Functionalization of Surfaces by Plasmas at Low and High Pressures

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The functionalization of surfaces is a requirement for a variety of processes from atomic-layer-deposition for microelectronics fabrication to biocompatible coatings for tissue engineering. Although many of these processes are often performed at low pressure, it is also desirable to use high pressure, atmospheric pressure plasmas which can be applied in more economical manner. The difficulty in using atmospheric pressure plasmas is obtaining uniform treatment. The functionalization of surfaces having complex shapes will be discussed using results from a multidimensional model.
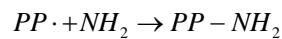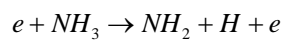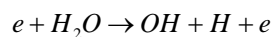
1. Introduction

Low pressure plasmas are used to functionalize surfaces when producing high value materials. For example, capacitively and inductively coupled plasmas similar to those used for microelectronics fabrication are used to produce biocompatible coatings.[1] Atmospheric pressure plasmas are routinely used to treat large areas of commodity polymer films (e.g. polypropylene) to improve surface properties such as adhesion and wettability.[2] Biocompatible materials as used for scaffolding for tissue engineering often have their surfaces treated to achieve similar functionality as commodity polymers to promote, for example, cell adhesion. Using results from a computational investigation, we discuss whether commodity plasma processes, such as atmospheric pressure corona discharges, can be applied to the functionalization of biocompatible materials requiring high degrees of uniformity. The example we use is functionalization of polypropylene with amine groups from ammonia plasmas.

2. Description of the Model

The model used in this investigation is a variant of nonPDPSIM described in Ref. 3. The fundamental equations we solve are for charge density on surfaces and in materials, continuity equations for all charged and neutral species, Navier-Stokes for hydrodynamic fluid motion and Poisson's equation for the electrostatic potential. A Monte Carlo simulation is used to follow the trajectories of secondary electrons emitted from surfaces. A radiation transport module is used to account for photoionization, secondary emission from surfaces and photon-initiated surface chemical reactions. A surface kinetics model is employed at every point on surfaces in contact with the plasma. An unstructured mesh resolves a dynamic range of 1000 in dimension.

We examine the functionalization of polypropylene (PP) with amine groups to enable cell adhesion by using an atmospheric pressure corona discharge sustained in a $He/H_2O/NH_3$ mixture. In this process, electron impact dissociation of H_2O produces OH radicals which can efficiently extract H atoms from the PP backbone, $[CH_2-CH_2-CH-CH_3]_n$, thereby producing alkyl radical sites. These sites are then passivated with NH_2 produced by electron impact dissociation of NH_3.

$$e + H_2O \rightarrow OH + H + e$$
$$e + NH_3 \rightarrow NH_2 + H + e$$
$$OH + [CH_2 - CH_2 - CH - CH_3] \rightarrow PP\cdot + H_2O$$
$$PP\cdot + NH_2 \rightarrow PP - NH_2$$

The plasma source is a linear corona as used in web treatment of polymer sheets and is schematically shown in Fig. 1. The upper wedge-shaped dielectric structure, symmetric across the centerline, has an embedded powered electrode exposed to the gas at the tip. The PP is on the lower flat grounded electrode creating a dielectric barrier discharge configuration. Roughness on the polymer surface is resolved with strand-like features having many micron length scales.
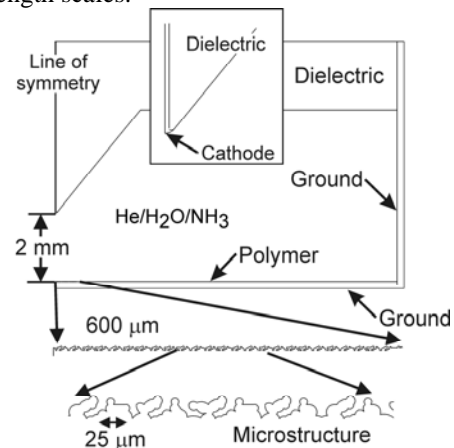

Figure 1 – Schematic of the corona discharge.

3. Functionalization of Polypropylene

The density of electrons and amine radicals (NH_2) during a single corona discharge -5 kV pulse is shown in Fig. 2 for $He/H_2O/NH_3$ =98.9/1/0.1. The peak electron and amine densities exceed 10^{13} cm^{-3}. Surface coverage of amine groups (PP-NH_2) are shown in Fig. 3 for $He/H_2O/NH_3$ =88.9/10/0.1 when operating at 10 kHz for 0.1 s. Since the rate of functionalization is limited by hydrogen abstraction reactions that produce alkyl sites, a large fraction of water is used to produce a large amount of OH radicals. There is a factor of two variation in the amine surface coverage resulting from sites that have large

and small view angles to the plasma. Locations that have large view angles on the "tips" of surface roughness are rapidly converted to alkyl and then amine sites. Those locations with small view angles (in the crevices of the surface structure) have lower surface coverage of amine.
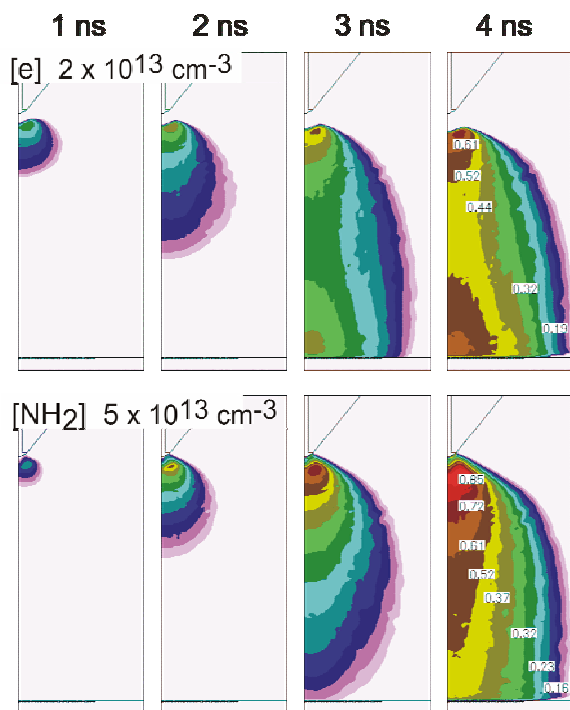

Figure 2 – Densities of (top) electrons and (bottom) amine radicals during a single discharge pulse.
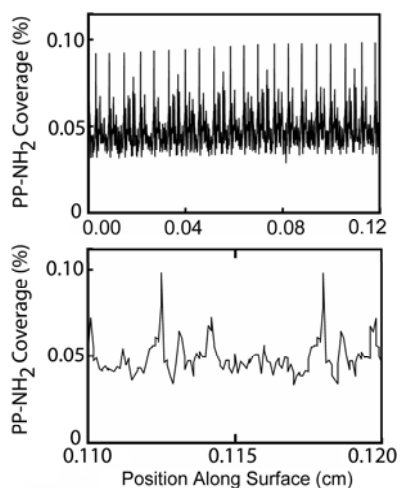

Figure 3 – Surface coverage of amine groups on poly-propylene (PP-NH_2). The variation results from differences in the view angle of the surface site.

Another application is the functionalization of porous microspheres for protein binding for drug delivery or gene therapy.[4] In this example, PP beads 90 μm in diameter are placed on the lower surface and treated in the He/H_2O/NH_3=88.9/10/0.1 corona discharge. Typical results are shown in Fig. 4. The penetration of electrons into the porous network of the beads depends on the orientation of the openings to the pores and their size. The electrons initially penetrate when they have an advantageous view angle, and then retreat as the surface is charged. NH_2 radicals are produced inside the pore by electron impact

reactions although only a small density is produced this way. The majority of the NH_2 later diffuses into the pores, as shown in Fig. 5, for different pore sizes.
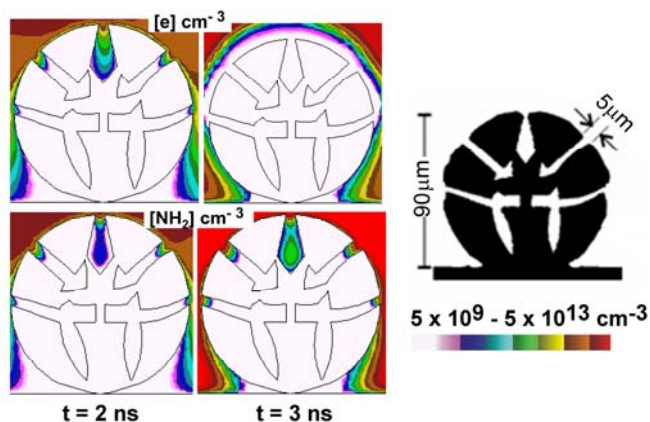

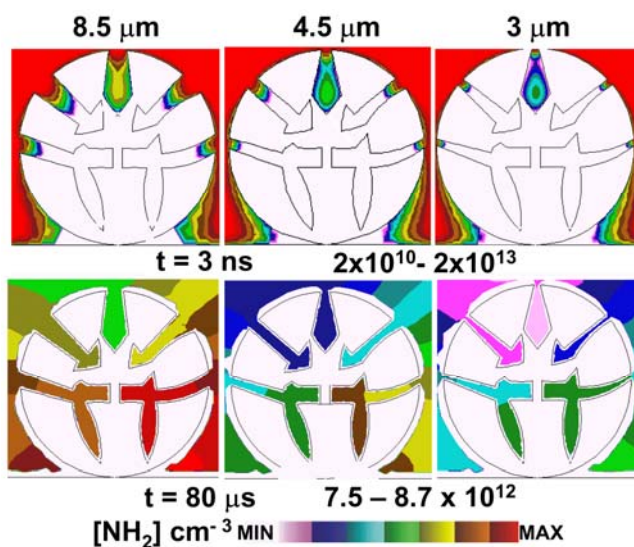Figure 5 – (top) Electron and (bottom) NH_2 density around and inside a porous bead.

Figure 5 – NH_2 density after the discharge pulse and after 80 μs for different pore sizes.

4. Concluding Remarks

The functionalization of rough surfaces and beads of polypropylene with amine groups was computationally investigated for atmospheric pressure discharges. We found that surface treatment depends on the local topography and orientation of the surface.

References

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[4] See, for example, http://www.ciphergen.com .