

# Surface Modification of a Group of Polymers Using a Low Temperature Cascade Arc Torch

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**ABSTRACT:** Surface modification treatments were performed on six different types of polymers using low temperature cascade arc torch (LTCAT) of Ar with or without adding reactive gas of O<sub>2</sub> or H<sub>2</sub>O vapor. The effects of the treatments on the wettability enhancement, surface degradation from oligomer formation, and surface stability from the mobility of surface moieties and hydrophobic recovery were investigated. Surface characterization techniques included the static Sessile droplet method and dynamic Wilhelmy balance method. Experimental results indicated that Ar LTCAT treatments of the polymers with shorter treatment times (2 s in most cases) resulted in stable and hydrophilic surfaces without any surface damage from oligomer formation, with the exception of nylon-6. The excellent results from Ar LTCAT treatments were attributed to the CASING effect (crosslinking via activated species of inert gas). Addition of O<sub>2</sub> into Ar LTCAT resulted

in greater wettability of the treated surfaces, but increased surface damage from oligomer formation. Adding H<sub>2</sub>O vapor into Ar LTCAT produced extremely hydrophilic surfaces on the polymers, but pronounced surface damage. The surface oligomer formation was attributed to alkoxy degradation reactions and chain scission from overexposure to high energy species. Comparisons of the treatment outcomes for each type of polymer are discussed with respect to the degree of wettability enhancement, the stability of the treated surfaces, and the susceptibility to degradation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 360–372, 2007

**Key words:** surface modification; plasma treatment; cascade arc torch; contact angle; Wilhelmy; polymethylmethacrylate; polystyrene; polycarbonate; polyoxymethylene; silicone rubber; nylon-6

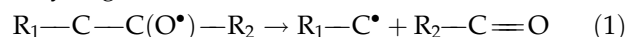
## INTRODUCTION

Plasma treatments have found wide applications in surface modification of polymers to improve their adhesive properties, enhance wettability, biocompatibility, barrier properties, optical reflection, susceptibility to harsh agents, and to reduce friction, among other objectives.<sup>1–7</sup> Plasma techniques offer advantages over other techniques because of the effectiveness and versatility of the treatments and the environmentally benign nature of the plasmas. However, traditional plasma techniques involve surface bombardment by high-energy species, such as ions, electrons, and VUV/UV photons, which can bring about significant degradation on the polymer surfaces. In addition, the complex nature of the plasma makes it difficult to selectively isolate beneficial surface reaction mechanisms and minimize detrimental effects.

Much is still unknown regarding the complex reaction mechanisms at the plasma–polymer inter-

face during plasma surface modification. Consequences of plasma treatments used for chemical modification (excluding deposition processes) include surface functionalization, in which new surface functional groups are created, surface crosslinking by the CASING (Crosslinking via Activated Species of INert Gases) effect, etching of surface material into volatile species, and the scission of surface polymer chains into loosely-bonded oligomers or Low Molecular Weight Oxidized Material (LMWOM).<sup>8</sup> The degradation of a polymer surface into a layer of oligomers can occur from bombardment of high-energy species that induce chain scission or via the formation and degradation of alkoxy radicals. The alkoxy degradation reaction is shown below, which results in scission of a polymer chain:

alkoxy degradation:



Alkoxy radicals can be formed on polymer surfaces in the presence of oxygen-containing plasmas through several routes originating from reactions with oxidizing species, such as O<sub>2</sub>, O, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HO<sub>2</sub>, and OH.<sup>9</sup>

Plasma surface modification studies have found that the outcome of the treatment depends on the

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polymer chemical structure and the polymer's susceptibility to the plasma conditions. For example, some studies have shown that the presence of oxygen in the polymer's chemical structure increases the polymer's susceptibility to degradation.<sup>5,10</sup> On the other hand, aromatic rings in the polymer (both in the backbone and in pendant groups) provide some resistance to etching reactions.<sup>10–13</sup> Polymethylmethacrylate (PMMA) is a polymer that easily undergoes oxidative degradation in a plasma environment,<sup>13,14</sup> while polystyrene (PS) is highly stable toward degradation.<sup>11,13,15</sup> Silicon-containing polymers are particularly resistant to photodegradation and oxidative degradation, yet degrade very easily in fluorine-containing plasmas, because of the formation of stable and volatile Si–F compounds.<sup>16</sup>

Low Temperature Cascade Arc Torch (LTCAT) plasma provides a beam of mainly electronically excited Ar<sup>\*</sup> species directed at the polymer surface, making it an ideal glow discharge process for the surface modification of polymers. With the absence of an external electric field in the substrate chamber, the low density of ions that escape the arc generator are not significantly accelerated to the substrate surface. In addition, the application of Ar LTCAT to polymer surfaces induces the CASING effect and any un-reacted surface free radicals that are present after treatment can be quenched by oxygen upon exposure to atmosphere to create hydrophilic moieties. The combination of these two processes results in the creation of new surface functional groups anchored to a stable, crosslinked surface layer.<sup>16</sup>

Investigations in our laboratory have involved the application of LTCAT plasma technology to polymer surface modification, which have resulted in successful wettability enhancement with less surface damage than traditional plasma and greater surface stability.<sup>6,7</sup> In addition, LTCAT is a fast and cost-effective treatment that can easily be scaled-up for high throughput in industrial settings. Previous studies have demonstrated the effectiveness of LTCAT in modifying the surfaces of polytetrafluoroethylene (PTFE)<sup>7</sup> and low density polyethylene LDPE.<sup>6</sup> The objective of this investigation is to uncover the effects of the polymer structure on the outcomes of LTCAT treatments by examining the wettability changes, surface stability, and surface degradation of a group of polymers with representative chemical structures. Polymers that were examined in this study include PS, which contains a stabilizing benzene ring, PMMA and polyoxymethylene (POM), with oxygen functionalities that may cause enhanced sensitivity to degradation in plasma, and polycarbonate (PC), which contains both benzene rings and oxygen in the backbone. In addition, polymers that exhibit surface crosslinking under radiation are also examined, including nylon-6 and silicone rubber

(SR).<sup>17</sup> The plasma treatments include Ar LTCAT, Ar LTCAT with O<sub>2</sub> addition, and Ar LTCAT with H<sub>2</sub>O vapor addition. The surface changes upon plasma treatment were examined using static and dynamic surface contact angle measurements, which can be related to other surface characteristics, such as surface energy and adhesive properties.

## EXPERIMENTAL

### Materials

The polymeric substrates that were used in the LTCAT treatments consisted of 1-mm thick sheets of PC, POM, PMMA, nylon-6, and SR and 1.2 mm thick sheets of PS, which were purchased from Goodfellow Cambridge Limited (Cambridge, England). The sheets were cut into 1 × 2 cm<sup>2</sup> pieces for the static sessile-drop contact angle measurements and 2 × 2.5 cm<sup>2</sup> for the dynamic Wilhelmy measurements. Prior to treatment, all samples were washed in a solution containing 5% detergent in de-ionized water, which was placed in an ultrasonic bath for 30 min. The samples were then thoroughly rinsed with de-ionized water, dried in ambient air for 1 day, and stored in a dry desiccator. The Ar and O<sub>2</sub> gases were obtained from Praxair (St. Louis, Missouri). The water vapor consisted of de-ionized water obtained from treating in-house distilled water through a Culligan de-ionization system.

### LTCAT treatments

The LTCAT system consisted of an arc generator that created a plasma jet into a vacuum chamber. Previous publications have presented detailed schematics and operational procedures of LTCAT.<sup>18,19</sup> The arc generator contained a narrow gas channel formed by a series of copper disks that were connected by polymer insulators. The vacuum chamber was pumped down to the base pressure of 1 mTorr before each treatment. The arc generator was cooled to 10°C prior to starting each experiment. Ar flowed through the narrow channel at a rate of 1000 sccm and direct current was supplied to ignite the discharge. Steady discharges were created within seconds of ignition. The electric field was confined to the arc generator and the species in the glow discharge stream consisted of ground-state neutral species, electronically excited neutral species, Ar<sup>\*</sup>, and a low density of positive ions and electrons. For some trials, reactive gases were added to plasma jet, and were then activated and dissociated by the electronically excited Ar<sup>\*</sup> species.

Single samples were placed on a substrate clip at the end of a sliding bar that could be moved into and out of the plasma jet. To complete plasma treatment, the polymer samples were immersed in the plasma jet for a preset treatment time. For static con-

TABLE I  
Chemical Structures and Surface Contact Angles of the Untreated Polymers:  
Polystyrene (PS), Polymethylmethacrylate (PMMA), Polyoxymethylene (POM),  
Polycarbonate (PC), Silicone Rubber (SR), and Nylon-6

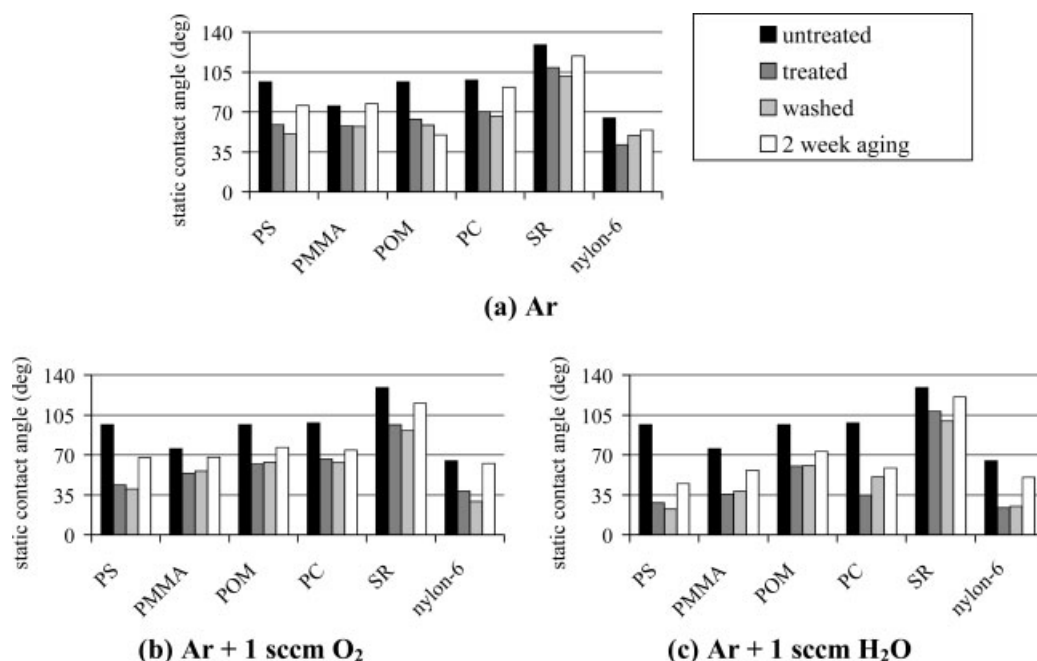
Polymer	Repeating unit	Static contact angle (°)
PS	$\begin{array}{c} \text{H} \\   \\ \text{---CH}_2\text{---C---} \\   \\ \text{C}_6\text{H}_5 \end{array}$	97 ± 3.1
PMMA	$\begin{array}{c} \text{CH}_3 \\   \\ \text{---CH}_2\text{---C---} \\   \\ \text{C=O} \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array}$	75 ± 2.7
POM	$\text{---CH}_2\text{---O---}$	97 ± 2.9
PC	$\begin{array}{c} \text{CH}_3 \\   \\ \text{---C---} \\   \\ \text{CH}_3 \end{array} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{---O---(C=O)---O---} \end{array}$	98 ± 1.5
SR	$\begin{array}{c} \text{CH}_3 \\   \\ \text{---O---Si---O---} \\   \\ \text{CH}_3 \end{array}$	129 ± 2.8
Nylon-6	$\text{---NH---(C=O)---(CH}_2\text{)}_5\text{---}$	65 ± 1.8

tact angle measurements, each type of polymer was LTCAT treated under 21 sets of experimental conditions, which include varied plasma exposure time and three different reactive gas flow rates for oxygen (1 sccm, 2 sccm, and 7 sccm) and water vapor (1 sccm, 2 sccm, and 10 sccm). The experiments were performed in random order for each polymer.

#### Wettability and surface stability of polymeric surfaces

The wettability and surface stability of the polymers were determined using static and dynamic contact angle measurements. For the static analysis, a VCA 2500XE system (Advanced Surface Technologies, Billerica, MD) was used to place a sessile droplet of

0.3  $\mu\text{L}$  de-ionized water on the surface of the treated polymers and to obtain an optical image of the water droplet. The computer user manually traced the arc that was created by the droplet on the polymer surface and a computer program was used to calculate the two contact angles that the water made with the polymer surface. Six measurements for each sample were done and the average number was reported in this study. The experimental error for the static contact angle measurement was within  $\pm 3.0^\circ$  from the average value. The static contact angle measurements on LTCAT treated samples were immediately performed after the treatment. Then the samples were placed in an ultrasonic bath of de-ionized water for 4 min to allow any surface oligomers or LMWOMs, if present, to wash away. The samples were then hung



**Figure 1** The average static contact angles of the polymers treated with (a) Ar LTCAT, (b) Ar LTCAT + 1 sccm O<sub>2</sub>, and (c) Ar LTCAT + 1 sccm H<sub>2</sub>O. Measurements were obtained from the untreated polymers (black), immediately after treatment (dark gray), after washing in DI water and drying in ambient air (light gray), and after aging in ambient air for 2 weeks (white). The other treatment conditions were 1000 sccm Ar, 4.0 A arc current, and 2 s treatment time.

dry in ambient air for 10 min before performing another contact angle measurement. Static surface analysis was also performed at different aging times after treatment to examine any hydrophobic recovery of the treated surfaces. The results of the static analysis were used to determine suitable treatment conditions for each polymer that would be used for the dynamic surface analysis.

Dynamic surface analysis was performed on samples treated using the treatment conditions chosen for each polymer based on the static contact angle data. The Wilhelmy balance method was used with a Sigma 70 tensiometer (KSV Instruments, Helsinki, Finland) that measured the force exerted on the treated sample during immersion and emersion in de-ionized water. The data obtained can be used to determine dynamic contact angles, along with intrinsic hysteresis, which is an indication of mobile surface moieties, and overshooting between cycles, which indicates the presence of LMWOM. A detailed description of the method is presented in a previous publication.<sup>6</sup>

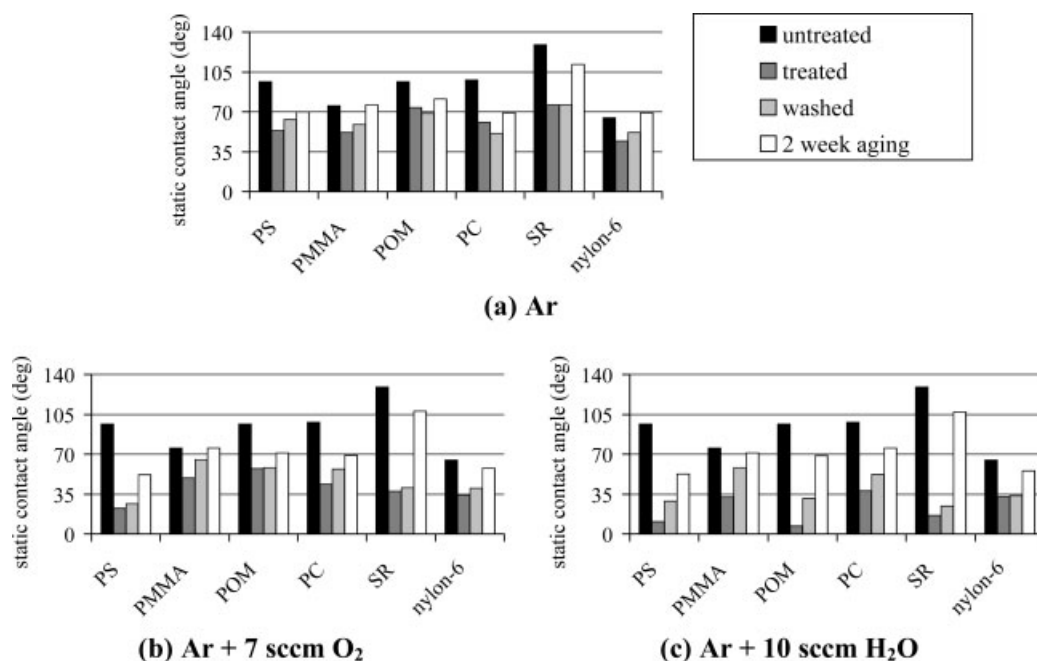
## RESULTS AND DISCUSSION

### Static contact angles of LTCAT-treated polymers

Static contact angle measurements were obtained from the samples that were treated using exposure times of 2, 5, and 10 s for Ar LTCAT, Ar LTCAT +

O<sub>2</sub> with O<sub>2</sub> flow rates of 1, 2, and 7 sccm, and Ar LTCAT + H<sub>2</sub>O with H<sub>2</sub>O flow rates of 1, 2, and 10 sccm. Thus, a total of 21 treatments were performed for each polymer and the measurements were conducted on each treated specimen before and after washing and after aging in ambient air for 2 days, 1 week, and 2 weeks. The static contact angle measurements were used to examine the effects of the LTCAT treatments on the surface wettability, surface damage from oligomer formation, and hydrophobic recovery of the treated polymers. The complete results from the static contact angle analysis are given in the Appendix of reference,<sup>20</sup> while some of the results are presented below. From the static contact angle results, three sets of suitable treatment conditions were determined for each polymer for Ar LTCAT, Ar LTCAT + O<sub>2</sub>, and Ar LTCAT + H<sub>2</sub>O. The conditions were chosen based on a high degree of wettability achieved with minimized surface damage. Samples were then treated under the chosen conditions and analyzed using the Wilhelmy balance method. Table I summarizes the polymer structures and the measured static contact angles of the untreated polymers.

The results from the static contact angle measurements on LTCAT-treated polymers are summarized in Figures 1 and 2. Figure 1 contains the treatments using the shortest treatment time (2 s) and the lowest reactive gas addition flow rates, when applied (1 sccm O<sub>2</sub> or 1 sccm H<sub>2</sub>O), and Figure 2 contains



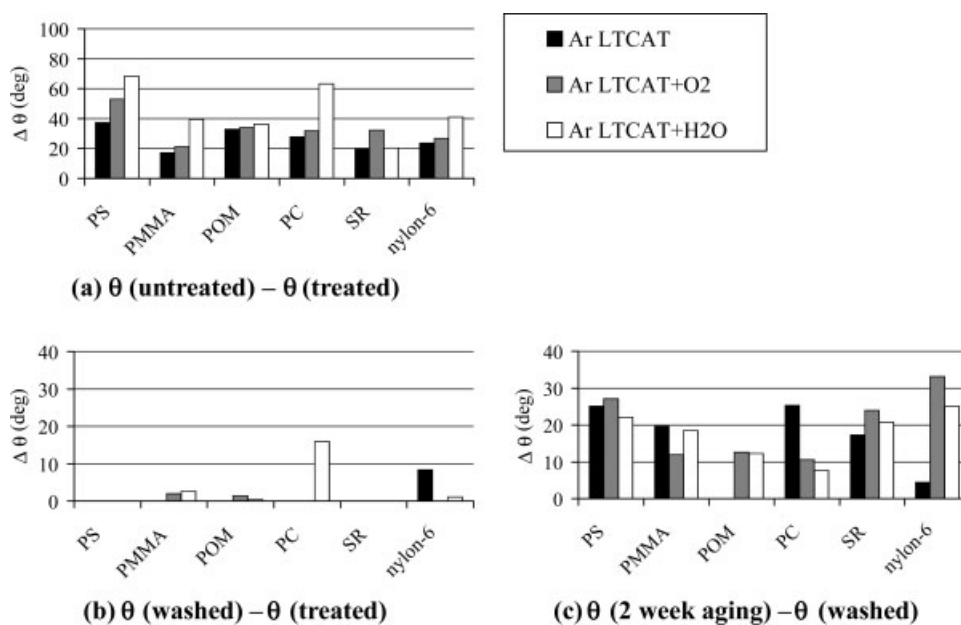
**Figure 2** The average static contact angles of the polymers treated with (a) Ar LTCAT, (b) Ar LTCAT + 7 sccm O<sub>2</sub>, and (c) Ar LTCAT + 10 sccm H<sub>2</sub>O. Measurements were obtained from the untreated polymers (black), immediately after treatment (dark gray), after washing in DI water and drying in ambient air (light gray), and after aging in ambient air for 2 weeks (white). The other treatment conditions include 1000 sccm Ar, 4.0 A arc current, and 10 s treatment time.

the results from the longest treatment time (10 s) and the highest reactive gas addition flow rates, when applied (7 sccm O<sub>2</sub> or 10 sccm H<sub>2</sub>O).

The effects of the reactive gas addition on the different types of polymers are further elucidated in Figures 3 and 4, the data of which were obtained by manipulation of the data from Figures 1 and 2, respectively. The extent of wettability change is presented in Figures 3(a) and 4(a), which contain the contact angle differences between each treated sample and the corresponding untreated polymer. The degree of surface damage is given in Figures 3(b) and 4(b), which contain the contact angle differences between each washed/dried sample and the corresponding treated sample. The extent of hydrophobic recovery was examined by calculating the contact angle differences between each aged sample and the corresponding washed/dried sample, which are shown in Figures 3(c) and 4(c). The extent of hydrophobic recovery can also be gauged by the static contact angle difference between the aged sample and the untreated polymer as shown in Figures 1 and 2. It should be noted that both previous observations should be used to assess hydrophobic recovery; in some cases, the value in Figures 3(c) or 4(c) is relatively low, but the contact angle after 2 weeks has been completely restored to the value of the untreated polymer, that is, complete hydrophobic recovery occurred.

From Figures 1–4, some general trends can be observed regarding the Ar LTCAT treatments and

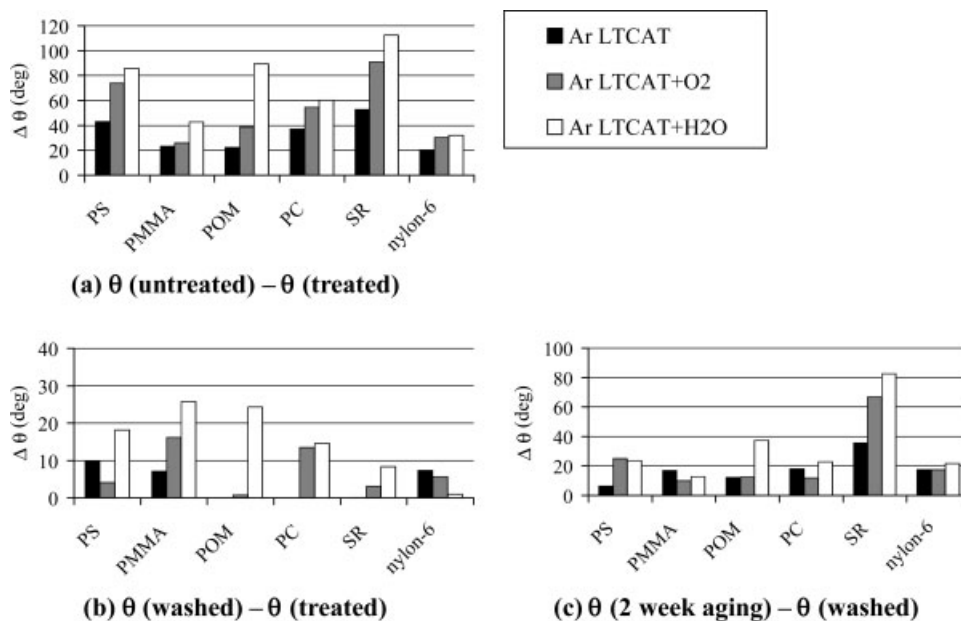
those with reactive gas addition. As shown from Figure 1(a), a short treatment of 2 s by Ar LTCAT typically improved the wettability of the polymers without surface damage (except for nylon-6, which showed certain surface damages because of the hydrophobic recovery after washing). The excellent surface stability that was observed for most of the polymers indicates that the CASING effect induced during Ar LTCAT treatments can occur on various polymeric surfaces. The LTCAT treatments with H<sub>2</sub>O vapor addition were the most effective in enhancing wettability immediately after treatment, followed by the Ar LTCAT + O<sub>2</sub> treatments, and then the Ar LTCAT treatments. However, the extent of surface damage on the treated polymers also followed a similar trend, in which the H<sub>2</sub>O vapor addition induced the most surface damage, followed by O<sub>2</sub> addition, and then Ar LTCAT (with mostly no damage for 2 s treatment time). In most cases, increasing treatment time or reactive gas flow rate enhanced wettability, but also increased surface damage. Some of the high energy species that react with the polymer during LTCAT treatments, including ions, could induce chain scission and overexposure to them could enhance the degradation effects, resulting in significant surface oligomer formation. Furthermore, the addition of oxygen-containing reactive gases would enhance the reaction mechanisms that lead to the alkoxy degradation reaction in Reaction (1) and subsequent chain scission.



**Figure 3** The differences in static contact angles,  $\Delta \theta$ , of the polymers treated with Ar LTCAT (black), Ar LTCAT + 1 sccm O<sub>2</sub> (gray), and Ar LTCAT + 1 sccm H<sub>2</sub>O (white) with 2 s treatment time. For (a), a higher value represents greater wettability enhancement. The degree of surface damage is evaluated in (b), in which a higher value indicates greater surface damage from LMWOM formation. The chart in (c) gives the extent of hydrophobic recovery, in which a higher value represents greater hydrophobic recovery. The other treatment conditions were 1000 sccm Ar and 4.0 A arc current.

Although generalizations were observed regarding the effects of the LTCAT treatments on all of the polymers, the LTCAT treatments affected each polymer in a different manner and those distinctions are

discussed below. PS is a polymer that has exhibited relative resistance to degradation during plasma treatments.<sup>11,13,15</sup> The LTCAT treatments of PS enhanced the wettability very greatly and the treated



**Figure 4** The differences in static contact angles,  $\Delta \theta$ , of the six types of polymers treated with Ar LTCAT (black), Ar LTCAT + 7 sccm O<sub>2</sub> (gray), and Ar LTCAT + 10 sccm H<sub>2</sub>O (white) with 10 s treatment time. For (a), a higher value represents greater wettability enhancement. The degree of surface damage is evaluated in (b), in which a higher value indicates greater surface damage from LMWOM formation. The chart in (c) gives the extent of hydrophobic recovery, in which a higher value represents greater hydrophobic recovery. The other treatment conditions were 1000 sccm Ar and 4.0 A arc current.

**TABLE II**  
**Treatment Times and Gas Flow Rates Used for Ar LTCAT, Ar LTCAT + O<sub>2</sub>, and Ar LTCAT + H<sub>2</sub>O Treatments of the Polymers**

Polymer	Ar LTCAT treatment time (s)	Ar LTCAT + O <sub>2</sub>		Ar LTCAT + H <sub>2</sub> O	
		O <sub>2</sub> flow rate (sccm)	Treatment time (s)	H <sub>2</sub> O flow rate (sccm)	Treatment time (s)
PS	2	7	2	10	2
PMMA	2	1	2	1	2
POM	2	1	2	1	2
PC	10	1	5	10	5
SR	15	2	5	1	5
Nylon-6	2	1	2	2	2

The other treatment conditions were 1000 sccm Ar and 4.0 A current.

PS samples exhibited resistance to damage with shorter treatment times and lower reactive gas flow rates. Slight damage was induced on PS surfaces using longer treatment times and higher reactive gas flow rates, with moderate hydrophobic recovery in all cases.

PMMA is a polymer that degrades easily in a plasma environment.<sup>13,14</sup> Ar LTCAT treatments of PMMA, however, enhanced the surface wettability without surface damage using 2 s treatment time, but hydrophobic recovery was nearly complete after 2 weeks aging for most of the conditions. Thus, for application of Ar LTCAT to PMMA, such as for adhesion to another surface, the treated PMMA should be applied immediately after surface treatment due to its short lifetime. PMMA was very sensitive to degradation using higher treatment times and addition of reactive gas, especially at greater flow rates, which induced significant surface damage.

POM can be etched into volatile species very readily in a plasma environment,<sup>5</sup> but compared with other polymers, has shown relative resistance to the formation of LMWOMs in O<sub>2</sub> and H<sub>2</sub>O vapor plasmas. During LTCAT treatments, POM exhibited resistance to surface degradation in Ar LTCAT and Ar LTCAT + O<sub>2</sub>, with exception of a longer treatment in Ar LTCAT + H<sub>2</sub>O shown in Figure 2(c). No C—C bonds are present in the POM polymer chain, so the alkoxy degradation reaction could not occur. Thus, the surface oligomer formation induced during longer treatment times and higher reactive gas flow rate was due to other reaction pathways that lead to chain scission, such as effects from high energy ions. Hydrophobic recovery for POM was moderate after 2 weeks of aging in ambient air for all of the treatment conditions examined.

PC treated by Ar LTCAT exhibited enhanced wettability and surface stability, with no damage observed for all treatment times. For PC treated with Ar LTCAT with reactive gas addition, some surface damages occurred for the higher O<sub>2</sub> flow rates and for all of the H<sub>2</sub>O vapor treatments. The hydropho-

bic recovery of LTCAT-treated PC was moderate after aging for 2 weeks in ambient air.

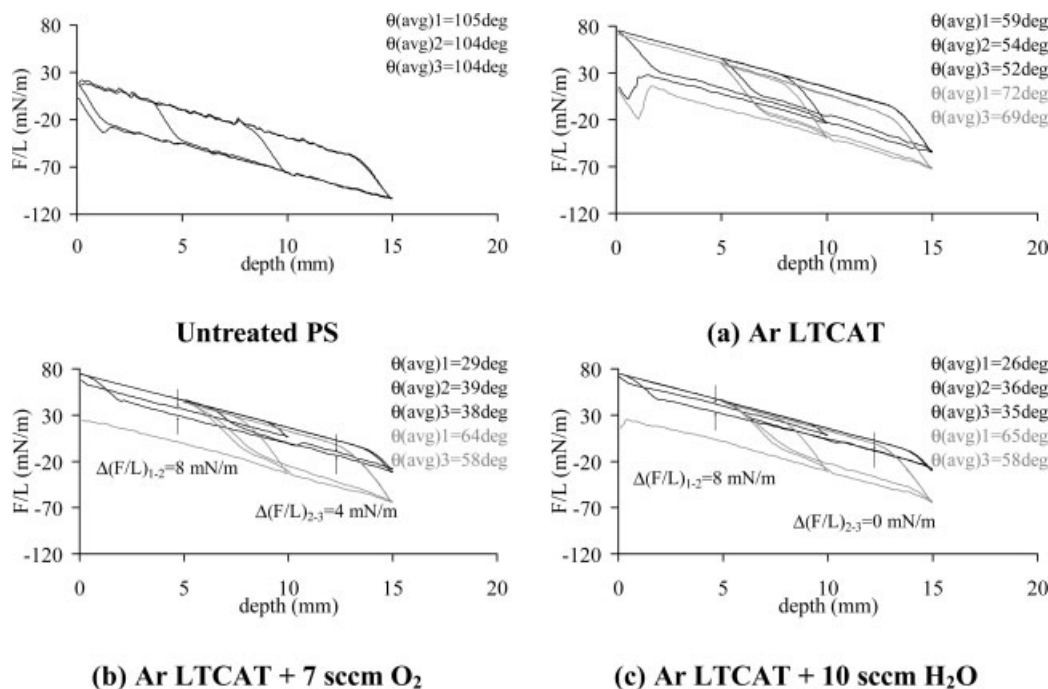
SR demonstrated great enhancement in wettability from LTCAT treatments using longer treatment times and higher reactive gas flow rates. Although the surface damage induced on SR was generally low, hydrophobic recovery was very high and nearly complete for all treatments, which can be seen from Figures 1 and 2. Thus, the lifetime of LTCAT-treated SR was very short, which must be considered when applying LTCAT treatments to SR surfaces.

The surface of nylon-6 is hydrophilic and the LTCAT treatments lowered the contact angle even further, but not to the extent of some of the other polymers. In addition, LTCAT treatments of nylon-6 induced surface damage for most of the conditions and nearly complete hydrophobic recovery occurred after aging for 2 weeks for most of the conditions applied.

#### Wilhelmy data comparison of LTCAT-treated polymers

Wilhelmy analysis was performed on each polymer treated with Ar LTCAT, Ar LTCAT + O<sub>2</sub>, and Ar LTCAT + H<sub>2</sub>O using the conditions chosen from the static contact angle analysis, which are given in Table II. The conditions were chosen based on the enhancement of wettability achieved and the surface stability. Figures 5–10 contain the Wilhelmy force loops for all six polymers, along with the advancing contact angles of the samples that were obtained immediately after treatment (black) and after aging in ambient air for 2 weeks (gray). Overshooting, when present, is indicated by the difference between the average force/length for subsequent cycles,  $\Delta F/L$  (mN/m).

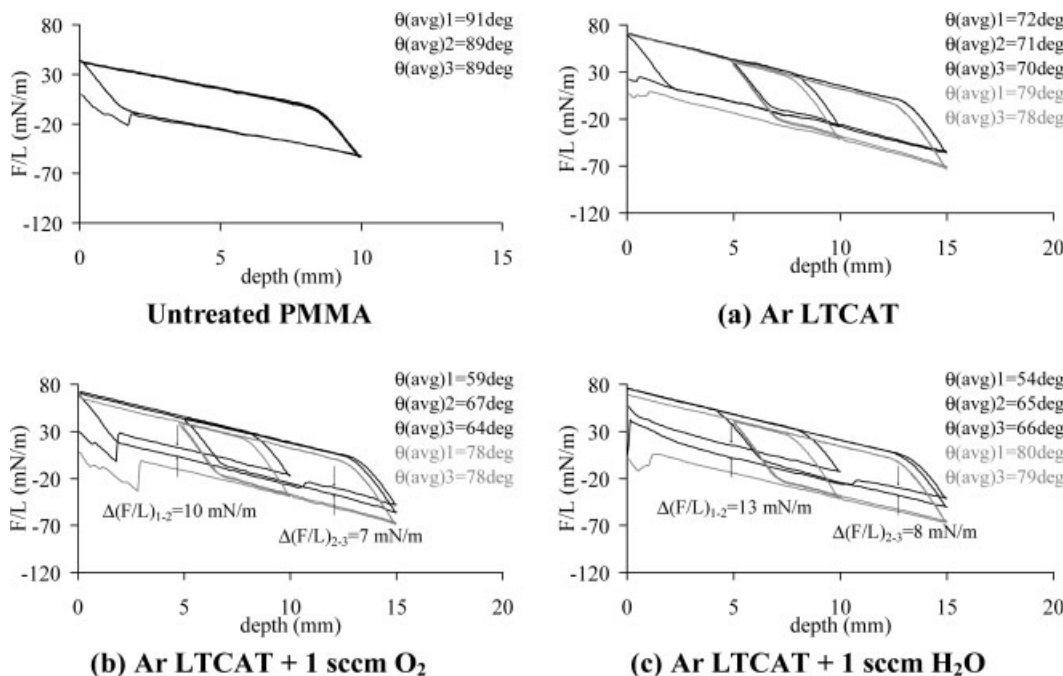
The Ar LTCAT treatments, in general, enhanced the surface wettability and produced stable surfaces with relatively low hydrophobic recovery, compared with the reactive gas addition treatments. The exception is nylon-6 in Figure 10, which exhibited overshooting for all treatments. Figure 11 contains the advancing contact angles that were obtained from



**Figure 5** The Wilhelmy force loops of untreated PS and Ar-LTCAT treated PS with (a) no reactive gas addition, (b) O<sub>2</sub> addition, and (c) H<sub>2</sub>O vapor addition. 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 ambient air. The other treatment conditions were 1000 sccm Ar, 4.0 A arc current, and 2 s treatment time.

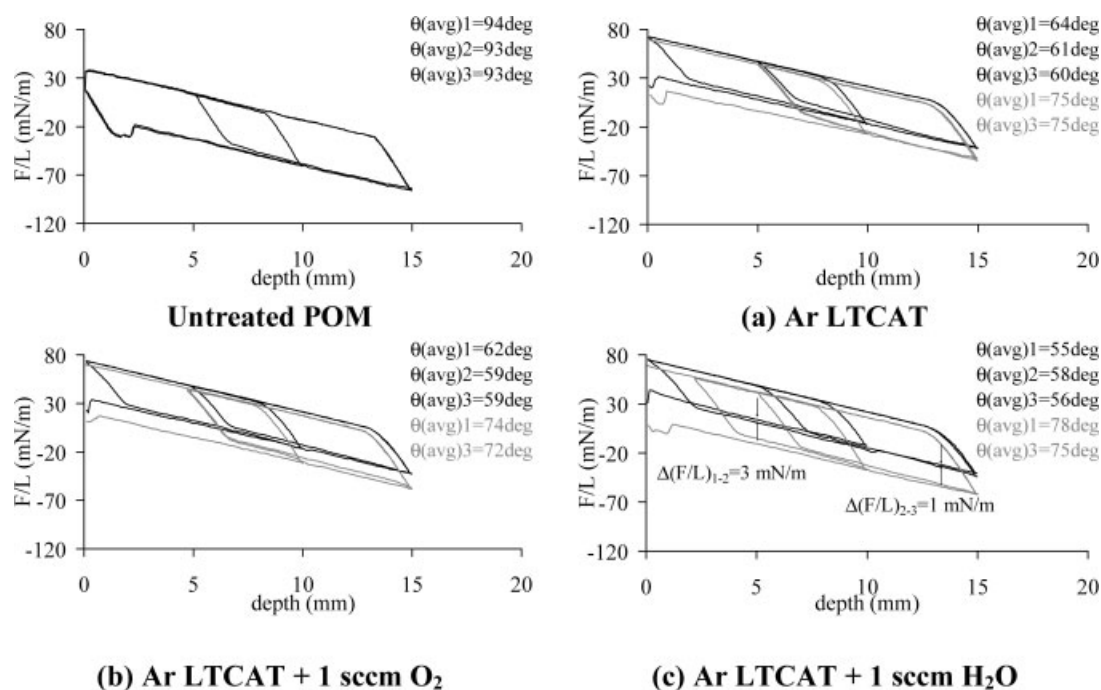
the Wilhelmy force loops of the untreated polymers (black), Cycle 1 of the treated polymers (dark gray), Cycle 2 of the treated polymers after drying in ambi-

ent air for 10 min (light gray), and Cycle 1 of the treated polymers after aging in ambient air for 2 weeks.



**Figure 6** The Wilhelmy force loops of untreated PMMA and Ar LTCAT-treated PMMA with (a) no reactive gas addition, (b) O<sub>2</sub> addition, and (c) H<sub>2</sub>O vapor addition. 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 ambient air. The other treatment conditions were 1000 sccm Ar, 4.0 A arc current, and 2 s treatment time.

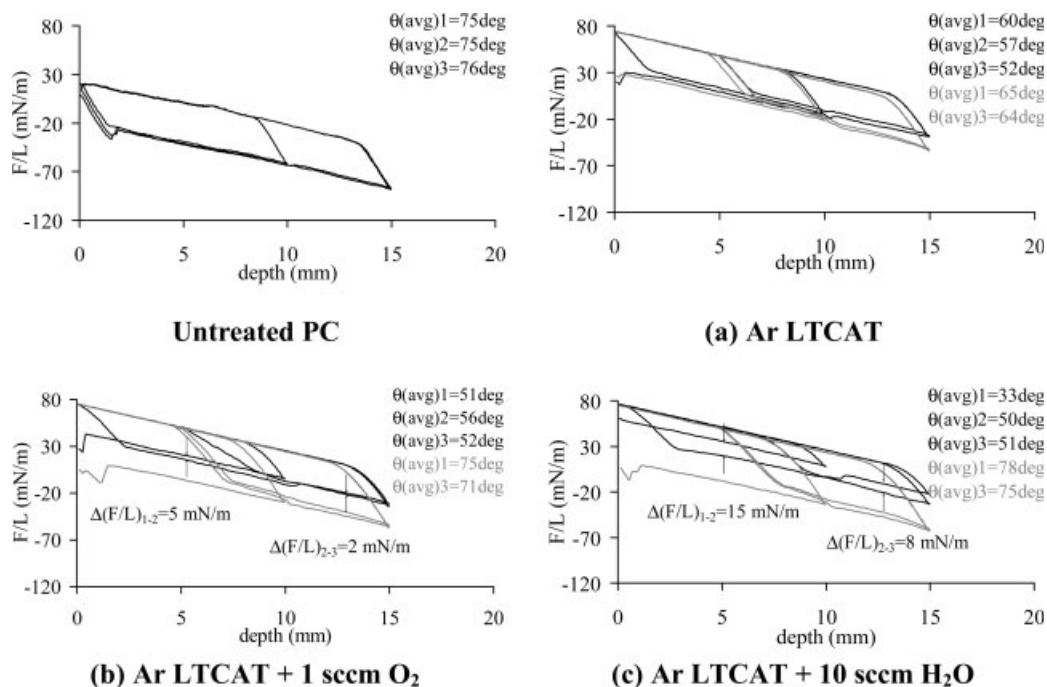




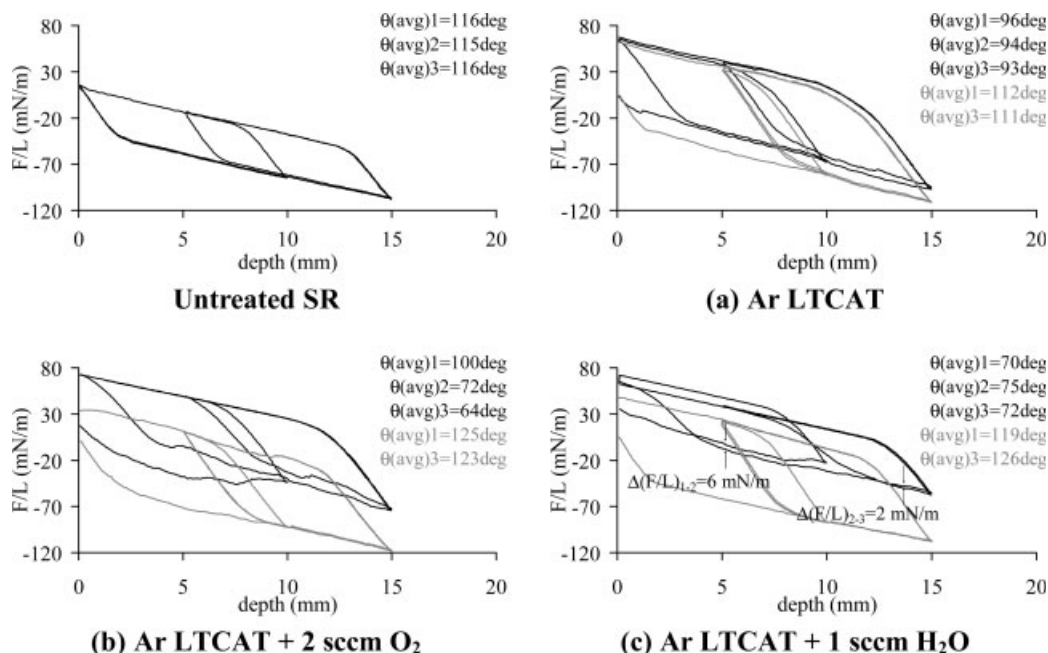
**Figure 7** The Wilhelmy force loops of untreated POM and Ar LTCAT-treated POM with (a) no reactive gas addition, (b) O<sub>2</sub> addition, and (c) H<sub>2</sub>O vapor addition. The black lines show the force loops obtained immediately after treatment and the gray lines show the force loops obtained after 2 weeks of aging in ambient air. The other treatment conditions were 1000 sccm Ar, 4.0 A arc current, and 2 s treatment time.

Figure 12 contains a comparison of the extent of intrinsic hysteresis and overshooting that was exhibited by the treated polymers, which was calculated

by subtracting the average of  $F/L$  in the advancing stage of Cycle 2 from the average  $F/L$  in the advancing stage of Cycle 1. Positive values indicate that



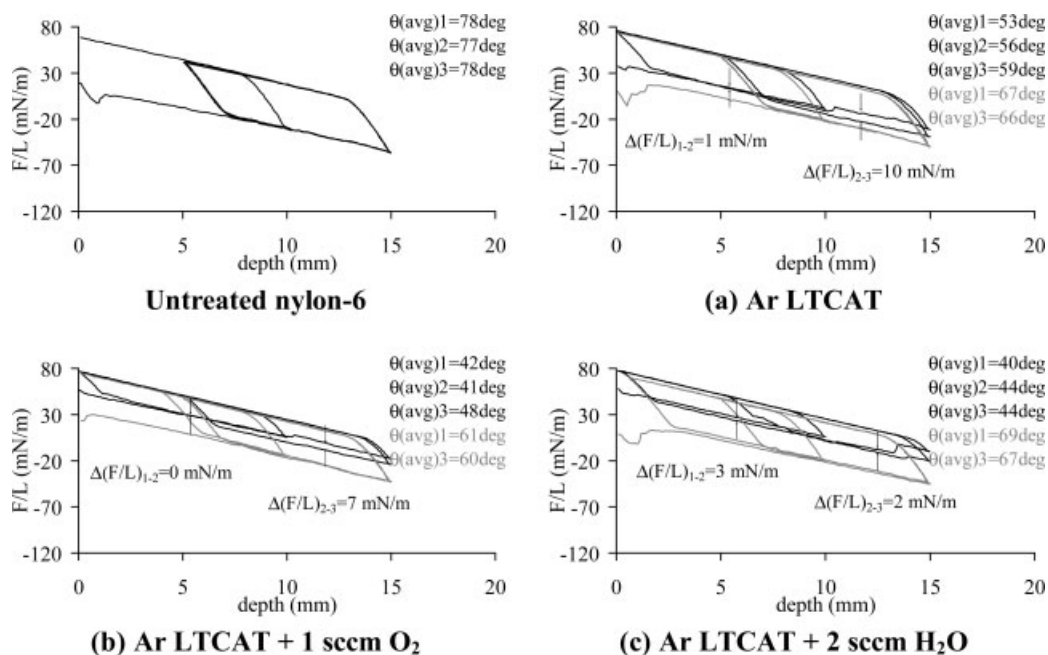
**Figure 8** The Wilhelmy force loops of untreated PC and Ar LTCAT-treated PC with (a) no reactive gas addition and 10 s treatment time, (b) O<sub>2</sub> addition and 5 s treatment time, and (c) H<sub>2</sub>O vapor addition and 5 s treatment time. The black lines show the force loops obtained immediately after treatment and the gray lines show the force loops obtained after 2 weeks of aging in ambient air. The other treatment conditions were 1000 sccm Ar and 4.0 A arc current.



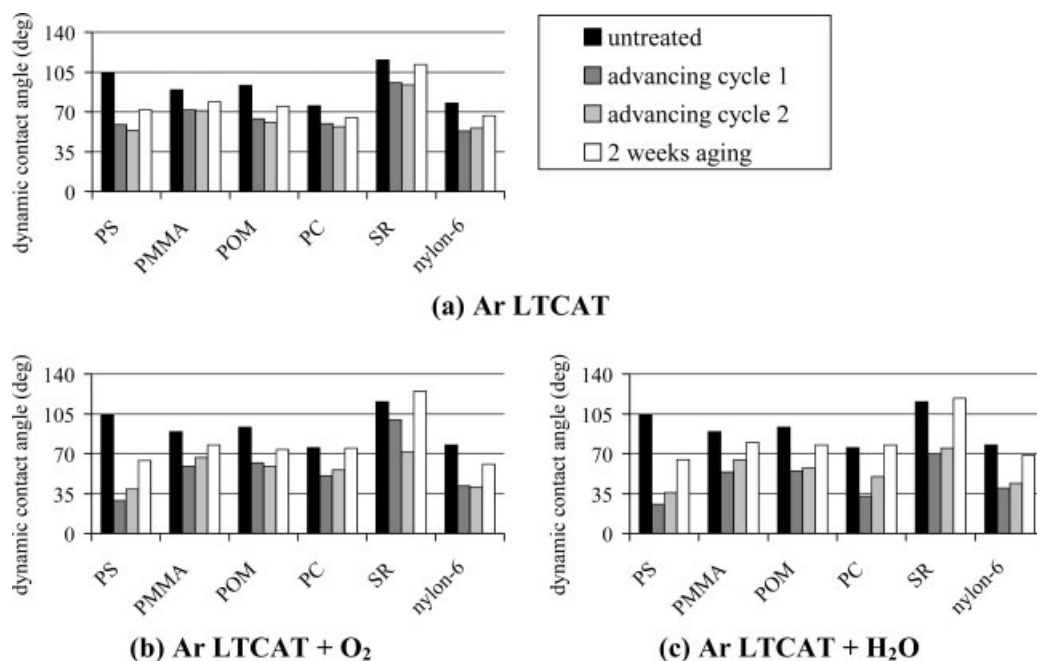
**Figure 9** The Wilhelmy force loops of untreated SR and Ar LTCAT-treated SR with (a) no reactive gas addition and 15 s, (b) O<sub>2</sub> addition and 5 s, and (c) H<sub>2</sub>O vapor addition and 5 s. The black lines show the force loops obtained immediately after treatment and the gray lines show the force loops obtained after 2 weeks of aging in ambient air. The other treatment conditions were 1000 sccm Ar and 4.0 A arc current.

intrinsic hysteresis was present due to mobility of surface moieties and negative values correspond to overshooting from washing away of surface oligomers or LMWOMs during the first immersion. Ar LTCAT-treated PS, POM, PC, and SR exhibited

higher surface mobility, in comparison with the others. Interestingly, Ar LTCAT-treated PMMA exhibited the greatest surface stability without damage from oligomer formation. In a traditional plasma environment, volatile species that are ablated from



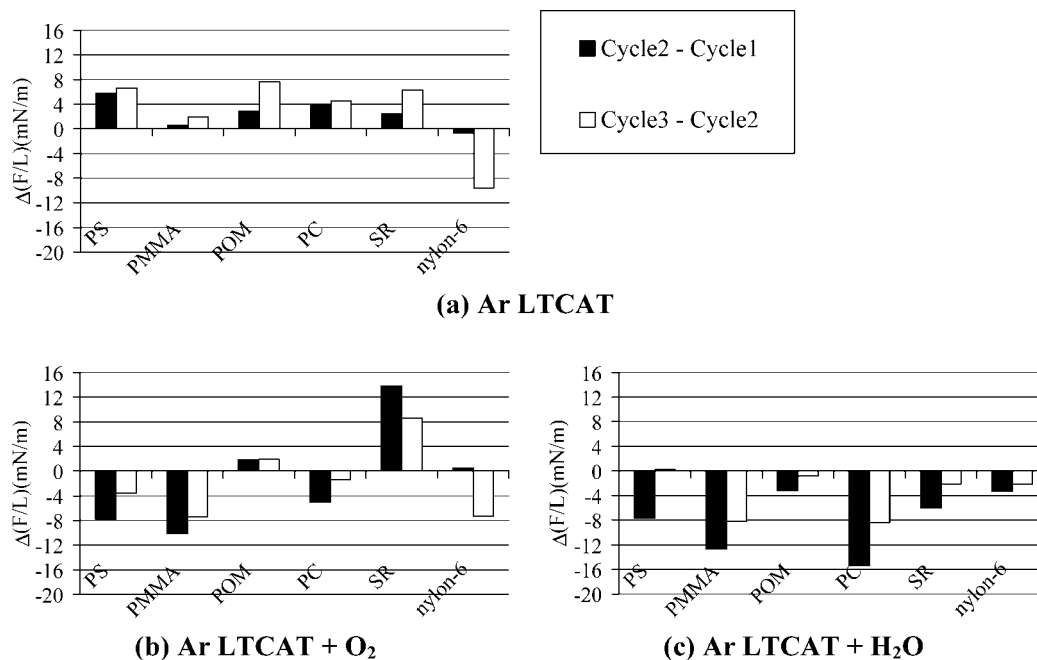
**Figure 10** The Wilhelmy force loops of untreated nylon-6 and Ar LTCAT-treated nylon-6 with (a) no reactive gas addition, (b) O<sub>2</sub> addition, and (c) H<sub>2</sub>O vapor addition. The black lines show the force loops obtained immediately after treatment and the gray lines show the force loops obtained after 2 weeks of aging in ambient air. The other treatment conditions were 1000 sccm Ar, 4.0 A arc current, and 2 s treatment time.



**Figure 11** The dynamic contact angles of the polymers treated with (a) Ar LTCAT, (b) Ar LTCAT + O<sub>2</sub>, and (c) Ar LTCAT + H<sub>2</sub>O using the conditions given in Table II. Measurements were obtained from the untreated polymers (black), 1<sup>st</sup> advancing Wilhelmy cycle of the treated samples (dark gray), 2<sup>nd</sup> advancing Wilhelmy cycle after drying for 10 min (light gray), and the 1<sup>st</sup> advancing Wilhelmy cycle after aging in ambient air for 2 weeks (white). The other treatment conditions were 1000 sccm Ar and 4.0 A arc current.

the substrate can contaminate the interface and subsequently react with the substrate. In the case of PMMA, oxygen atoms that are ablated from the

side-group can react with polymer chains to form alkoxy radicals and subsequently induce polymer chain scission. In LTCAT, however, the high flux of



**Figure 12** The differences in the average values of  $F/L$  (mN/m) for Wilhelmy cycles of the polymers treated with (a) Ar LTCAT, (b) Ar LTCAT + O<sub>2</sub>, and (c) Ar LTCAT + H<sub>2</sub>O using the conditions given in Table II. The  $\Delta(F/L)$  values were calculated between cycle 2 and cycle 1 (black), in which the polymer sample was allowed to dry in ambient air for 10 min between the cycles. The  $\Delta(F/L)$  values between cycle 3 and cycle 2 (white) were obtained without a break in motion. A positive value represents intrinsic hysteresis, while a negative value indicates that LMWOM was removed from the treated sample surface between cycles. The other treatment conditions were 1000 sccm Ar and 4.0 A arc current.

neutral species that are directed to the polymer surface can eliminate the contamination by ablated species. Thus, treatment of PMMA by Ar LTCAT minimizes surface contamination and damage from ablated species and results in a stable surface at a lower treatment time (2 s). Nylon-6 is the only polymer in this study that exhibited overshooting after Ar LTCAT treatment.

The dynamic surface analysis results also show that the reactive gas addition treatments were more effective in increasing the polymer surface wettability, especially for H<sub>2</sub>O vapor treatments. However, surface damage was also significantly induced by reactive gas addition and generally was highest for H<sub>2</sub>O vapor addition. As mentioned previously, reactive gas addition can enhance LMWOM formation through the production of alkoxy radicals and subsequent chain scission. PMMA exhibited the highest overshooting for O<sub>2</sub> addition and the second highest for H<sub>2</sub>O vapor addition among the treated polymers. It should be noted that the lowest reactive gas flow rates and treatment times were used for PMMA and POM, unlike the other polymers. Thus, even using very low flow rates of O<sub>2</sub> and H<sub>2</sub>O, PMMA underwent significant degradation from oligomer formation. PS, which showed resistance to degradation at lower reactive gas flow rates and treatment times from the static analysis, exhibited overshooting at the higher reactive gas flow rates. Based on the static contact angle results, decreasing the reactive gas flow rates for treatment of PS decreased and eliminated the surface damage. POM showed relative resistance to degradation from LMWOM formation with reactive gas addition and exhibited no overshooting from the oxygen addition treatment. SR also showed some resistance to oligomer formation; however, the polymer is not rigid and did not completely hold its shape during the Wilhelmy cycles. Thus, the Wilhelmy data for SR contains an added degree of error.

## CONCLUSIONS

Ar LTCAT is an energetically mild and effective surface treatment technique that can be applied to various polymers to enhance wettability without surface degradation from LMWOM formation, while maintaining good surface stability. The exception in this study was nylon-6, which was damaged under all treatment conditions. The excellent wettability and surface stability was attributed to the CASING effect combined with the quenching of unreacted surface free radicals upon atmospheric exposure, which resulted in the formation of new hydrophilic functional groups anchored to stable, crosslinked surfaces. Most of the polymers exhibited some extent of

surface damage at longer treatment times, which was ascribed to overexposure to high-energy species that induce chain scission and polymer degradation.

The addition of oxygen and water vapor to Ar LTCAT significantly enhanced the polymer wettability, but at the cost of greater surface damage from LMWOM formation. The enhanced surface damage was attributed to an increase in alkoxy degradation reactions from the surface reactions with oxygen-containing plasma species, in most cases. Shorter treatment times and lower reactive gas flow rates generally resulted in a decrease in surface damage. However, each polymer exhibited different treatment effects during LTCAT treatments and the treatments should be optimized separately for each polymer and application. Hydrophobic recovery occurred to some extent on all of the polymers treated by LTCAT. Thus, the lifetime of a treated polymer surface must be considered when applying LTCAT to any polymer.

The surface of PS was readily modified by LTCAT and was resistant to degradation at shorter treatment times and lower reactive gas flow rates. In addition, LTCAT-treated PS surfaces exhibited relatively low hydrophobic recovery. Ar LTCAT treatment of PMMA with 2 s treatment time resulted in wettability enhancement and high surface stability, as indicated by the lowest amount of intrinsic hysteresis. However, PMMA was the most susceptible to degradation with the reactive gas addition treatments. In addition, LTCAT-treated PMMA surfaces exhibited pronounced hydrophobic recovery. POM generally exhibited resistance to degradation from LMWOM formation during Ar LTCAT and Ar LTCAT + O<sub>2</sub> treatments, but not using Ar LTCAT + H<sub>2</sub>O. PC had a moderate enhancement of wettability with good surface stability. SR was readily modified by LTCAT, but the treated surfaces had low lifetimes with very high hydrophobic recovery. Nylon-6 experienced surface damage from all of the LTCAT treatments.

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