Plasma-Surface Modification of Materials

The Effects of Plasma Treatment on the Material Properties of Materials at a Microscopic Scale

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Background info

Plasma-surface modification is a very effective surface treatment technique which allows the ability to alter specific material properties while leaving the base attributes of said material unchanged. The use of this fourth state of matter can influence changes in material properties such as the rise of the surface energy of a material. This can then influence the wettability characteristics of a material, creating a surface better suited for bonding and biocompatibility within the material itself.. There are numerous applications for this type of surface modification in the real world, especially in the biomedical department, and we plan to continue our research to discover all the ways plasma-surface modification can be utilized on a microscopic plane.

Rationale

The use of plasma to change the surface properties of various materials seemed to appropriately qualify this topic for our report on microfluidics. From the beginning of the semester we have been covering topics regarding wettability, contact angle, and surface tension, which plasma treatment is directly correlated to. Along with changing the hydrophilic properties of materials, plasma-surface modification (PSM) can also change properties such as metal adhesion, dyeability, refractive index, chemical inertness, lubricity, and biocompatibility all on a microscopic scale. We also plan to venture our research towards the application of “Blown-Arc Atmospheric Plasma Treatment” which uses a flow of atmospheric air to blow an electrode induced plasma arc to be used in multiple surface treatment devices in many fields. It is from all these qualities of PSM that we can rationalize our decision of picking it as a topic of research.

Research scope/Planning

In our research, the overall approach will be to figure out the correlation between numerous plasma treatment techniques and the wettability of various materials. In addition to this, we will look into the relationship between the overall surface energy and wettability that is created through each of the plasma-surface modification techniques. We also plan to go more in depth on the application of “Blown-Arc Atmospheric Plasma Treatment,” as this is a treatment directly related to microfluidics and the wetting properties of materials.

Understanding Surface Energy and Wettability

The way that liquids interact with a surface is oftentimes primarily affected by attributes such as surface energy and surface tension. It has been proven that altering the surface energy of a given substrate can directly influence its wettability and lead to a more hydrophobic or hydrophilic surface depending on your chosen method of treatment. Before we can begin understanding the best way to change surface energy, we must first acknowledge the process of determining the surface free energy (SFE) of a material and which attributes affect its resultant.

One of the most commonly used methods for calculating SFE is known as the Owens-Wendt-Rabel-kaelble (OWRK) equation, which uses contact angle measurements to determine a material's surface energy. This model uses the sum of a dispersive component (YD) and polar components (YP) to determine both a liquids surface tension and a solid’s SFE respectively. Combining this summation with our knowledge of contact angles between liquids and solids (theta) between liquid and solids we can construct the Owens-Wendt-Rabel-Kaelble equation listed below.

$$\gamma_{LV}(1+\cos\theta) = 2[(\gamma_{SV}^{D}\gamma_{LV}^{D})^{1/2} + (\gamma_{SV}^{P}\gamma_{LV}^{P})^{1/2}]$$

This equation helps us construct a numerical relationship between the surface energy of solid materials, the surface tension of liquids, and their water contact angle and visualize how the manipulation of one may affect the other. This correlation can be graphically represented in a figure known as a “wetting envelope”. Essentially a wetting envelope is a model used to interpret how changing polar and dispersive components will affect (theta).

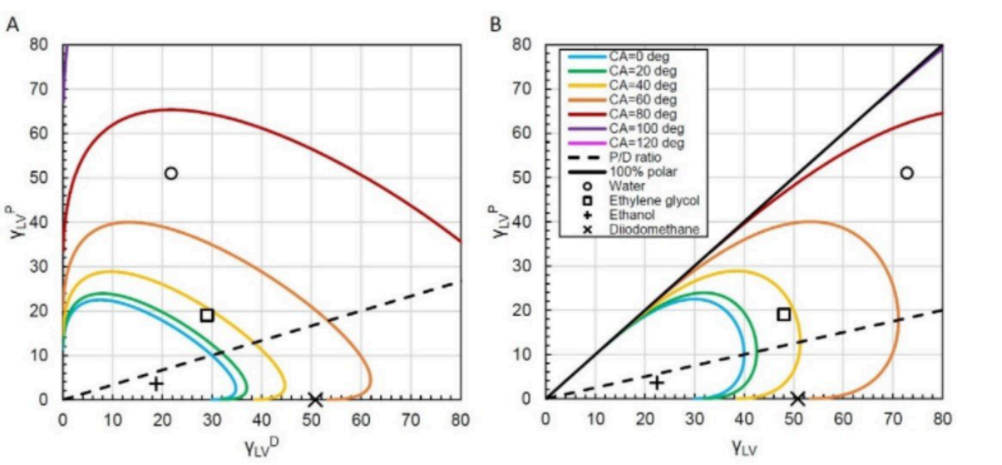

Fig. 1 Wetting Envelope

It is from the application of both the wetting envelopes and the OWRK model that we can determine what modifications need to be made to make a surface increase wettability (decrease theta) or increase wettability (increase theta) by modifying the solid or the liquid. For the purposes of our research we will focus on the modification of a solid using one of the most effective and well-known techniques; plasma treatment.

Treatment Processes

The entire reason for there being a plasma treatment process is if the surface of a given substrate has a very low amount of surface energy. This low surface energy is directly related to wettability, in that the overall wettability of the substrate is poor, created by a scarce amount of coating adhesion. To improve overall wettability and make the substrate surface more hydrophilic, a plasma surface treatment can be utilized to increase the surface energy of the substrate. A few of the treatment processes used to achieve a higher surface energy are corona, flame, and atmospheric plasma. Corona treatment is used to raise surface energy within materials such as plastic films, foils and paper to improve wettability. The overall application of this treatment can improve things such as printing and coating quality of specific materials that may need this characteristic. Flame treatment is a treatment that is created by a combination of air and a flammable gas to produce a blue flame. When particles on a substrate's surface are exposed to this blue flame plasma field, the surface molecules undergo an oxidation process and become polarized. Like corona treatment, flame treatment also promotes a surface with better adhesion and wettability properties. Atmospheric plasma treatment or APT is a process that achieves the same desired outcome as the other processes mentioned, where a substrate's surface is improved by increasing the surface energy and in turn producing a surface with increased wettability properties. This process in particular increases surface energy at a substantial rate without having to worry about backside treatment or pin-holing (tiny holes in finish or imperfections). How the APT process works is by first exposing a polymer to a glow discharge with a low temperature and high density. The figure below represents this discharge process taking place, where the glowing parts indicate gas reacting to an Enercon plasma treater.

From this discharge, the plasma created is a partially ionized gas consisting of large concentrations of excited atomic and molecular species. These excited species then can interact with a solid surface which results in a chemically and physically modified material surface.

Ablation, Crosslinking, and Activation

In the ablation process, a polymer surface of a substrate is struck with free radicals, electrons, ions, and radiation that break the covalent bonds of the polymer. Through this process, the polymer will ultimately have polymer chains that are lower in molecular weight. When these molecular components become shorter, volatile oligomer and monomer by-products will eventually ablate. In the crosslinking process, an inert gas is introduced either Argon or Helium in most cases. A bond breaking process will then occur on a polymer surface. Through this chemical process, there are no free-radicals present so bonds can be formed with nearby radicals on a different chain or crosslink. Through the activation process, surface polymer functional groups are replaced with atoms or chemical groups from the plasma itself. The plasma in this process contains very high-energy UV radiation. This UV radiation is able to create several free radicals on the polymer being treated. The radicals on the polymer surface are thermodynamically unstable which are able to quickly and effectively react with other free-radical species that may be present to form covalently bonded atoms or more complex functional groups.

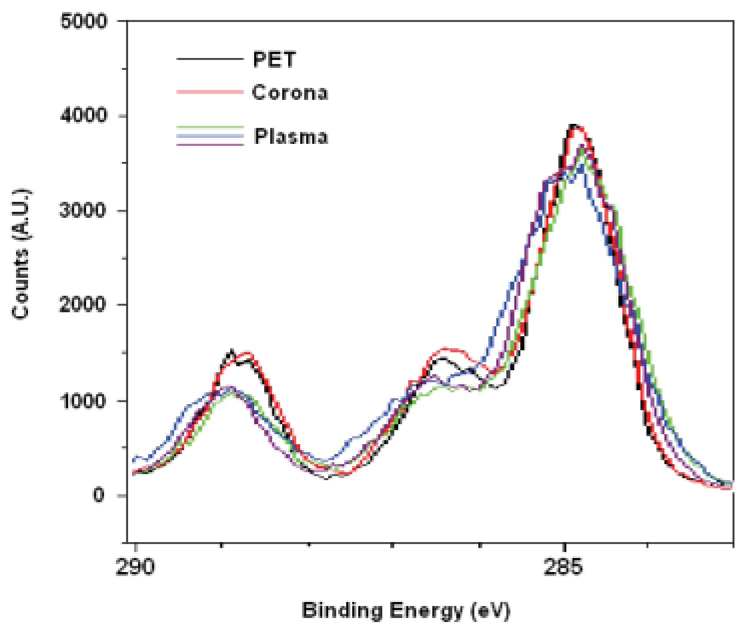

Fig. 2 Counts vs. Binding Energy for Treated and Untreated PET

From Figure (2) it can be seen that there are three different sized peaks present. The intensity of the highest peak seems to decrease after plasma treatment, whereas when corona treatment is involved, there is little to no change. In the case of the corona treated sample of PET, the second peak is strongly increased in intensity. The third peak illustrated at about 286 eV does not change or alter after the corona treatment process, however, it is broadened and reduced by plasma treatment.

Conclusion

Throughout this research of plasma surface modification of materials, there have been several treatment processes that can be applied to a wide range of polymeric surfaces. These treatment processes have the ability to increase or decrease surface energy on a substrate's surface ultimately creating a surface with increased or decreased wetaility depending on the intended application. The plasma treatment process can be operated at low temperatures as well as atmospheric pressure. The surface energies of various substrates have been proven to show substantial increases and with this, the wettability has in turn been improved without physically changing the makeup of the material being treated. Plasma treatment overall provides advantages for several materials that have expanded our technological knowledge and what possibilities are now readily available for humankind.

Research papers/Website sources

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