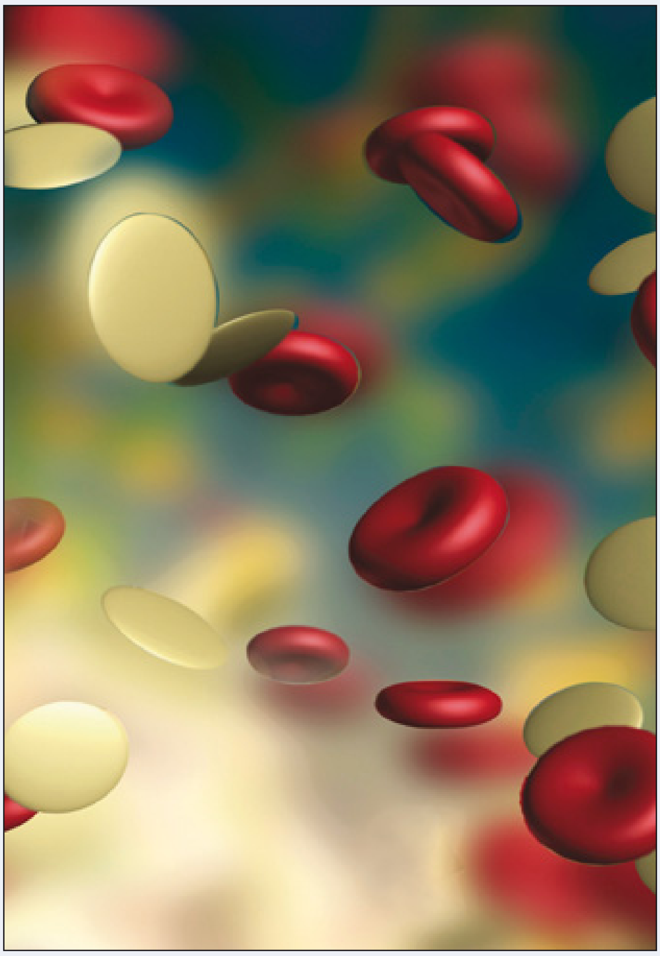
Plasma processing polymers for medical applications

Many applications make use of polymers. To use these polymers, their surface needs to be modified. **Dr. C. A. Bishop of C. A. Bishop Consulting Ltd** explains the nano scale exploration of plasma for surface treatment in vacuum.

Polymers are found in a variety of applications throughout the medical environment such as drug delivery systems, dressings and implants. However, to make the polymers suitable for use, they often have to be modified; in particular the surface often has to be modified. Surfaces can be modified in a variety of ways of which plasma processing is one of the most versatile. Surfaces can be physically modified by etching which can either smooth or roughen the surface depending on the plasma conditions. Not only can the surface be physically modified but it can also be chemically changed. In this way the same polymer can have the surface energy changed and be made to be either hydrophobic or hydrophilic. All of this is may be done using just the original polymer and the gases used in the plasma. Additional surface modification may take place by using the plasma to graft or deposit additional material onto the surface. Thus the option for customising polymer surfaces is considerable.

Plasma is just an excited gas

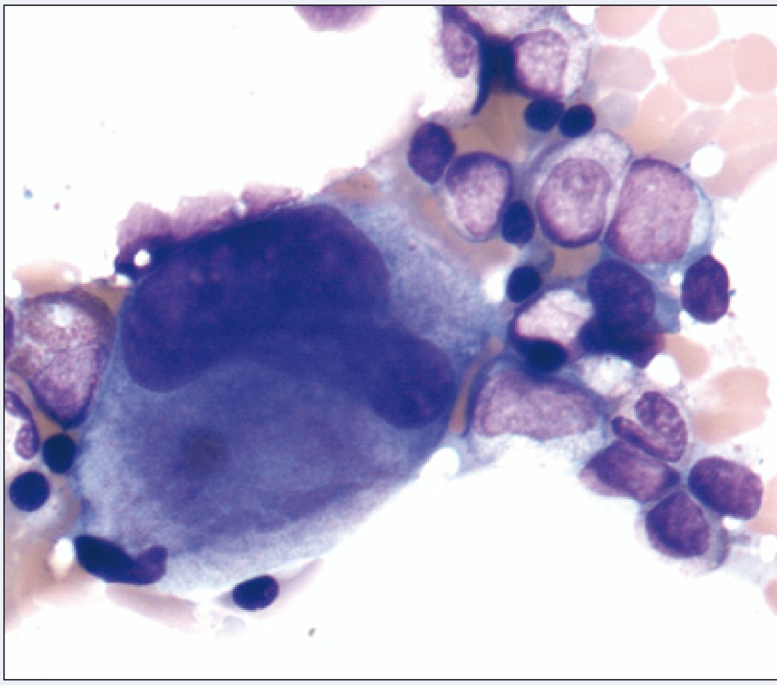
If we look at plasma processing, this has a number of options. Plasma is just an excited gas that contains ions and electrons. The type of plasma can be defined by the density and temperature of electrons in the gas. There are many types of plasma that can be used for polymer modification including flame, corona, and atmospheric or vacuum plasma. The cheapest and simplest plasma processing is probably flame treatment. The flame can either be oxidising or reducing depending on the gas composition and the position of the polymer in the flame. Typically it is used for simple surface cleaning and activation. Once the requirement are for more precise control of the surface chemistry the closer control available from electrically



stimulated plasma is necessary. Corona treatment uses a high voltage electrical discharge to produce the plasma across the polymer surface. Generally this type of process uses oxygen to both clean and chemically modify the surface. The plasma uses air which breaks down and the ozone provides an aggressive surface treatment. With both of these processes the chemistry available tends to be limited. Atmospheric plasma is somewhat more flexible and allows for a greater variety of surface chemistry to be used. The superior control of the power supply enables the arcing that is often seen with corona treatment to be minimised thus reducing the process variability and substrate damage. In addition most atmospheric plasma systems use an inert gas blanket which can allow the exclusion of oxygen and moisture which can further widen the available chemistry. This process being at atmospheric pressure is often cheaper than using vacuum plasma treatment. Atmospheric plasma treatments are relatively recent developments and consequently the systems have not yet been fully developed and hence the costs are currently higher than could be expected in the future once the systems have been optimised. For instance helium is often used to help stabilise the plasma but this can be a relatively high cost consumable gas. It is expected that in future systems either the control will have improved to dispense with the helium or that it will be possible to recycle the helium thus reducing the operating costs.

Treating Polymers

Vacuum plasma treatment has a number of advantages in treating polymers. The system having been evacuated has a reduced oxygen and water vapour content which, for some processes, are major contaminants. Having removed the air the desired gas can then be introduced to provide the etching, surface modification or deposition required. The lower pressure also reduces the effective temperature of the plasma and so the possibility of thermal damage to the polymer surface is reduced. Plasma treatment for medical applications can require a number of attributes such as sterilisation, disinfection, biocompatibility or anti-microbial coating as well as the more typical surface modifications used elsewhere. The typical processes at the polymer surface include ablation, micro-etching or chain scission. The breaking of chains and removal of atoms from the surface allows for cross linking or grafting and functionalisation of the polymer surface. The gas or gases in the plasma can be used to not only bombard the surface but also combine with the atoms at the surface either to convert atoms to a gaseous form that can be pumped away or to provide the chemical modification that changes the surface characteristics. In addition the plasma produces a high level of ultra violet (UV) radiation which may be used for sterilisation. The starting point in deciding what treatment to give the surface is to define the compatibility requirements. Polymers that are in intimate contact, such as contact lenses, may require a different treatment to those that have blood or skin contact. Where cell proliferation is required such as in diagnostic kits what is good for one test may be toxic for another. Thus there is no universal surface treatment for medical applications. Typically implants that have blood contact will have blood plasma proteins sticking to the polymer surface. These proteins may then cause inflammation or other unfavourable reactions. It was found that the preferred polymer surface had a high surface energy and hence high level of wetting. In work done at Dublin City University it was found that it was possible to control the level of hydrophilicity or hydrophobicity by modifying the power and composition of the plasma. Using hexamethyl disiloxane (HMDSO) in the plasma meant that a coating containing Si, H, C and O could be created. Using a low power to the plasma the coating had a higher level of C and H content and was hydrophobic. As the power was increased the levels of C and H were reduced as the higher energy plasma further fragmented the HMDSO and the coating more closely approached silica. If the plasma gas content is then further modified using the additional of titanium isopropoxide (TIP) the effect is to further increasing the coating polarity and improving the hydrophilicity. The wetting of the surface was measured by the contact angle method and for the low power plasma deposited HMDSO only surface a contact angle of 105^{o} was produced. As the power was increased and some additional oxygen introduced this contact angle was reduced towards 65^{o} and with the addition of TIP it was further reduced to 40^{o} showing high hydrophilicity.



The use of hydro gels

Another material that is finding many medical applications is hydro gels. These are materials made up of a polymer matrix that contains a large amount of water and can be used in wound dressings, for tissue repair or drug release systems. In some cases these hydro gels contain up to 95 vol % water. As might be imagined these hydro gels are very fragile and so to make them more easily handled they are bonded to a polymer backing such as polypropylene. These hydro gels do not have good adhesion to the polymer and so the polymer surface needs to be treated to optimise. In some work at the Ecole Polytechnique, Montreal on a hydro gel made using a soy albumin protein as a cross linking agent and Polyethylene Glycol (PEG) and containing 96% water it was found that the adhesion could be significantly improved by using a nitrogen plasma to treat the polypropylene surface. The plasma increased the nitrogen content at the surface to around 15 % primarily through the inclusion of amine groups that are believed to form covalent bonds to the hydrogel. It was also found that the plasma treatment smoothed the surface of the polymer, cleaning by removing poorly bonded material as well as some amorphous surface material, which suggested that the increase in adhesion was purely chemical and not related to any increase in surface area because of surface roughening.

A simple sterilisation process has been developed that requires the materials to be placed in a vacuum and evacuated and then a quantity of hydrogen peroxide to be introduced into the vacuum system. The liquid is vaporised and will contact all surfaces. A plasma is then struck which then removes any surface contamination as well as exposing the surfaces to the sterilising UV light.

As can be seen from the above examples plasma processing offers a very wide range of options for modifying both the physical and the chemical and biological properties of polymer surfaces making them a versatile material for medical use.

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