical treatments and mechanical roughening. Plasma processes are versatile and environmentally benign methods for polymeric surface modification.[5]

Plasma treatments of polymers that involve chemical surface modification can induce surface functionalization, in which new surface functional groups are created, surface crosslinking, and degradation. Plasma processes can have significant drawbacks for polymer surface treatment, though, due to the difficulties in optimization of certain desirable reactions and in minimization of undesired consequences, such as surface degradation.[7] Many species exist in low-pressure plasmas, including high-energy ions, electrons, vacuum ultraviolet (VUV) and ultraviolet (UV) photons, excited neutral species, reactive free radicals, and neutrals. Bombardment from high-energy species, such as ions, can result in significant ablation of surface moieties, chain scission, and surface degradation.[8–10] Degradation can occur in the form of etching into volatile species, which could be desirable or tunable to fit the application, or the scission of surface macromolecular chains into oligomers or low molecular weight oxidized materials (LMWOM), which form a weak boundary layer on the surface that is detrimental to adhesion and stability.

Recent studies[1,11] have demonstrated many unique advantages of low-temperature cascade arc torch (LTCAT) over traditional plasma techniques, including significant reduction of degradation on polymer surfaces and enhanced surface stability. In addition, LTCAT treatment is fast and effective, in the case of Ar LTCAT, 2 s exposure time was reported to be sufficient for the surface modification of low density polyethylene (LDPE), which was much faster than the 120 s that was required for Ar RF plasma treatment.[1] LTCAT consists of a beam of mainly excited neutral species of a noble gas, whereas most of the ions and electrons are contained in a DC arc generator.[12,13] However, some ions and low energy electrons (0.3–1.5 eV)[14] escape the discharge generator and remain in the beam that

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expands into the substrate chamber. It was reported that Ar LTCAT treatments applied to LDPE surfaces induced some surface damage from LMWOM formation.[1] In Ar LTCAT without reactive gas addition, the likely sources of surface degradation include effects from high-energy Ar ions (>15 eV) that escape the arc generator and the effects of VUV/UV radiation.

Although it may be possible to reduce plasma-induced polymer surface damage by lowering the power and treatment time, there is a practical lower limit on these factors. In this study, we chose to place a stainless steel mesh in the LTCAT beam in an attempt to remove ions from the discharge before interacting with the polymer substrates and to study the disturbance effects of the mesh. Furthermore, the mesh was placed in the reactor chamber, which is absent of an external electric field, and thus, no ion regeneration occurred between the mesh and the substrate. The treatment conditions included Ar LTCAT, Ar LTCAT + O_2, and Ar LTCAT + H_2O with the mesh placed at grounded or floating potential for each experiment. The changes in light emitting species were examined by optical emission spectroscopy (OES) and the treatment effects were observed by dynamic surface characterization of the treated polymer samples using the Wilhelmy balance method. The treated samples in this investigation were compared with the results from our previous study,[1] which was conducted without any disturbances in the beam.

EXPERIMENTAL

Materials

LDPE sheets with thickness of 1 mm were purchased from Goodfellow Cambridge Limited (Cambridge, UK) and cut into 20 × 30 mm plates. The samples were ultrasonically cleaned in 5% detergent in deionized water for 30 min, rinsed in deionized water, and dried in ambient air for 30 min. The clean dry samples were then stored in a desiccator. Stainless steel mesh was obtained from McNichols (Atlanta, GA) in sizes mesh 8 and mesh 24. The mesh was cut into 5 × 5 in pieces and ultrasonically cleaned in acetone for 30 min. The argon and oxygen gases, with purities of 99.997 and 99.5 %, respectively, were obtained from Praxair (St. Louis, MO). The water used in the Wilhelmy balance method and in the water vapor reactive gas that was added to Ar LTCAT was obtained from a Culligan deionizing system attached to in-house distilled water.

LTCAT reactor conditions

A detailed description and the operational procedures of the LTCAT reactor were reported in previous investigations.[11,13] The LTCAT reactor consisted of an arc generator, Pyrex glass cross vacuum chamber, and an Edward (Grand Island, NY) High-Vacuum EH500A/E2M80 combination pump. The arc generator was mounted on one port of the cross vacuum chamber and consisted of a narrow channel (2 mm) formed by a series of copper disks that were separated by silicone rubber insulators. A copper needle cathode was placed at the upstream end of the arc generator and the last metal disk was grounded. Before performing each experiment, the copper disks were cooled to 15°C using an ethylene glycol–water mixture.

For each treatment, the LTCAT reactor was evacuated for 10 min to about 1 mtorr pressure. The leak rate of the reactor was around 0.04 sccm, which was about 0.004% of the Ar flow rate. Ar flowed through the narrow channel at 1000 sccm, which created supersonic gas velocity in the narrow channel that forced the glow discharge into the vacuum chamber in the form of a luminous plasma torch. A MDX-5K direct current power supply was used to ignite and sustain the argon discharge inside the arc generator. Previous studies[12,13] have shown that the electric field inside the arc generator confines most of the charged species, and as a result, the discharge torch consists mainly of electronically excited neutral species of argon. Reactive gas, such as O_2 and H_2O vapor can be added to the LTCAT discharge, in which the electronically excited noble gas species transfer energy to the reactive gas species, resulting in dissociation and excitation of the reactive gas molecules. Ionization of the reactive gas molecules and dissociated fragments can be neglected in the discharge vacuum chamber because of the relatively low energy of the electronically excited Ar energy carriers.

The LDPE samples were placed at 21 cm distance from the arc generator outlet and a stainless steel mesh was placed about 1 cm upstream the polymer location or 1 cm downstream the polymer location. In addition, the mesh was either placed at floating potential or at ground potential, depending on the experiment. Treatment times and the flow rates of the reactive gases that were added to the discharges were varied.

Wilhelmy balance method

The Wilhelmy balance method was used to examine the surface characteristics of the plasma-treated polymers. Our previous investigation outlines the theory and method of the dynamic wettabiltiy analysis.[1] A KSV Instruments (Helsinki, Finland) Sigma 70 tensiometer was used to obtain dynamic contact angles of the polymers during several wetting cycles by measuring the total force exerted on the polymer

sample plate although immersed in water. The immersion and emergence speed of the samples was fixed at 5 mm/min, which was 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 to obtain the advancing and receding contact angles for each immersion cycle.

The stability of the polymer surfaces was examined by observing the intrinsic hysteresis or overshooting between cycles. Intrinsic hysteresis occurs when the surface during one cycle exhibits greater wettability than in the previous cycle, which is attributed to mobile hydrophilic functional groups that bend toward the polymer surface during the first wetting, making the surface more wettable for the next wetting cycle. Overshooting is exhibited by a polymer when the treated surface contains loosely-bonded, nonvolatile oligomers that display hydrophilic behavior during the initial wetting cycle and wash into the water during immersion, which exposes a more hydrophobic surface layer in the next wetting cycle. Wilhelmy force loops were obtained immediately after treatment, 1 day after treatment, 1 week after treatment, and 2 weeks after treatment. In this article, only the representative Wilhelmy data obtained immediately after treatment and 2 weeks aging after treatment was presented. Hydrophobic recovery, when it occurred for a treated polymer, was observed by comparing the immediate Wilhelmy force loop to the loops obtained after allowing the samples to age. The overall stability of a treated polymer surface was gauged from the degree of intrinsic hysteresis, overshooting in the initial force loop, and hydrophobic recovery. A surface is considered stable when each of the three phenomena is minimized.

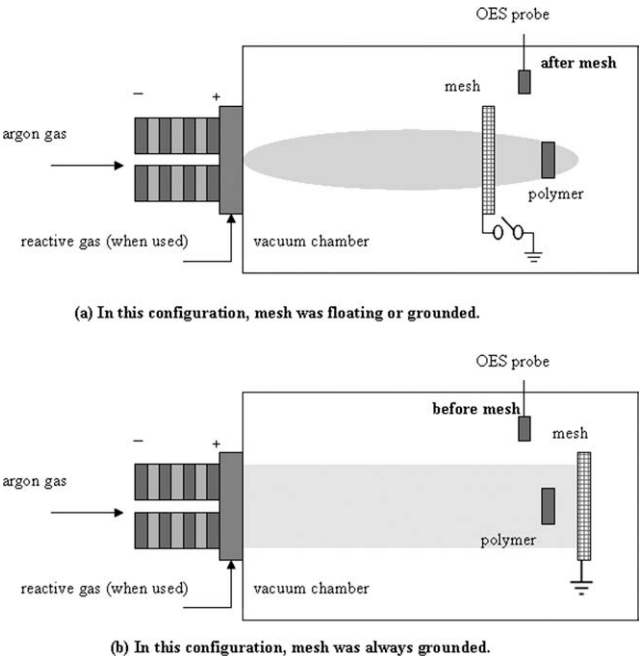

Figure 1 A pictorial representation of the LTCAT configuration, which illustrates the positions of the polymer substrate and OES probe with respect to the stainless steel mesh. In (a), the mesh was placed at floating or grounded potential and in (b), the mesh was grounded.

Optical emission spectroscopy

OES was used to examine the photoemitting species that were present in the glow of the discharges upstream and downstream the mesh screen that was set at floating or grounded potential. The OES equipment was manufactured by Jarrell Ash Corporation (now Thermo Electron in Minneapolis, MN) with a control and data acquisition system from Princeton Instruments (Trenton, NJ). The exposure time for the OES spectra was 5 min for all cases.

RESULTS AND DISCUSSION

The effects on the LTCAT discharges and treatments of LDPE substrates from the placement of a stainless steel mesh in the beam at floating or grounded potential were investigated. The types of discharges included Ar LTCAT and Ar LTCAT with reactive gas addition of O_2 or H_2O. Figure 1 illustrates the placement of the LDPE substrates and the OES probe with respect to the stainless steel mesh screen. For the configuration in Figure 1(a) with a floating mesh, both the OES spectra and Wilhelmy loops for the treated polymer surfaces are presented. When a grounded mesh was placed in the configuration shown in Figure 1(a), however, the glow after the mesh disappeared from both visual inspection and the OES spectra, which showed no significant peaks. Thus, the OES spectra after a grounded mesh are

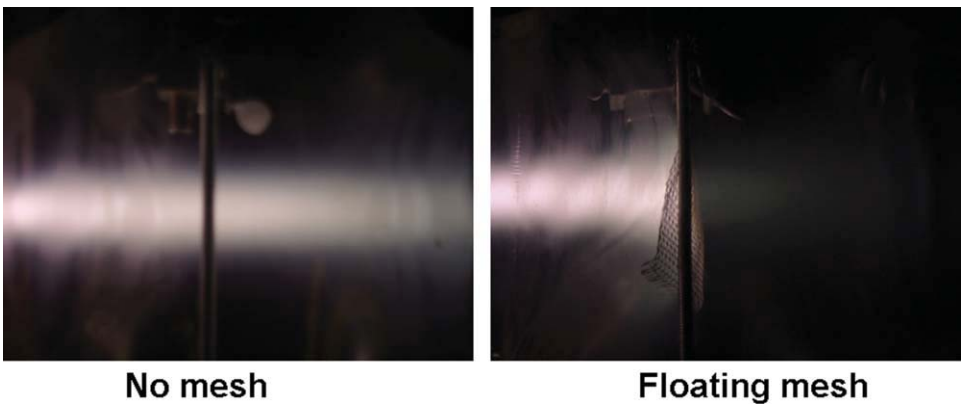

Figure 2 Optical photographs showing the effects of placement of a floating stainless steel mesh on the visible glow of Ar LTCAT discharge under the conditions of 1000 sccm Ar and 4 A arc current. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

not given, but the Wilhelmy loops of the treated samples placed after the grounded mesh are presented. For the configuration shown in Figure 1(b) with a grounded mesh, the OES spectra of LTCAT and some of the Wilhelmy force loops of the treated samples placed in this position are presented. For comparison, OES spectra and Wilhelmy loops for LDPE substrates treated without the placement of a mesh in LTCAT discharges are also presented. The Wilhelmy force loops for LDPE treated without the mesh were obtained from our previous results.[1] Wilhelmy loops were also obtained after aging the samples in ambient air for 2 weeks, to evaluate the possible hydrophobic recovery of the plasma-treated surfaces.

The effects of placing a floating mesh in LTCAT

A mesh size 8 was placed upstream from the LDPE sample position in Ar LTCAT, Ar LTCAT + O_2, and Ar LTCAT + H_2O discharges. Figure 2 contains an optical photograph of the effects of the floating mesh placed in the beam of Ar LTCAT discharge. It is obvious from Figure 2 that the mesh created a

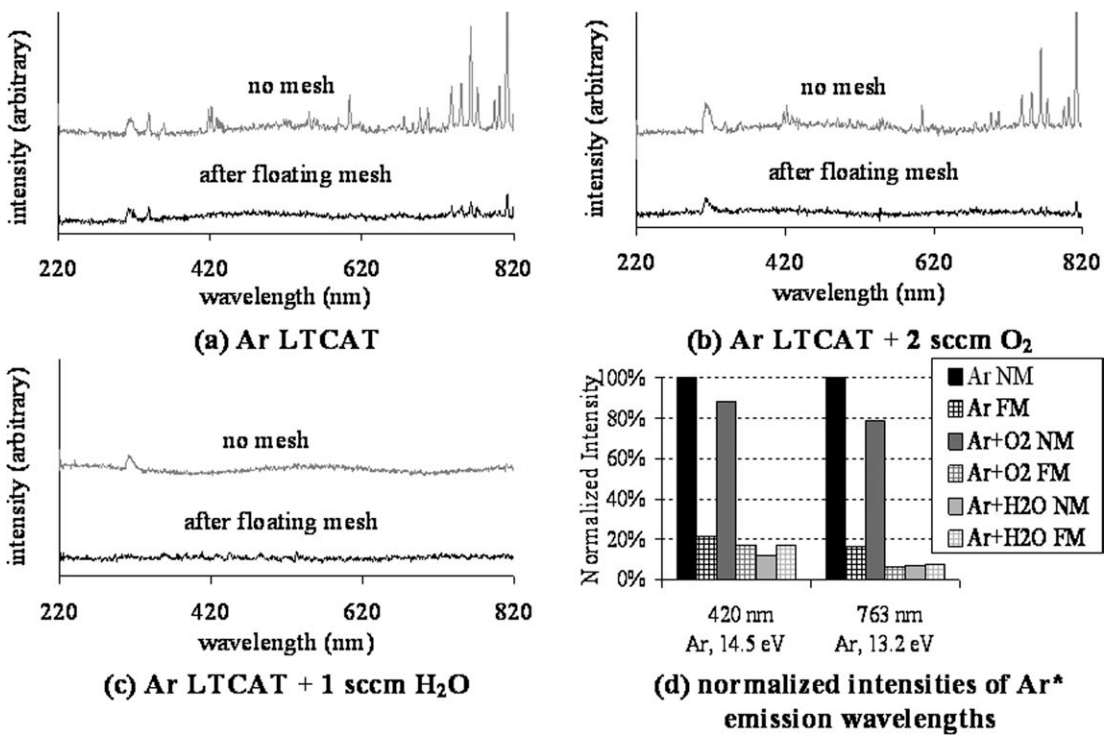

Figure 3 The OES spectra of (a) Ar LTCAT, (b) Ar LTCAT + 2 sccm O_2, and (c) Ar LTCAT + 1 sccm H_2O discharges at the sample position without a mesh (grey) and after a floating stainless steel mesh (black), and (d) a comparison of the normalized intensities of two Ar* emission wavelengths. The other LTCAT conditions include 1000 sccm Ar and 4 A arc current. The OES exposure time was 5 min. Code: NM = no mesh; FM = floating mesh.

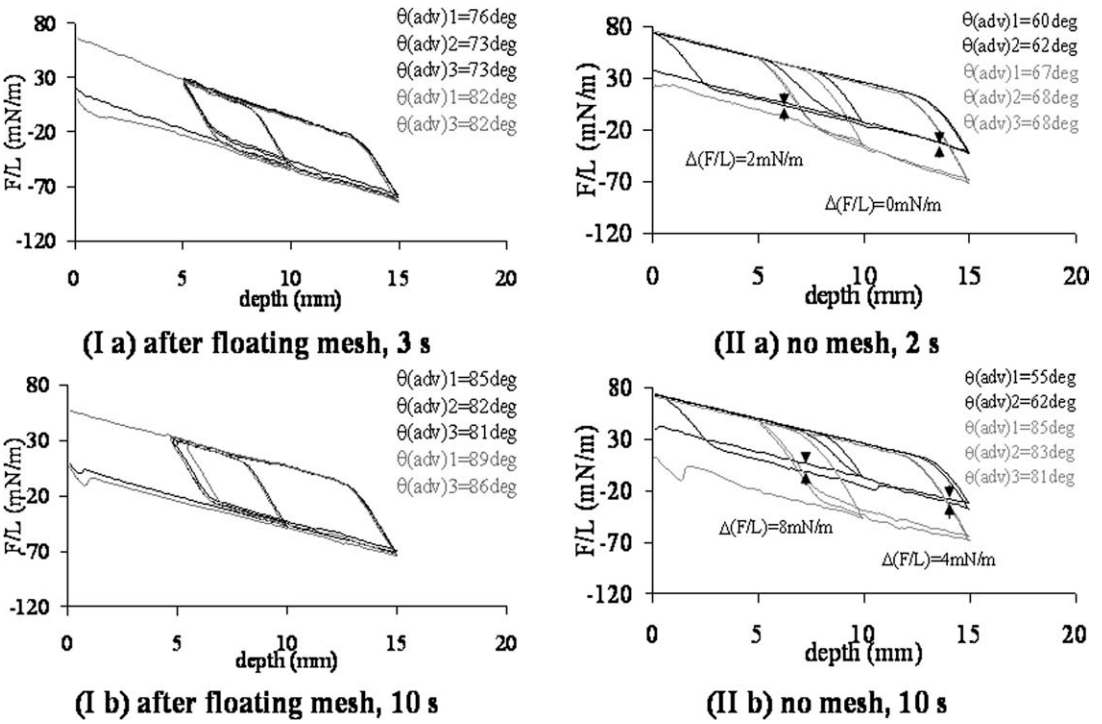

Figure 4 The Wilhelmy force loops of Ar LTCAT-treated samples that were placed (I) downstream from a floating stainless steel mesh and (II) in a discharge without a mesh with various treatment times. The black lines show the force loops obtained immediately after treatment and the grey lines show the force loops obtained after 2 weeks of aging in ambient air. The other LTCAT conditions included 1000 sccm Ar and an arc current of 4 A. The Wilhelmy force loops obtained without a mesh were obtained from Ref. [1].

significant disturbance in the LTCAT discharge and much of the beam seems to be reflected by the mesh, even though the mesh size was relatively large ($\sim$ 2.5 mm). OES spectra of the discharges without the mesh and after the floating mesh [configuration Fig. 1(a) with floating mesh] were obtained to examine the changes in photoemitting species induced by the mesh. Figure 3 contains OES observations of (a) Ar LTCAT, (b) Ar LTCAT + 1 sccm O_2, and (c) Ar LTCAT + 1 sccm H_2O vapor discharges obtained without a mesh (grey) and after a floating mesh (black). To clearly elucidate the changes in Ar* after the floating mesh screen, the normalized intensities for two wavelengths corresponding to Ar* (420 and 763 nm) were obtained for each discharge using the emission intensities from Ar LTCAT without a mesh. Thus, the normalized intensities for the two chosen wavelengths for Ar LTCAT without a mesh were equal to 1. The OES data indicate that the intensity of electronically excited Ar atoms, Ar*, was greatly reduced for all discharges by the placement of the floating mesh upstream from the substrate.

Some of the discharge passed through the floating mesh, however, and polymer samples were surface treated in this fainter glow region. The effects of treatment time in the Ar LTCAT discharge were examined using Wilhelmy force loops of LDPE surfaces placed after the floating, stainless steel mesh [configuration Fig. 1(a) with floating mesh] and were compared with those treated without a mesh placement in Figure 4. No overshooting was observed for the samples treated after the floating mesh, whereas all of the samples treated without a mesh exhibited some overshooting. Recall that overshooting in the Wilhelmy loop indicates surface damage in the form of LMWOM.[1] However, the surface wettability was lower using the treatment by the discharge after the floating mesh as indicated by the higher advancing contact angles. Thus, the placement of the floating mesh in front of the sample in Ar LTCAT eliminated surface damage from LMWOM formation for at least up to 20 s treatment time, but the desired wettability enhancement was significantly reduced, as also apparent by paired *t*-test of the dynamic contact angles measured at depths of immersion, in which the *P*-value is <0.0001.

The addition of O_2 to the Ar LTCAT discharge with the LDPE substrates placed after the floating stainless steel mesh [configuration Fig. 1(a) with floating mesh] was investigated and the effects of O_2 flow rate on the dynamic surface characteristics of the treated samples are shown in the Wilhelmy loops of Figure 5. The lower flow rates of 1 sccm and 2 sccm O_2 with the floating mesh did not induce

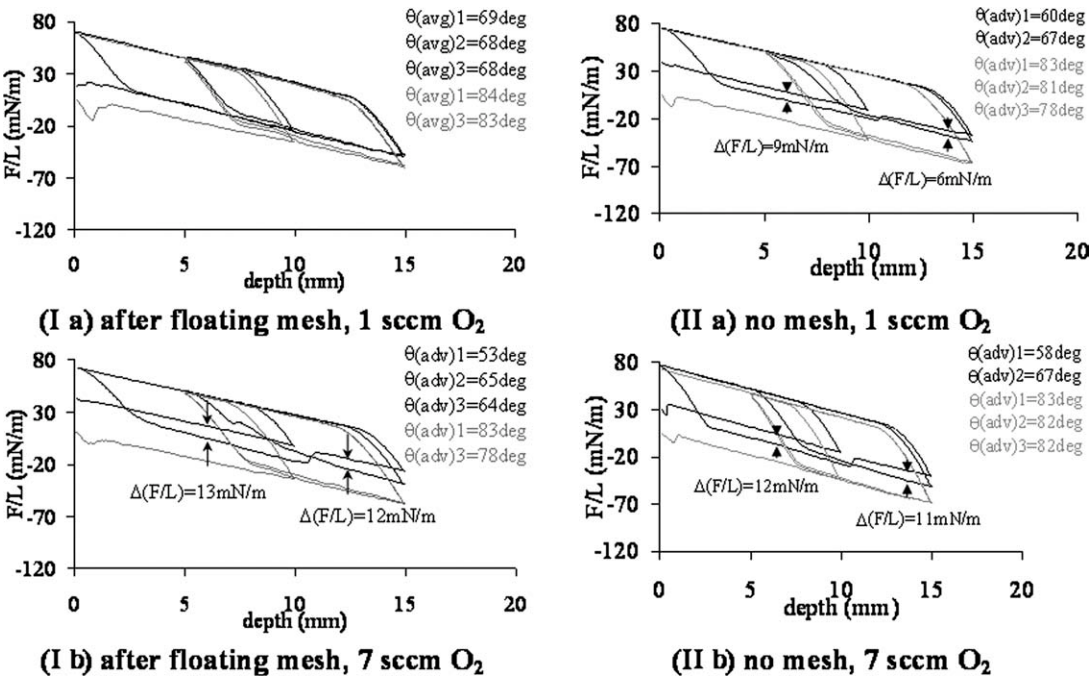

Figure 5 The Wilhelmy force loops of Ar LTCAT + O_2-treated samples that were placed (I) downstream from a floating stainless steel mesh and (II) in a discharge without a mesh with various O_2 flow rates. The black lines show the force loops obtained immediately after treatment and the grey lines show the force loops after 2 weeks of aging in ambient air. The other LTCAT conditions included 1000 sccm Ar, 2 s treatment time, and an arc current of 4 A. The Wilhelmy force loops obtained without a mesh were obtained from Ref. [1].

as much damage as in similar discharge conditions without the mesh, as observed from overshooting. However, using the higher flow rate of 7 sccm O_2, the dynamic surface characteristics of the treated LDPE were very similar to those induced by treatments of the same conditions, but without the floating mesh. With lower flow rates of O_2, both the Ar species and the reactive oxygen species contribute to surface modification, because of incomplete quenching of Ar* by the O_2. At higher flow rates, however, more of the Ar* species are quenched by O_2 and at some high flow rate, the reactive oxygen species become the main contributors to surface modification effects, including degradation from LMWOM formation. Because the treatment effects are similar using the higher O_2 flow rate in both cases (without a mesh and after a floating mesh), it is likely that the reactive oxygen species are not significantly affected by the placement of a floating mesh, unlike the Ar* species.

The treatment time effects were examined using Ar LTCAT + 1 sccm O_2 with the LDPE samples placed after a floating mesh [configuration Fig. 1(a) with floating mesh] and the data are shown in Figure 6. The Wilhelmy loops show that for the discharges with and without a mesh, increasing treatment time not only enhanced the wettability but also resulted in increased surface damage as shown by overshooting. However, less overshooting was observed on the samples treated in LTCAT after the mesh than without the mesh, which was also less effective in wettability improvement.

A comparison of Ar LTCAT + H_2O treatments of LDPE placed after the floating mesh [configuration Fig. 1(a) with floating mesh] to the discharge without the mesh is given in the Wilhelmy loops in Figure 7. No damage is induced on the LDPE treated after the floating mesh, unlike the significant damage induced by the discharge without a mesh, but the wettability is only moderately enhanced. This indicates that the reactive Ar species and H_2O species that induce wettability enhancement and surface damage were significantly affected by the floating mesh.

The effects of the grounded mesh on the LTCAT discharges

Changing the mesh potential from floating to ground produced significant changes in the nature of the discharge. Instead of a steady, narrow, bright torch in Ar LTCAT, the discharge expanded between the arc generator outlet and the mesh with a decrease in visual glow intensity and a detectable color change. Figure 8 contains a comparison of optical photographs of Ar LTCAT, Ar LTCAT + O_2, and Ar LTCAT + H_2O discharges with a floating mesh and a grounded mesh. The OES spectra obtained after the grounded mesh [configuration Fig. 1(a) with

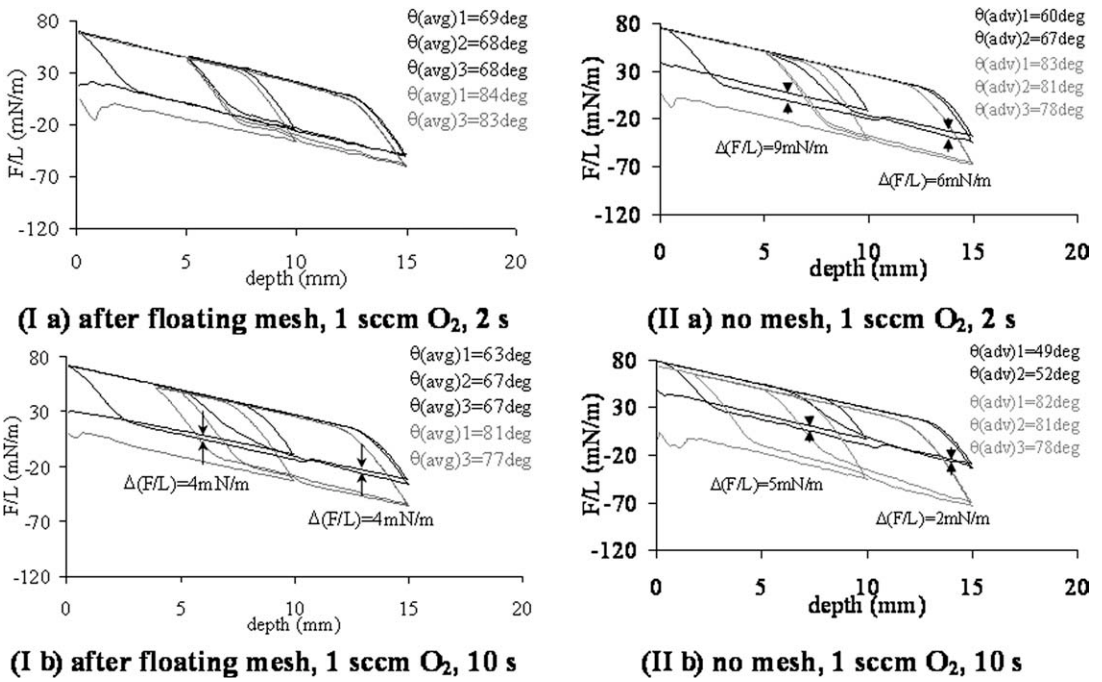

Figure 6 The Wilhelmy force loops of Ar LTCAT + O_2-treated samples that were placed (I) downstream from a floating stainless steel mesh and (II) in a discharge without a mesh with various treatment times. The black lines show the force loops obtained immediately after treatment and the grey lines show the force loops after 2 weeks of aging in ambient air. The other LTCAT conditions included 1000 sccm Ar, 1 sccm O_2, and an arc current of 4 A. The Wilhelmy force loops obtained without a mesh were obtained from Ref. [1].

grounded mesh] did not show any peaks, however, the OES spectra obtained before the grounded mesh [configuration Fig. 1 (b)] are presented in this section.

Figure 9 contains OES spectra from (a) Ar LTCAT, (b) Ar LTCAT + 1 sccm O_2, and (c) Ar LTCAT + 1 sccm H_2O vapor discharges obtained without a mesh (grey) and before a grounded mesh [black,

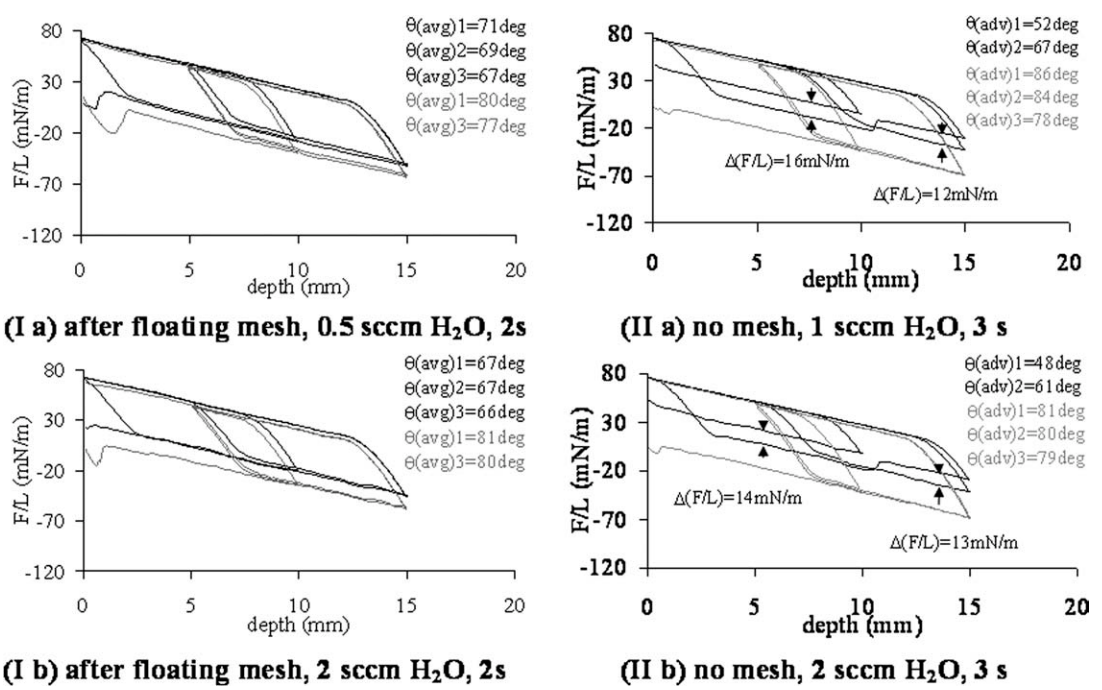

Figure 7 The Wilhelmy force loops of Ar LTCAT + H_2O-treated samples that were placed (I) downstream from a floating stainless steel mesh and (II) in a discharge without a mesh with various H_2O flow rates. The black lines show the force loops immediately after treatment and the grey lines show the force loops after 2 weeks of aging in ambient air. The other LTCAT conditions included 1000 sccm Ar and an arc current of 4 A. The Wilhelmy force loops obtained without a mesh were obtained from Ref. [1].

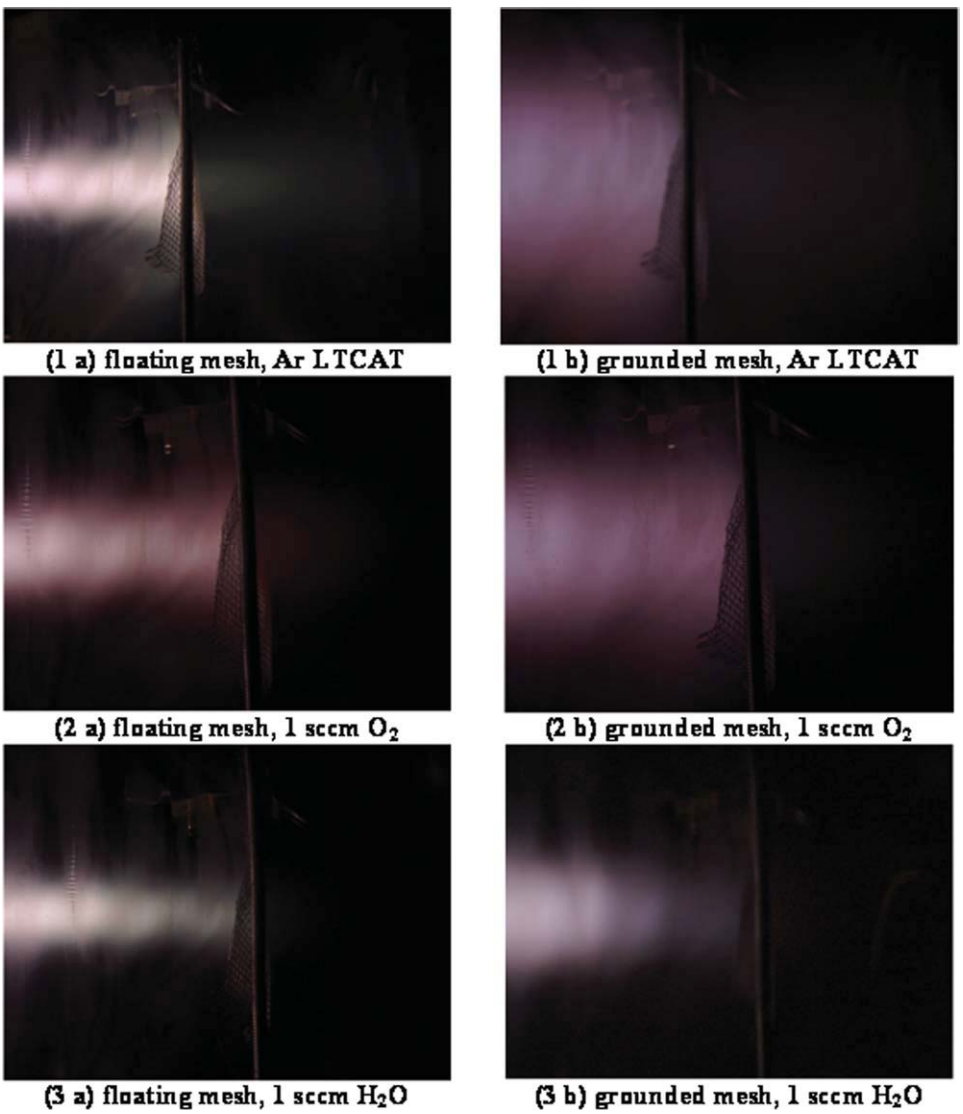

Figure 8 Optical photographs of the effects of placement of (a) floating and (b) grounded stainless steel mesh on the visible glow of (1) Ar LTCAT, (2) Ar LTCAT + O_2, and (3) Ar LTCAT + H_2O discharges. The other conditions include 1000 sccm Ar and 4 A arc current. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

configuration Fig. 1 (b)]. For the Ar* emission wavelength at 811 nm, the emission intensity obtained by OES from each discharge was normalized using the emission intensity obtained from Ar LTCAT without a mesh, which thus had a normalized intensity equal to 1. For the O emission wavelength at 777 nm, the emission intensities were normalized using the emission intensities obtained from Ar LTCAT + 7 sccm O_2 before the grounded mesh, which produced the highest emission intensities of the O species for all of the discharges examined by OES. These normalized intensities of each discharge are compared in Figure 9. Grounding the mesh greatly changed the emission intensities in the discharge, as shown by the decrease in the Ar* emission intensities. In the case of O_2 addition, the Ar* emission intensity decreased and the O emission intensities greatly increased. This indicates that when a grounded mesh was added to the discharge of Ar LTCAT + O_2, greater energy transfer to the O_2 occurred. The dissociation energy of O_2 is 5.1 eV, in which a portion of the electrons in LTCAT discharges contain enough energy to cause dissociation of O_2 molecules.[14] It is possible that the grounded mesh enhanced the number of electrons that escaped from the arc generator, which would have increased the rate of dissociative collisions between electrons and oxygen. Further investigation with a Langmuir probe could determine the changes in electron density of the discharge induced by the grounded mesh placement.

Samples were treated in the downstream of the grounded mesh [configuration Fig. 1(a) with grounded mesh] for Ar LTCAT, Ar LTCAT + O_2,

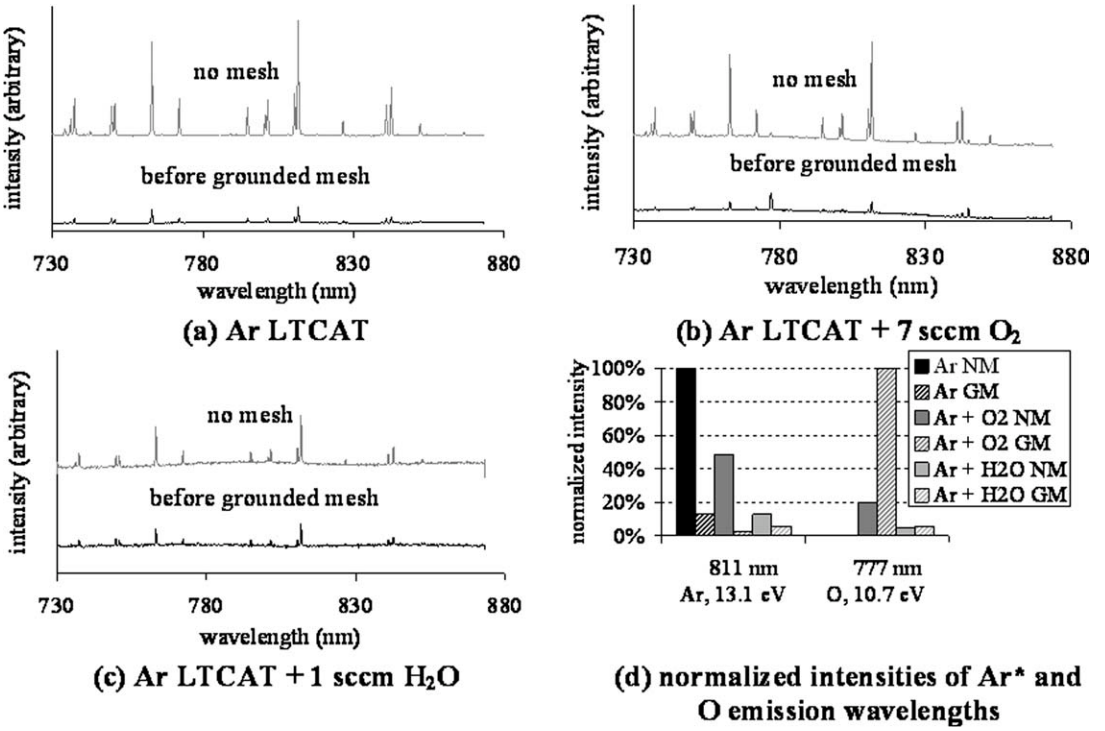

Figure 9 The OES spectra of Ar LTCAT (a), Ar LTCAT + 7 sccm O_2 (b), and Ar LTCAT + 1 sccm H_2O (c) discharges obtained at the sample position without a mesh (grey) and before a grounded mesh (black) and (d) a comparison of the normalized intensities of Ar* and O emission wavelengths.. The other LTCAT conditions include 2000 sccm Ar and 4 A arc current. The OES exposure time was 5 min.

and Ar LTCAT + H_2O and in the glow region before the grounded mesh [configuration Fig. 1 (b)] for Ar LTCAT discharges. For the LDPE treatments after the mesh, comparisons of Wilhelmy force loops from using a grounded and floating mesh are shown for Ar LTCAT in Figure 10, Ar LTCAT + O_2 in Figure 11, and Ar LTCAT + H_2O in Figure 12. For Ar LTCAT and Ar LTCAT + O_2, the discharges after the floating mesh induced greater wettability on the treated polymer surfaces. In Ar LTCAT + H_2O, the polymers placed after the grounded mesh achieved greater wettability than the polymers treated in without a mesh. Furthermore, the treatment after the grounded mesh with 0.5 sccm H_2O induced no surface damage from LMWOM and produced wettability similar to the best condition previously reported for Ar LTCAT [see Fig. 4 (IIa)]. However, increasing the flow rate of H_2O induced surface damage, which also increased with increasing H_2O flow rate.

From visual inspection and OES data, the nature of the discharge emanating from the arc generator between the arc generator outlet and the mesh appeared to have a significantly altered nature when the mesh was grounded, which was not observed with the floating mesh. LDPE samples were placed in this discharge of Ar LTCAT before the grounded mesh [configuration Fig. 1 (b)] to study the treatment effects of this altered discharge on LDPE samples, the results of which are given in Figure 13 as compared with the results obtained without a mesh.[1] The Wilhelmy force loops in Figure 13 show that the wettability of the treated LDPE samples is reduced with the addition of a grounded mesh in the discharge, also evident from paired *t*-test analysis of the contact angle at depths of immersion, which produced a *P*-value <0.0001. This evidence, along with the OES spectra, clearly indicates that placing a grounded mesh in the LTCAT discharge alters the nature of the discharge and possibly changes the plasma density.

The effects of the discharges and the mesh placement on the surface treatment of the LDPE are compared in Table I. In general, the addition of a floating mesh inhibited surface damage and the presence of LMWOM, however, the initial wettability was not as greatly enhanced. With O_2 addition into the plasma, greater surface damage was induced on the polymers placed in the discharge after the floating mesh than after the grounded mesh. For Ar LTCAT + H_2O, however, the effect was reversed; the treatments on polymers placed after the floating mesh were less effective in enhancing the wettability of LDPE surfaces and were also less prone to induce surface damage. It seems that the grounded mesh inhibited the flux of the reactive Ar and oxygen species to the substrate more significantly than the floating mesh. On the

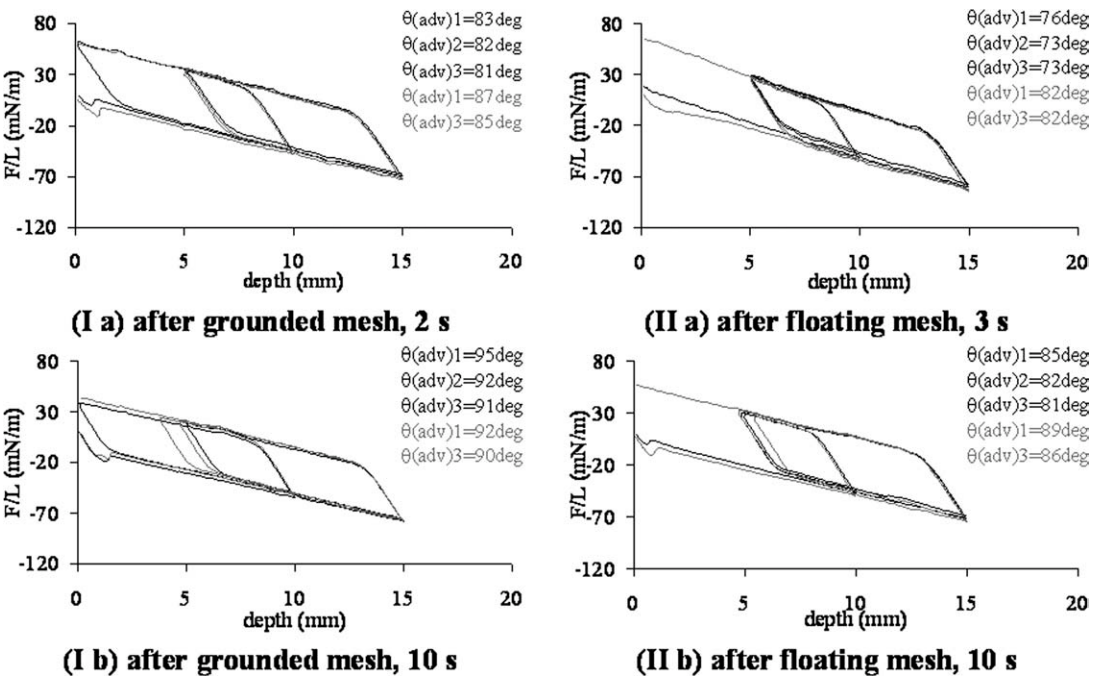

Figure 10 The Wilhelmy loops of Ar LTCAT-treated LDPE samples that were placed downstream from (I) a grounded stainless steel mesh and (II) a floating stainless steel mesh. The black lines show the force loops obtained immediately after treatment and the grey lines show the force loops obtained after 2 weeks of aging in ambient air. The other LTCAT conditions included 1000 sccm Ar and an arc current of 4 A.

other hand, the greater wettability enhancement and increased surface damage induced on the LDPE placed after the grounded mesh than the floating mesh in the Ar LTCAT + H_2O discharges indicated a greater penetration of H_2O reactive species through the mesh in the grounded case.

Surface damage with formation of LMWOM is not desirable in surface treatment applications. The

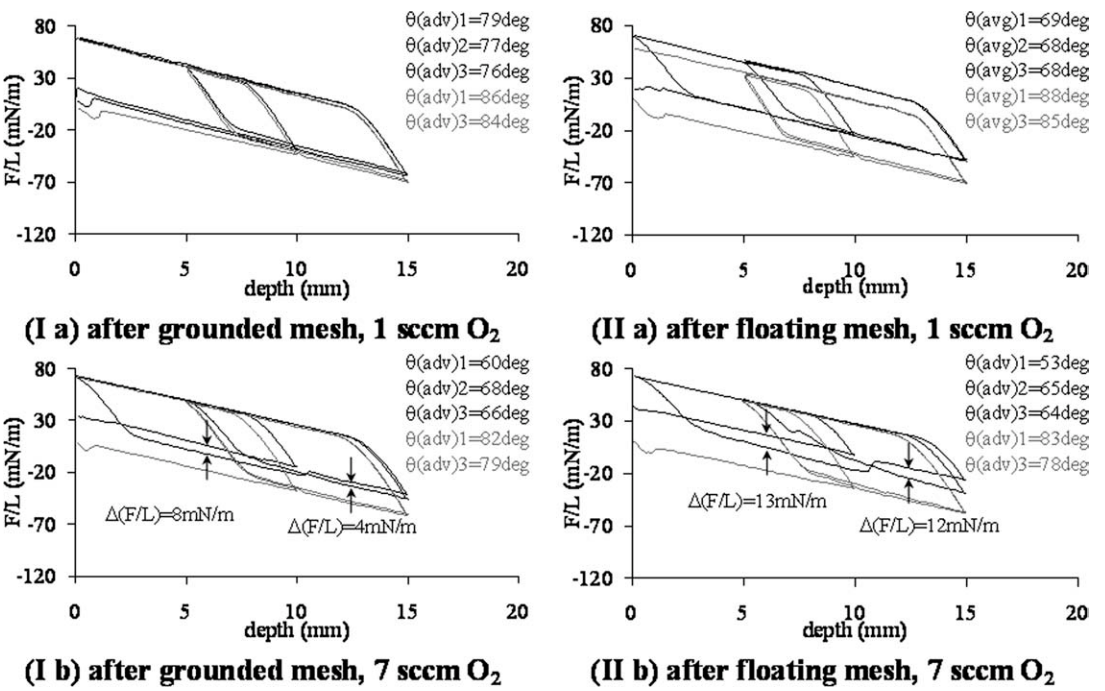

Figure 11 The Wilhelmy loops of Ar LTCAT + O_2-treated LDPE samples that were placed downstream from (I) a grounded stainless steel mesh and (II) a floating stainless steel mesh. The black lines show the force loops obtained immediately after treatment and the grey lines show the force loops obtained after 2 weeks of aging in ambient air. The other LTCAT conditions included 1000 sccm Ar, an arc current of 4 A, and 2 s treatment time.

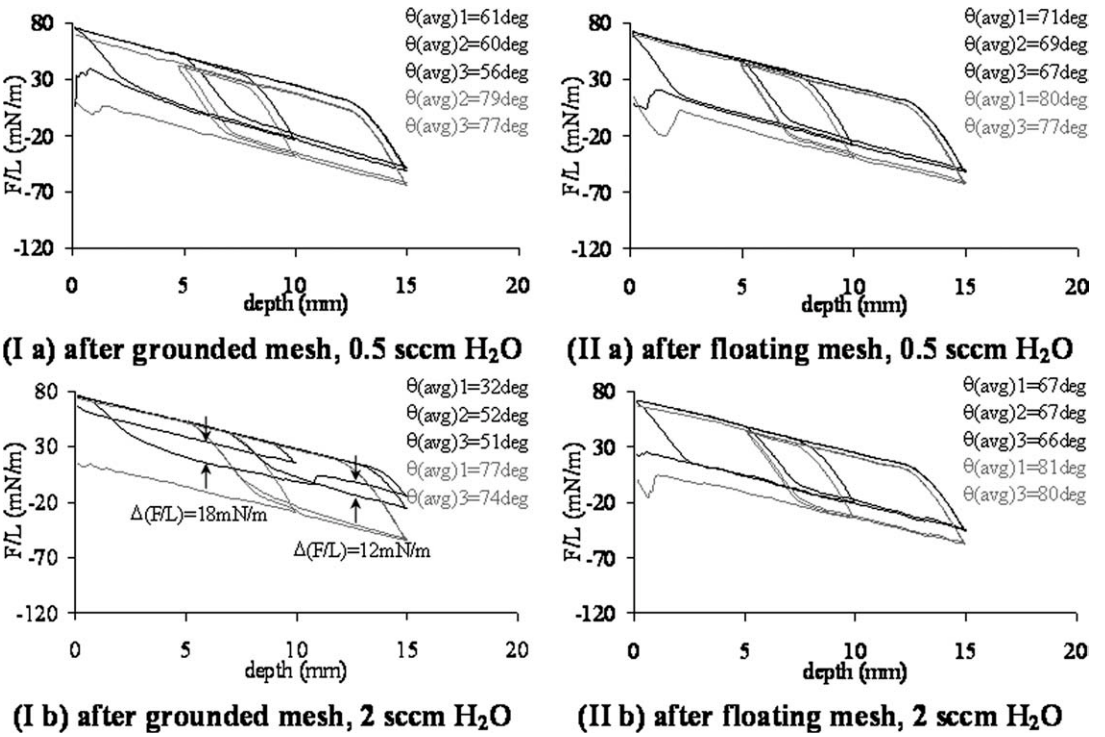

Figure 12 The Wilhelmy loops of Ar LTCAT + H_2O-treated LDPE samples that were placed downstream from (I) a grounded stainless steel mesh and (II) a floating stainless steel mesh. The black lines show the force loops obtained immediately after treatment and the grey lines show the force loops obtained after 2 weeks of aging in ambient air. The other LTCAT conditions included 1000 sccm Ar, an arc current of 4 A, and 2 s treatment time.

greatest wettability that was achieved from the trials without surface damage was Ar LTCAT + H_2O downstream of a grounded mesh. Hydrophobic recovery is present in all cases, however, and the treated polymers should undergo the subsequent application shortly after surface treatment.

CONCLUSIONS

In this study, a stainless steel mesh was placed in the discharges of LTCAT for surface modification of LDPE to distinguish the effects of ions in the discharge from those of the other species, especially the electronically excited Ar species, Ar*. However, optical photography and OES data indicated that much of the photoemitting species were significantly reduced from the placement of the mesh in LTCAT. Furthermore, when the mesh in LTCAT was grounded, the nature of the LTCAT discharge was significantly changed. OES data indicated that in the case of Ar LTCAT + O_2, the emission intensities of O species in the discharge created by the grounded mesh increased, whereas the Ar peaks were reduced for all discharges. This indicates that the grounded mesh placement resulted in greater energy transfer to the oxygen species, possibly from an increase in the number of electrons released from the arc generator. Further investigation of the changes in the discharge by a grounded mesh using Langmuir probe analysis could shed more light on the sources of the altered nature of the discharge.

The Wilhelmy force loop data indicated that placing a floating mesh screen in the Ar LTCAT beam inhibited LDPE surface damage from LMWOM formation, but did not enhance the wettability as effectively as it would without placing the mesh. Although it is possible that the mesh may have consumed ions in the torch, the reduction of the emission intensities of Ar* species that reached the samples position was unfavorable for wettability enhancement of LDPE. The best wettability that was achieved without surface damage was in the downstream of Ar LTCAT + H_2O after the floating mesh. Hydrophobic recovery is present in all cases and should be managed by application of the treated surface shortly after treatment.

The Wilhelmy loops of the LDPE samples treated after the mesh in Ar LTCAT + O_2 discharges revealed that the reactive oxygen species were not affected by the floating mesh, but were significantly reduced after the grounded mesh, as indicated by poor wettability enhancement of the plasma treated LDPE. The reactive species in Ar LTCAT + H_2O discharges, however, were greatly reduced after the floating mesh, as indicated by the decrease in

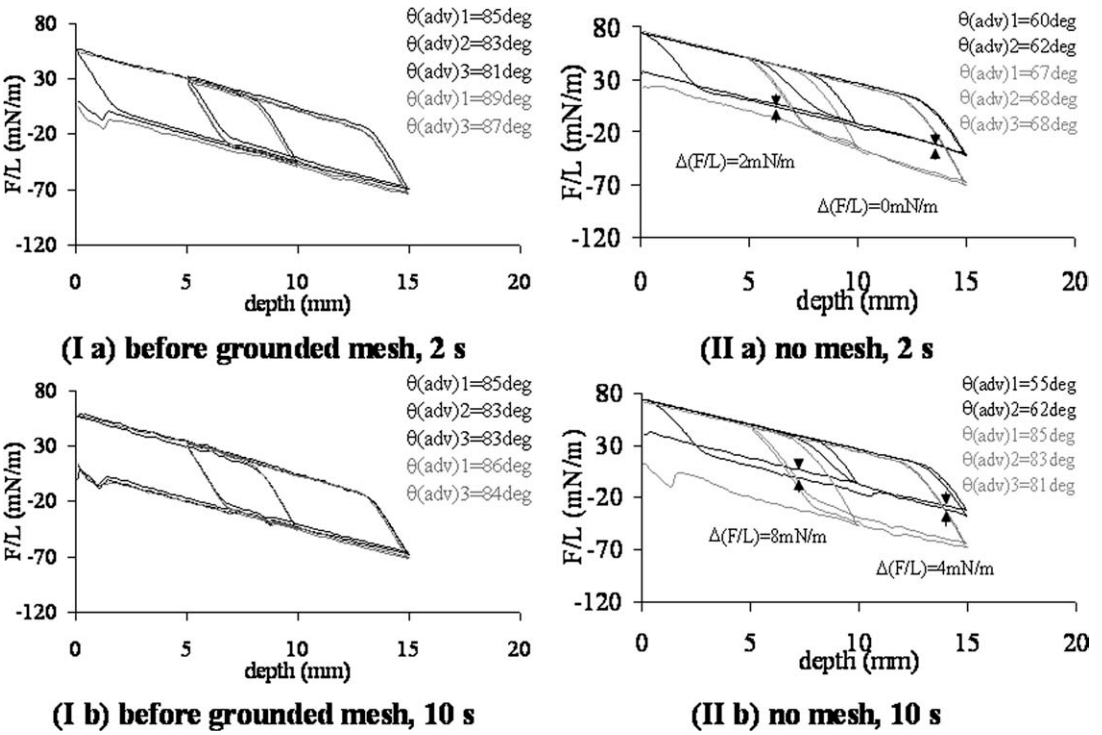

Figure 13 The Wilhelmy loops of Ar LTCAT-treated samples that were placed (I) in the discharge created between the arc generator and a grounded, stainless steel mesh and (II) in a discharge without a mesh with various treatment times. The black lines show the force loops obtained immediately after treatment and the grey lines show the force loops obtained after 2 weeks of aging in ambient air. The treatment conditions were 1000 sccm Ar and 4 A arc current. The Wilhelmy force loops obtained without a mesh were obtained FROM Ref. [1].

wettability and surface damage on the treated polymers. LDPE samples treated after a grounded mesh in the Ar LTCAT + H_2O discharges, however, exhibited much improved wettability enhancement with less surface damage than those treated without using a mesh or after a floating mesh. For samples treated in the Ar LTCAT discharge before a grounded mesh, the wettability enhancement and induced surface damage were significantly reduced in comparison with the treatments without a mesh. A natural continuation of this study would involve investigation of the chemical and physical surface changes resulting from the plasma treatments.

These findings indicate a most important message, which is that careful consideration needs to make when applying any such disturbance in a plasma discharge because the nature of the discharge as well as the desirable process outcomes can be significantly altered.

TABLE I
Summary of Surface Changes Induced from LTCAT Plasma Treatments

		Placement position of LDPE samples			
Plasmas	Evaluation	No mesh	Downstream of floating mesh	Downstream of grounded mesh	Upstream of grounded mesh
Ar LTCAT (2 and 3 s)	Initial contact angle	θ = 60°	θ = 76°	θ = 83°	θ = 85°
	Overshooting (LMWOM damage)	θ increase by 2°	Not present	Not present	Not present
	Hydrophobic recovery	θ increase by 6°	θ increase by 7°	θ increase by 4°	θ increase by 4°
Ar LTCAT +1 sccm O_2 (2 s)	Initial contact angle	θ = 60°	θ = 69°	θ = 79°	n/a
	Overshooting (LMWOM damage)	θ increase by 7°	Not present	Not present	n/a
	Hydrophobic recovery	θ increase by 16°	θ increase by 15°	θ increase by 7°	n/a
Ar LTCAT + 2 sccm H_2O (2 and 3 s)	Initial contact angle	θ = 48°	θ = 67°	θ = 32°	n/a
	Overshooting (LMWOM damage)	θ increase by 13°	Not present	θ increase by 20°	n/a
	Hydrophobic recovery	θ increase by 20°	θ increase by 14°	θ increase by 25°	n/a

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