

Investigation of Dow Cyclotene 4026 Surface Amination by Downstream Plasma Treatment

Lijiang Wang, Gregory Raupp

Department of Chemical & Material Engineering, Arizona State University, Tempe, Arizona 85287-6006

Received 14 May 2004; accepted 8 November 2004

DOI 10.1002/app.21948

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Dow Cyclotene 4026 surfaces were treated by downstream ammonia cold plasma with and without argon plasma pretreatments. The modified polymer surfaces were characterized by X-ray photoelectron spectroscopy, Fourier transform infrared-attenuated total reflection, and atomic force microscopy (AFM). A 2^{4-1}_{IV} fractional factorial design was developed to identify the optimal processing parameters. Further experimental investigation has also been conducted to optimize the operating conditions. The combined results show that the extent of surface amination of Cyclotene grows with increase of power, pressure, and temperature of ammonia plasma treatments both with and without argon plasma pretreatments. For the treatment time effect, the results indicate that N/C (nitrogen/carbon) ratios increase with time and then start to slightly decrease at the

~4-min point, which may be tentatively explained by a competition between the modification process and the degradation process on the polymer surfaces. AFM results suggest that the upper limit of the operating condition to obtain a desirable surface topography is 175°C. Based on all the results from Design of Experiment, experimental data, and AFM analysis, the optimum processing parameters have been suggested. Finally, the aging effect of aminated surfaces is discussed; further investigation of this effect is still underway. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2418–2427, 2005

Key words: cold plasma; surface amination; cyclotene; atomic force microscopy (AFM); aging

INTRODUCTION

Polymers have become widely accepted for *in vivo* and *in vitro* medical applications. Many of these materials have properties that lend themselves well to the manufacture of medical appliances or devices. Moreover, polymers are easily molded or formed into complex shapes and bulk physical properties may be selected from a wide range of parameters such as rigidity and temperature stability. Unfortunately, fabrication procedures that require bonding are difficult to achieve, and biological interface reactions within the body or in the laboratory can limit their *in vivo* and *in vitro* performance.

Plasma preparation of polymer substrates to enhance adhesion to the polymer surface is a proven technology¹ that has been used to attach biomolecules to substrates.^{2,3} This work has focused on surface amination using a downstream cold plasma apparatus.

Cyclotene has been widely used in various electronic packaging applications. This polymer is derived from B-staged bisbenzocyclobutene chemistry and has excellent physical, chemical, and electrical properties,⁴

which include low dielectric constant, good processability, low moisture absorption (< 0.2 wt %), and good adhesion. However, for the designed optimization of the performance of Cyclotene in biomedical device application, the ability to fabricate specific surface compositions tailored to a particular application, e.g., providing stable hydrophilic surfaces, protein repelling surfaces, or surfaces suitable for cell culture, has caused an extensive attention. For example, in neural implantation application, molecules from the bioenvironment approach the polymer surface and experience interfacial forces due to electrostatic interactions. These interfacial forces act across extremely short distance; thus, only the chemical groups located within a few Angstroms of the surface of the polymeric material exert a significant influence across the interface toward the environment. So it becomes possible to optimize the device performance by modifying the interfacial interactions of polymers. Modifying the surface of a material by cold plasma technique can improve its biocompatibility without changing its bulk properties.

In search of the “ideal” polymeric material for microelectronic device applications, several researchers^{5–7} have reported their work relating to the reliability and/or the processability of Cyclotene. These reports have shown that Cyclotene is a high-performance and reliable material. However,

Correspondence to: L. Wang (lj.wang@asu.edu).

Contract grant sponsor: DARPA Bio-Info-Micro program.

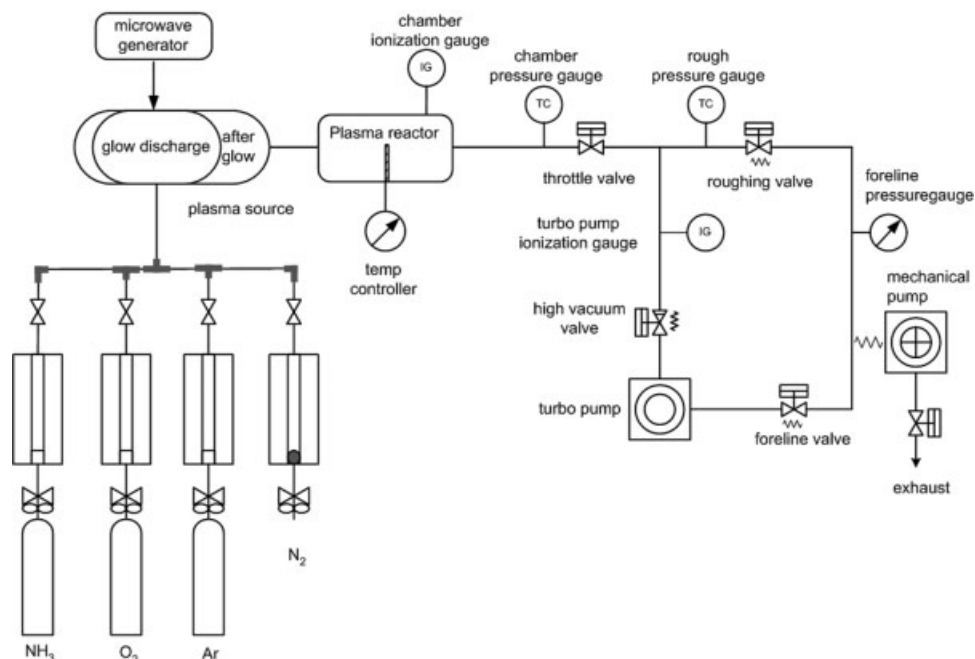


Figure 1 Schematic of the plasma reaction system.

informative work relating to Cyclotene surface amination using cold ammonia plasma is still lacking, and the investigation of the processing parameter optimization is even less due to the difficulty of process reproducibility and the thermal and chemical instability of modified Cyclotene surfaces. We have conducted the ammonia with/without argon plasma treatments on Cyclotene surfaces and have evaluated their performances in cell adhesion and spreading tests.⁸ This paper intends to obtain a desirable biocompatible surface that is stable and contains a controllable density of specific chemical groups by optimizing the operating conditions of plasma treatments, so that we can understand the fundamental biochemical basis for the improved performances.

EXPERIMENTAL

A downstream plasma system (schematically shown in Fig. 1) has been used to create a mixture of photons, electrons, ions, radicals, and atoms that have the potential to react with the substrate surfaces. For any gas composition, three simultaneous processes alter the outer molecular layers of the polymer: ablation, crosslinking, and activation (create functional groups). The effect of each depends on the chemical nature of the gas plasma, the polymer, and the processing parameters.

Materials

Cyclotene 4026–46 was obtained from Dow Chemical Company. Gases used for plasma treatment were of

commercial variety (NH₃ purity: class 4.5, Matheson gases; Ar purity: class 5, LIQUID AIR Corp.).

Sample preparation

The sample preparation procedure is the same as in our previous work.⁸ Immediately after cleaning, the sample was placed into a Specialty Coating Systems Model P-7608D programmable spin coater, and Dow AP3000 adhesion promoter was dispensed onto the sample surface using a clean, glass dropper bottle. After adhesion promoter application, the prewarmed Dow Cyclotene 4026–46 was dispensed onto the center of the sample surface; the spin program used was as follows: linear ramp to 800 rpm over 10 s; 800 rpm “spread” for 10 s; linear ramp to 2000 rpm over 10 s; 2000 rpm “spin” for 30 s; linear ramp to 0 rpm over 10 s. A typical postsoft-bake thickness of 13 μm was achieved using the 2000-rpm spin speed. Finally, the sample was transferred to a Thermco MB-80 Mini-brute furnace, where it was purged with N₂ at room temperature for 1 h to drive off all oxygen from the film; after the 1-h purge, the sample was cured in the inert atmosphere by rapidly raising the temperature to 250°C for 60 min (full cure for second Cyclotene layer).

Plasma system

The downstream plasma reactor (physical configuration is shown in Fig. 2) consists of a 2.54-GHz plasma source (ASTEX AX2000), 250-W microwave power generator, 4” stainless-steel chamber, and the pump-

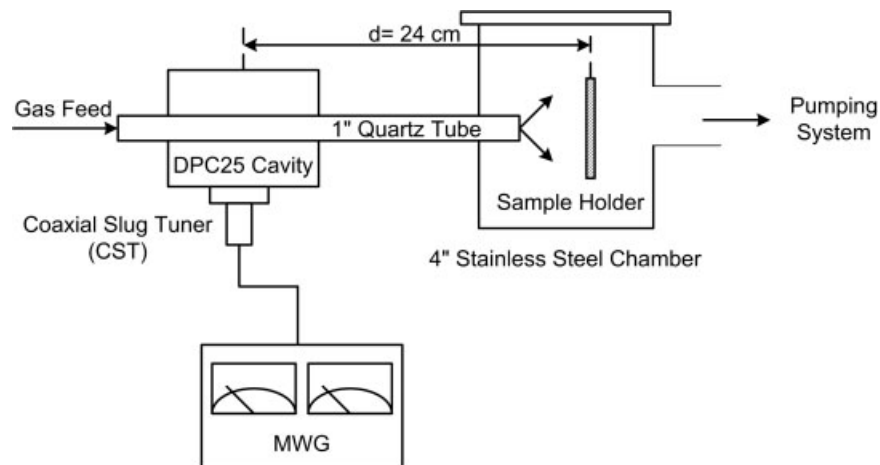


Figure 2 Schematic of the downstream reactor configuration.

ing system (a Pfeiffer/Balzers turbo pump TP180H backed by an Edwards E2M-18 two-stage mechanical pump). Typical base pressures are less than 7×10^{-7} Torr. Samples are mechanically mounted on an aluminum block. The argon and ammonia gases are introduced into the reactor through the mass flow meters (PFD-301), respectively. The plasma source is attached to a port on a 4-inch stainless-steel chamber by a 1-inch quartz tube. The distance d between the sample and the center of the discharge is 24 cm. In this way, all of the samples are downstream treated. Gas flows are controlled by using mass flow controllers over the 1–200 sccm range.

The major advantage of this type of system is the decreased number of excited state neutrals, ion reactions, and sputtering damage on surfaces treated by plasmas. While the plasma is a very efficient means to create new functions, this process is limited by the surface degradation, i.e., the bond breaking under the action of active species, which induces the loss of polymer fragments in the gas phase. The degradation rate is particularly high when the substrate is directly in the plasma because of the ion and electron bombardments. Therefore, whenever possible, the substrate is set in the flowing afterglow of the discharge to benefit from the functionalization while decreasing the degradation.^{9–12} Moreover, in the flowing afterglow, the substrate is reached only by long lifetime neutral species (at least microsecond lifetimes) and photons, and so only these species are expected to react with polymer surfaces. Therefore, it is easier to distinguish the effect of each active species and interpret the obtained results than directly in the plasma where the number of potentially active species is much higher and their synergy is not known.

Characterization techniques

Due to the complexity of the possible surface reactions with plasma treatment, a more comprehensive under-

standing of the surface chemistry requires the use of several surface-sensitive characterization techniques. In this study, the surface chemistry of the plasma aminated Cyclotene film was characterized with a combination of surface-sensitive spectroscopies: X-ray photoelectron spectroscopy (XPS), Fourier transform infrared-attenuated total reflection (FTIR-ATR), and atomic force microscopy (AFM).

XPS analyses were performed using a monochromatic Mg $K\alpha$ X-ray source (240 W). The take-off angle was 90° . The base pressure was 2×10^{-10} Torr and the pressure was 10^{-9} Torr while taking data. The infrared spectra were measured using a FTIR spectrometer (Bruker, IFS 66V/S) with the ATR attachment to obtain surface sensitive infrared-spectra. Typically 1024 scans with a resolution of 4 cm^{-1} were taken and coadded to get one spectrum. The samples were brought into contact with one side of the internal reflection element germanium (Ge) using an adjustable spring to ensure approximately the same pressures for all samples. In this paper, in addition to XPS and FTIR-ATR, the AFM technique was also used to monitor the surface topography of the modified Cyclotene surfaces.

The surface of a polymer used in a medical device is often the interface between the body and the device. By controlling the surface properties of the polymer, the medical device designer can enhance or inhibit various reactions of the body to the device. The interaction between the polymer and its environment depends in large part on surface composition and structure. Plasma treatments can produce the desired surface characteristics and topographies. Since surface composition and topography play such an important role in the performance of the polymer, precise surface characterization can be a large part in the rapid deployment of new materials or understanding of problems and behaviors in existing materials. AFM, with its high-resolution

TABLE I
Factors and Levels

	(A) Power (W)	(B) Pressure (torr)	(C) Treatment time (min)	(D) Temperature (°C)
Low level (-1)	50	0.2	1	Room temp.
Center point (0)	150	0.4	3	60
High level (1)	250	0.6	5	100

surface mapping capabilities, can be a key component of that characterization.

A NanoScope E MultiMode AFM (Veeco Digital Instruments, Santa Barbara, CA) and standard AFM cantilevers (Veeco Digital Instruments) with pyramidal Si_3N_4 tips were used to image surface structures of Cyclotene samples. The spring constant of the cantilevers employed for imaging was 0.12 Newtons per meter as reported by the manufacturer. The samples were imaged in air at room temperature. A 2×2 mm area was scanned at a rate of 4 Hz. The integral and proportional gain values were set to 2.0 and 3.0, respectively.

Experimental design

In this study, we experimentally investigated the efficiency of surface amination of Cyclotene using ammonia plasma with or without argon plasma pretreatment. A “one variable at a time” approach for experimentation would require a large number of experiments and yet may not provide a complete picture. In contrast, design of experiment (DoE) is a systematic, mathematically sound approach that uses fewer experiments, requires rigorous but easy-to-use analytical techniques, and yields more information such as second- or higher-order interactions. Thus, a two-level 2_{IV}^{4-1} fractional factorial (screening) experiment was conducted to identify significant factors and proper factor settings in the process of Cyclotene surface modification. The factors that may have effects on the amination of the surface are proposed as follows: microwave power, chamber pressure, treatment time, and sample temperature. The response character will be the efficiency of amination of Cyclotene surface, which is measured by XPS. The factors and levels are shown in Table I. This design is well suited for phenomenological modeling of measured responses as a

function of the four factors. Outside of this range, the limitations were either due to plasma source power delivery range, plasma stability, mass flow controller range, and accuracy or due to degradation of polymer.

The efficiency of amination of Cyclotene was measured by XPS analysis as the principal response.

In this experiment, we are interested in the extent of Cyclotene surface amination. The extent of amination is determined by XPS, which is a very sophisticated instrument to measure the ratio of N/C and binding energy. Thus, we take the ratio of N/C (efficiency of amination of Cyclotene) as the response measurement, which quantitatively represents the extent of amination of Cyclotene.

Considering all the limitations of surface amination experiments, we decided to apply a 2_{IV}^{4-1} fractional factorial design with single-replicate, two blocks, and two center points within each block. Design generator is $D = ABC$; block generator is $CD = AB$. The summary of this design is shown in Table II.

To minimize unintentional effects, every effort is made to keep the same intervals between treatment and XPS analysis. Due to the large amount of time required on XPS analysis, runs were performed on 2 different test days. Both the XPS analysis and the XPS operators were blocked in the design.

The result of the experiment will indicate which main effects and two-factor interactions are significant. The linear model provided by Design-Expert software will be given.

Microwave plasma treatment

Microwave plasma treatment took place at 2.45 GHz in a system described in the plasma system section. Gases used for plasma treatment were of commercial variety (NH_3 purity: class 4.5, Matheson gases; Ar purity: class 5, Liquid Air Corp.). For ammonia

TABLE II
Summary of Design

Experiment design	Block description	Number of runs
2_{IV}^{4-1} design	Block 1:	4 + 2
Two blocks	XPS analysis (test day 1)	
Single replicate	Block 2:	4 + 2
Two center points in each block	XPS analysis (test day 2)	
	Total run	12

TABLE III
Result of Matrix Design for Ammonia Plasma Treatments without Ar Pretreatments

Standard order	Run order	Block	A	B	C	D = ABC	Response: N/C ratio
4	1	Block 1	1	1	-1	-1	0.057
10	2	Block 1	0	0	0	0	0.040
6	3	Block 1	1	-1	1	-1	0.052
1	4	Block 1	-1	-1	-1	-1	0.026
9	5	Block 1	0	0	0	0	0.043
7	6	Block 1	-1	1	1	-1	0.035
8	7	Block 2	1	1	1	1	0.206
11	8	Block 2	0	0	0	0	0.036
5	9	Block 2	-1	-1	1	1	0.041
3	10	Block 2	-1	1	-1	1	0.018
12	11	Block 2	0	0	0	0	0.050
2	12	Block 2	1	-1	-1	1	0.086

plasma treatment, the plasma was maintained at a power of 50~250 W, a pressure of 0.2~0.6 Torr, a flow rate of 50~110 sccm, a treatment time of 1~5min, and a temperature of room temperature ~ 175°C. For the case with argon plasma pretreatment, the experiment was conducted with an argon plasma treatment at a power of 150 W, a pressure of 0.4 Torr, a flow rate of 35 sccm, a treatment time of 3 min, and a temperature of 60°C followed by an ammonia plasma treatment under the above operating conditions. After plasma treatments, the samples were immediately transferred to the "smart desiccator" with nitrogen gas flowing inside so that the possibility of oxidation and water uptake could be minimized. The samples were then characterized using XPS, FTIR-ATR, and AFM techniques.

RESULTS AND DISCUSSION

DoE results

For ammonia plasma treatments without argon pretreatments, the results of the DoE are summarized in Table III.

The final equation in terms of actual factors (from Design-Expert software output) is

$$\begin{aligned} \text{N/C ratio} = & 0.065 + 0.035 \times \text{power} + 0.014 \\ & \times \text{pressure} + 0.018 \times \text{time} + 0.023 \times \text{temp.} + 0.017 \\ & \times \text{power} \times \text{pressure} + 0.0140 \times \text{power} \times \text{time} \\ & + 0.023 \times \text{power} \times \text{temp.} \end{aligned}$$

The result implies that we can identify the following significant factors according to the order of significance coefficients: absorbed power, interaction between power and temperature, temperature, the interaction between power and pressure, chamber pressure, treatment time, interaction between power and time. Our reduced linear model indicates that the

extent of amination improves with increase of absorbed plasma power, chamber pressure, treatment time, and sample temperature and also improves with the increase of the following interaction effects: power and pressure, power and time, and power and temperature.

For ammonia plasma treatments with argon pretreatments, the DoE result is as follows.

The factors and levels are the same as those in Table I except that argon plasma pretreatments were used before ammonia plasma surface treatments. Argon plasma pretreatment conditions were as follows: power 150 W, pressure 0.4 Torr, treatment time 3 min, and temperature 60°C. The result of the matrix design is shown in Table IV.

The final equation in terms of actual factors (from Design-Expert software output) is

$$\begin{aligned} \text{N/C ratio} = & 0.098 + 0.046 \times \text{power} + 0.030 \\ & \times \text{pressure} + 0.006 \times \text{time} + 0.012 \times \text{temp.} + 0.032 \\ & \times \text{power} \times \text{pressure} + 0.003 \times \text{power} \times \text{time} + 0.012 \\ & \times \text{power} \times \text{temp.} \end{aligned}$$

The tendency of the N/C ratios with argon pretreatments is the same as that without Ar pretreatments. However, the N/C ratios are higher with Ar pretreatments than without Ar pretreatments. This may be explained because argon plasma can modify the polymer surface and create free radicals that could then react with ammonia to produce an aminated surface more easily. In addition, the order of the extent of different parameter effects on N/C ratios is different. For the case with argon pretreatments, the order is as follows: absorbed power, the interaction between power and pressure, chamber pressure, temperature, interaction between power and temperature, treatment time, interaction between power and time.

TABLE IV
Result of Matrix Design of Ammonia Plasma Treatments with Ar Pretreatments

Standard order	Run order	Block	A	B	C	D = ABC	Response: N/C ratio
4	1	Block 1	1	1	-1	-1	0.170
10	2	Block 1	0	0	0	0	0.052
6	3	Block 1	1	-1	1	-1	0.071
1	4	Block 1	-1	-1	-1	-1	0.047
9	5	Block 1	0	0	0	0	0.058
7	6	Block 1	-1	1	1	-1	0.056
8	7	Block 2	1	1	1	1	0.237
11	8	Block 2	0	0	0	0	0.049
5	9	Block 2	-1	-1	1	1	0.055
3	10	Block 2	-1	1	-1	1	0.050
12	11	Block 2	0	0	0	0	0.050
2	12	Block 2	1	-1	-1	1	0.099

Detailed investigation of effects of processing parameters on N-incorporation on Cyclotene surfaces

Further investigation of the different parameter effects on N/C ratios on the Cyclotene surface has been carried out. According to the results of DoE above, there are three significant interaction effects for both ammonia treatments alone and argon pretreatments cases. These three interaction effects are power \times pressure, power \times temperature, and power \times time effects. Based on this result, we especially investigated these three interaction effects by doing corresponding experiments. The N/C ratios versus chamber pressure, substrate temperature, and treatment time as a function of power with and without argon pretreatments are displayed in Figures 3–5.

Figures 3–5 show that for both cases (ammonia plasmas with and without argon plasma pretreatments),

the final N/C ratios increase with increasing power, operating pressure, and substrate temperature. Temperature is limited by the surface topography and damageability of the polymer. We observe that the nitrogen incorporation onto the polymer surface mainly occurs within the first 4 min for medium and low power; at high power, this activity occurs within first 3 min and then a slight decrease of N/C ratio can be seen. This behavior may be tentatively explained by a competition between the modification process and the degradation process on the polymer surface. Under identical processing conditions, the extent of nitrogen incorporation onto the polymer with argon plasma pretreatments is higher than that without argon plasma pretreatments. This behavior is most likely due to the CASING (crosslinking via activated species of inert gases) effect. Several researchers^{13–16} have reported that argon plasma can cause highly

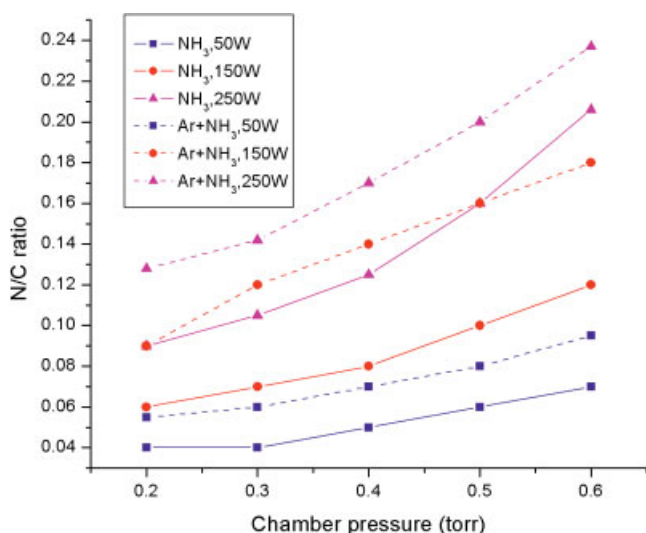


Figure 3 N/C ratios of the plasma-treated Cyclotene surfaces versus chamber pressure as a function of power with and without Ar pretreatments.

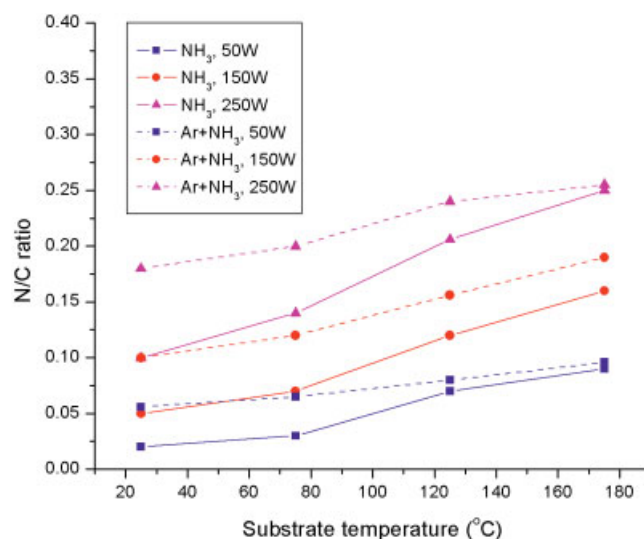


Figure 4 N/C ratios of the plasma-treated Cyclotene surfaces versus substrate temperature as a function of power with and without Ar pretreatments.

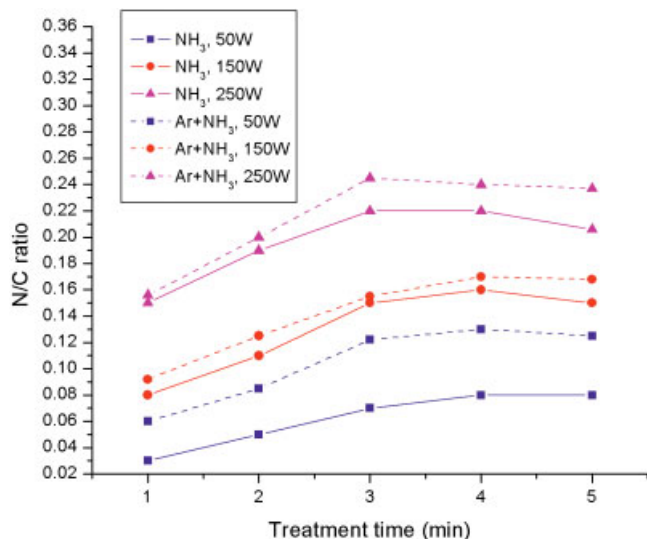


Figure 5 N/C ratios of the plasma-treated Cyclotene surfaces versus treatment time as a function of power with and without Ar pretreatments.

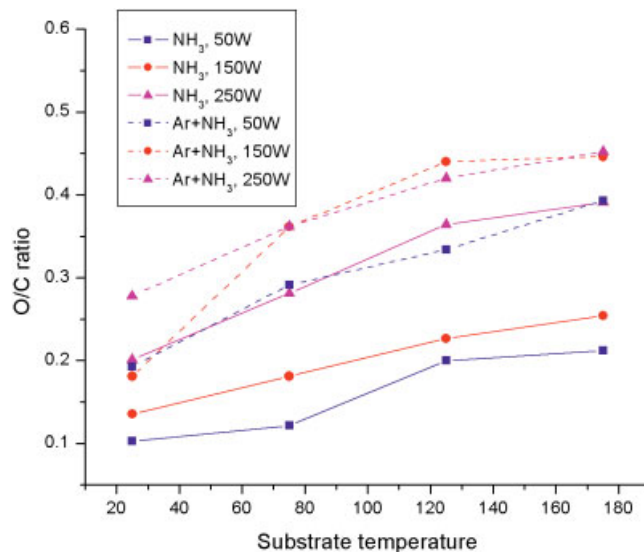


Figure 7 O/C ratios of the plasma-treated Cyclotene surfaces versus substrate temperature as a function of power with and without Ar pretreatments.

branched and crosslinked structures near the polymer surface. So it is reasonable to postulate that argon gas plays a role in modifying the polymer surface and creating free radicals that could then react with ammonia to produce an aminated surface more easily.

The O/C ratios can provide some insightful information on understanding the reaction mechanisms of the plasma surface modification process. The O/C ratios versus chamber pressure, substrate temperature, and treatment time as a function of power with and without argon pretreatments are shown in Figures 6–8.

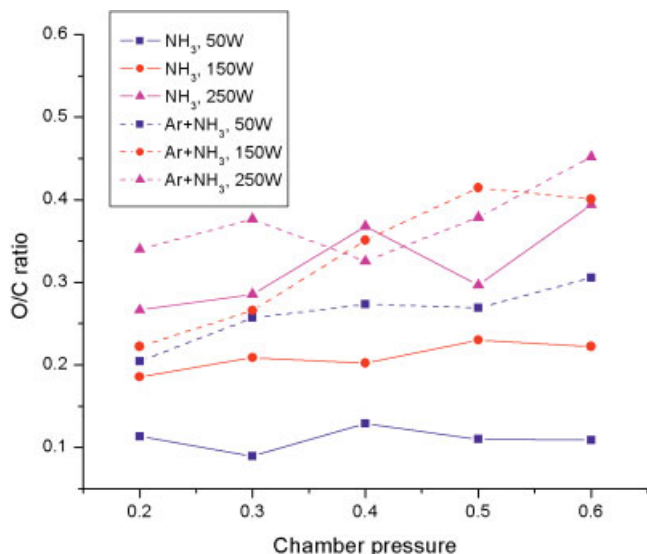


Figure 6 O/C ratios of the plasma-treated Cyclotene surfaces versus chamber pressure as a function of power with and without Ar pretreatments.

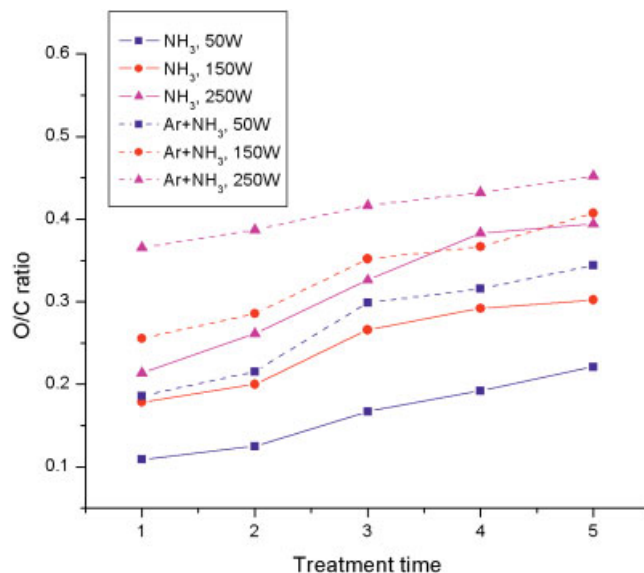


Figure 8 O/C ratios of the plasma-treated Cyclotene surfaces versus treatment time as a function of power with and without Ar pretreatments.

created by plasma exposure can, following venting of the plasma reactor, react with atmospheric oxygen. The addition of oxygen to carbon-centered radicals is a very fast process, and oxygen can diffuse rapidly through a few nanometers of the material probed by XPS. Gerenser et al.¹⁷ reported that substantial post-treatment oxygen incorporation into polyethylene was found after 30 s of exposure to the atmosphere.

In addition, the degree of oxygen incorporation for the case with argon pretreatments is higher than that without Ar pretreatments. This is most likely also due to the CASING effect, which means that argon gas can create free radicals that can react with both ammonia and impurity gases (including O₂) in the vacuum system during both plasma treatments and postoxidation periods, therefore causing more oxygen introduction. Furthermore, this effect enhances with plasma treatment time.

Aging effect

Another important phenomenon we observed during the detailed experimental exploration is the aging effect of the aminated polymer surfaces. Both N/C ratios and O/C ratios changed over time, which means that the modified polymer surfaces are unstable and the treatment effects decrease with time. The extent of the disappearance of treatment effects on storage varies with different materials and different treatment gases.^{18–21} Morra et al.¹⁸ reported that the O/C ratios correlated inversely with the extent of hydrophobic recovery in three plasma-treated hydrocarbon polymers and proposed that a high extent of oxygen incorporation into the surface was necessary to prohibit the hydrophobic recovery. However, this may not apply to all surface-modified polymer surfaces. Xie et al.²² found that water plasma-treated fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE) surface had very low oxygen concentration compared with ammonia plasma-treated FEP and PTFE, respectively. However, the former N/C ratios did not change with storage time while the latter N/C ratios decreased on storage. So there must be some alternative mechanisms for surface evolution. Genenbach et al.²² proposed a surface restructuring theory and explained that modified polymer surfaces generally are highly mobile and the mobility of polymer chain segments allows surface restructuring to occur, and this typically leads to a considerable decrease over time of the effects on the surfaces by nondepositing plasma treatments. The detailed aging effect study in our research group is still underway.

Surface characterization results

XPS results combined with FTIR-ATR spectra showed that possible species that were introduced by ammonia plasma treatments are amine (C–N), amide (O

= C–N), imine (C = N), and imide (O = C–N–C = O). The absence of specific Si–N peaks indicated that the new N-containing species were grafted to C only.

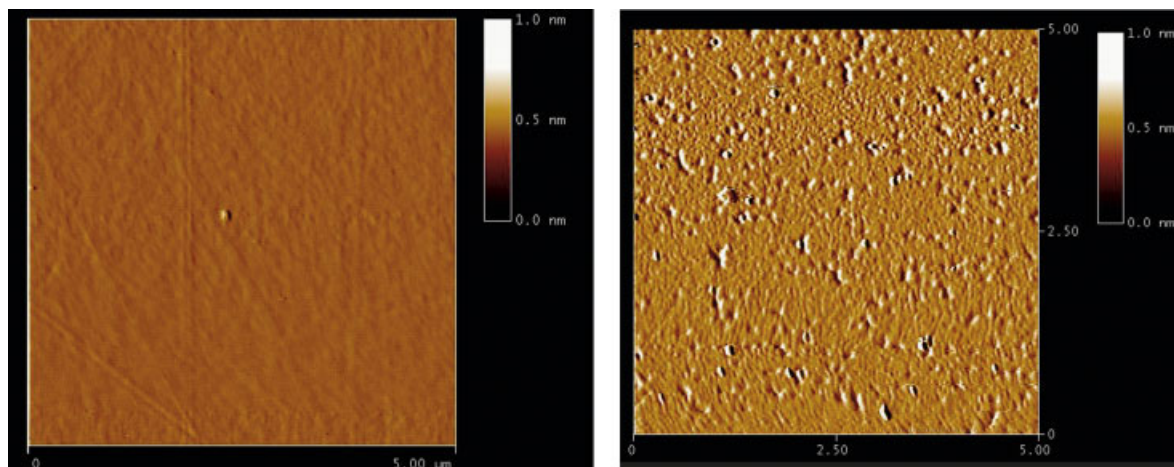
AFM results

Typical AFM images for untreated and plasma treated with/without argon plasma pretreated Cyclotene surfaces are presented in Figure 9. The difference between the treated and untreated samples is obvious and suggests that surface modification by ammonia plasma with and without argon pretreatments produces fine, bulge-like ridges and additional structure superimposed on the gentle undulations native to untreated Cyclotene film. Also, for the Cyclotene surface by ammonia plasma treatments with argon plasma pretreatments, the bulge-like ridges are obviously bigger than that with ammonia plasma treatments alone. Line scans were taken at several random locations across the areas. Figure 9 displays some representative examples. These line scans clearly show more detailed topography of the ammonia with/without argon plasma-pretreated surfaces.

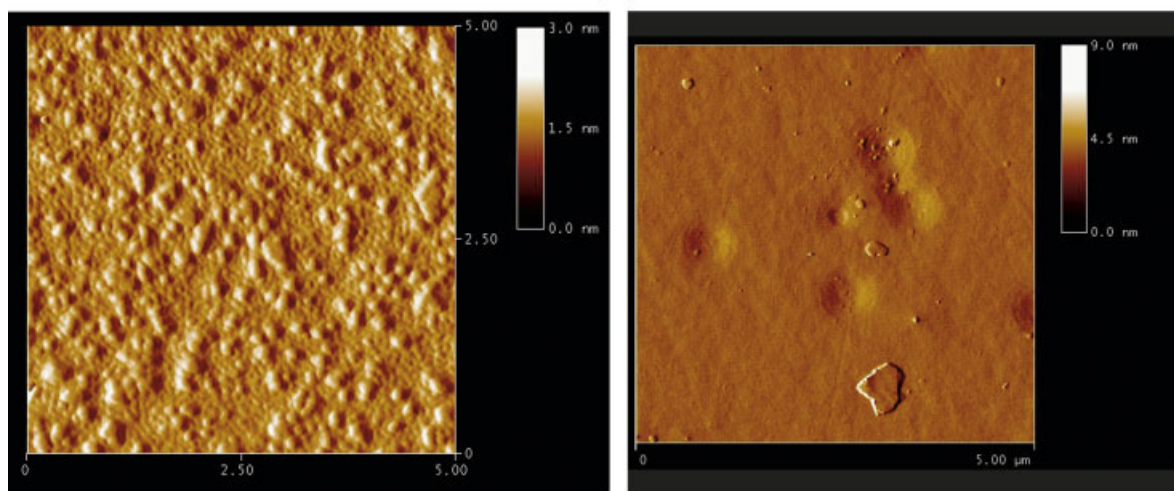
The root-mean-square (RMS) roughness of the surface for the control (untreated) case is about 2.5 nm (shown in Fig. 9a). The RMS of the image surface for ammonia treatments alone is 8.5 nm (shown in Fig. 9b) and the RMS for ammonia treatments with Ar pretreatments is about 25 nm (shown in Fig. 9c), which is much greater than that in ammonia treatments alone. However, for Figure 9d, the RMS is greater than 80 nm. Moreover, the roughness is very uneven, which implies that the surface topography of polymer is not desirable any more under such an operating condition. By observing all AFM pictures under different operating conditions, we found that 175°C is the temperature upper limit for ammonia plasma treatments.

CONCLUSIONS

The current experimental investigation leads to the following conclusions: XPS and FTIR-ATR characterization results indicate that nitrogen-containing functional groups have been introduced onto Cyclotene surfaces by ammonia with/without argon plasma pretreatments and the functional groups exist in the two most possible forms: amine and amide groups. DoE results show that the extent of surface amination improves with the increase of absorbed plasma power, chamber pressure, treatment time, and sample temperature for ammonia plasma treatments both with and without argon plasma pretreatments. There are also some second-order interactions in the final proposed models for both cases. The further experimental exploration with different processing parameters combined with the AFM results implies that the optimum



a) Untreated Cyclotene

b) Ammonia plasma treatments alone
(250 W, 0.6 Torr, 5 min, 100 °C)

c) Ammonia plasma treatments (250 W, 0.6 Torr, 5 min, 100 °C) with Ar plasma pretreatments (150 W, 0.4 Torr, 3 min, 60 °C)

d) Ammonia plasma treatments (250 W, 0.6 Torr, 5 min, 200 °C) with Ar plasma pretreatments (150 W, 0.4 Torr, 3 min, 60 °C)

Figure 9 AFM images for ammonia plasma-treated Cyclotene films. (a) Untreated Cyclotene. (b) Ammonia plasma treatments alone (250 W, 0.6 Torr, 5 min, 100°C). (c) Ammonia plasma treatments (250 W, 0.6 Torr, 5 min, 100°C) with Ar plasma pretreatments (150 W, 0.4 Torr, 3 min, 60°C). (d) Ammonia plasma treatments (250 W, 0.6 Torr, 5 min, 200°C) with Ar plasma pretreatments (150 W, 0.4 Torr, 3 min, 60°C).

operating condition so far is as follows: argon plasma pretreatments (absorbed power 150 W, chamber pressure 0.4 Torr, substrate temperature 60°C, treatment time 3 min), followed by ammonia treatments (absorbed power 250 W, chamber pressure 0.6 Torr, substrate temperature 175°C, treatment time 3 min). Under same processing conditions, the extent of nitrogen incorporation onto the polymer with argon plasma pretreatments is higher than that without argon plasma pretreatments. This is most likely due to the

CASING effect, which agrees with many other researchers' reports that argon plasma can cause highly branched and crosslinked structure near the polymer surfaces. It is reasonable to postulate that argon gas plays a role in cleaning the polymer surface and creating free radicals that could then react with ammonia to produce an aminated surface more easily.

This work was supported by the DARPA Bio-Info-Micro Program, Grant #MDA972-00-1-0027. The authors thank

Kee-keun Lee for his assistance with Cyclotene sample preparations and Jay Schwarts for his assistance with AFM analysis.

References

1. Kaplan, S. L.; Rose, P. W. *Int J Adhesion Adhesives* 1991, 11, 109.
2. Sipehia, R.; Chawla, A. S. *Biomater Med Dev Arti Organs* 1982, 10, 229.
3. Mutlu, M.; Mutlu, S.; Rosenberg, M. F.; Kane, J.; Jones, M. N.; Vadgama, P. *J Mater Chem* 1991, 1, 447.
4. The Dow Chemical Company,. <http://www.dow.com/cyclotene>.
5. Yang, D. Q.; Martinu, L.; Sacher, E.; Sadough-Vanini, A. *Appl Surf Sci* 2001, 177, 85.
6. Wong, S.; Loke, A.; Wetzel, J.; Townsend, P.; Vrtis, R.; Zussman, M. *Materials Research Society Spring Meeting E7.1*, San Francisco, CA, April 16, 1998.
7. Garrou, P. E.; Heistand, R. H.; Dibbs, M. G.; Manial, T. A.; Mohler, C. E.; Stokich, T. M.; Townsend, P. H.; Adema, G. M.; Berry, M. J.; Turlik, I. *IEEE Trans Components Hybrids Manufact Tech* 1993, 16, 46.
8. Lee, K.; He, J.; Wang, L. *Proc of the 26th Annual Intern Conf of the IEEE EMBS*, San Francisco, CA, September 1-5, 2004; p 4326.
9. Poncin-Epaillard, F.; Chevet, B.; Brosse, J-C. *Eur Polym* 1990, J26, 333.
10. Golub, M. A.; Wydeven, T.; Cormia, R. D. *Polymer* 1989, 30, 1571.
11. Foerch, R.; McIntyre, N. S.; Hunter, D. H. *J Appl Polym Sci* 1990, 40 1903.
12. Foerch, R.; Johnson, D. *Surf Interface Anal* 1991, 17, 847.
13. Sprang, N., Theirich, D.; Engemann, J, *Surf Coatings Technol* 1998, 98, 865.
14. Vallon, S.; Drévilion, B. *J Vac Sci Technol* 1996, A4, 3194.
15. Mason, M., Vercruysse, K. P., Kirker, K. R., Frisch, R., Marecak, D. M., Prestwich, G. D.; Pitt, W. G. *Biomaterials* 2000, 21, 31.
16. Zhao, Q.; Lu, H. Y.; Hess, D. W. *J Electrochem Soc* 1996, 143, 2896.
17. Gerenser, L. J. *J Adhesion Sci Technol* 1987, 1, 303.
18. Morra, M., Occhiello, E.; Garbassi, F. *Polymer-Solid Interfaces: Proceedings of the 1st International Conference*, Belgium, September 2-6, 1991.
19. Occhiello, E.; Morra, M., Cinquina, P.; Garbassi, F. *Polymer* 1992, 33, 3307.
20. Cross, E. M.; McCarthy, T. J. *Macromolecules* 1990, 23, 3916.
21. Van der Mei, H. C.; Stokroos, I.; Schakenraad, J. M.; Busscher, H. J. *J Adhesion Sci Technol* 1991, 5, 757.
22. Xie, X., Gengenbach, T. R.; Griesser, H. J. *J Adhesion Sci Technol* 1992, 6, 1411.