Environmentally Friendly Plasma-based Surface Engineering Technologies

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Abstract. Weakly ionised reactive plasmas are characterised by a very low degree of ionization, which rarely exceeds the order of $10^{-4}$, and by a very high degree of dissociation, which often reaches values above 50%. Thus the most numerous plasma species are free neutral atoms originated from the dissociation of the source gas molecules. Neutral atoms are chemically very reactive species, which makes such plasma suitable for material processing. At the same time the neutral atoms have a low kinetic energy and therefore they cannot penetrate into the bulk material, so their effect is restricted to the topmost atomic layers of the material surface hence weakly ionised, reactive plasmas are suitable for surface engineering. Here we present examples of weakly ionised plasma applications as environmentally friendly alternatives to processes that otherwise utilise aggressive chemicals and produce toxic waste.

1. Introduction

Surface engineering technologies, in which the chemical composition on the surface material is changed while the bulk of the material is left intact, are a growing filed in industry. They can either represent the final stages in an industrial processing or an important step that makes final stage processes possible or more efficient, thus aiding to more environmentally friendly processes. Surface activation, for example, leads to improved adhesive properties of materials, which reduces the amount of paint needed to coat a surface or enable the metallization of composite materials, which, in turn, allows them to be used as substitutes for metals in certain industrial applications, thus eliminating the need for metal.

However, the surface processing itself may not always be environmentally friendly as inducing chemical changes on the surface of a material requires a sufficiently reactive medium. This, as wet chemical treatment, uses acids, lye, solvents or liquid halogenated hydrocarbons, which presents a burden to the environment for several reasons, starting from the consumption of energy and other resources tied to the production and the purification of such chemicals, health hazards during transport, storage and the industrial process itself and to the problem of waste disposal after the process has been completed [1]. In this paper we present the possibility to replace chemical surface engineering technologies by alternatives that do not include the use of said aggressive chemicals.

2. Weakly Ionised Plasma

The plasma used in the processes described in this paper is often referred to as a weakly ionised one. Usually it is created at pressures ranging from 1 to 100 Pa using RF or MW discharges. It belongs to the class of cold plasmas, meaning that the temperature of the electrons is well above the temperatures of other plasma species. Whereas the temperature of electrons is typically between 4 and 5 eV, the
ions and the gas remain at room temperature or just slightly above. As the name suggests, the degree of ionisation is relatively low, typically it does not exceed $10^{-4}$. However, the degree of dissociation is rather high and often reaches 50% or even more [2].

As dissociation means breaking up of source gas molecules into neutral atoms, the neutral atoms are thus the most populous plasma species and their characteristics govern the total plasma characteristics. Their main properties are that they are chemically very active while their kinetic energy is small enough so that they cannot penetrate into the bulk of the processed material and thus their effect is restricted to the topmost atomic layers [3]. Therefore, weakly ionised plasmas can be used to induce chemical changes on the surface of a processed material while leaving its bulk properties intact and as such can be a very suitable tool for surface processing.

3. Plasma Based Surface Engineering Technologies

3.1. Surface activation

Surface activation stands for changing the chemical composition of the surface with the intent to modify its adhesion properties. Surface energies of nonpolar plastic materials are raised to levels which ensure a satisfactory adhesion before further processing such as painting, coating, laminating, printing, lacquering, gluing, etc. The increase of surface energies is a combined product of three effects:

- Removal of weak boundary layers.
- Cross-linking of surface molecules.
- Generation of polar groups.

Oxygen atoms remove the surface layers with the lowest molecular weight and oxidise the uppermost atomic layer of the polymer. The oxidation is responsible for the creation of polar groups, which are directly related to the adhesion properties of the surface. Furthermore, oxygen atoms combined with UV radiation help to break up bonds and promote a three-dimensional cross-linking of molecules close to the surface [4-12].

Plasma-based surface activation is already a relatively wide spread application in industry. Examples range from the automobile industry (rear-view mirror housings and bumpers are activated to meet the strict requirements for paint adhesion and polypropylene instrument consoles are activated prior to foaming with polyurethane) to the production of medical equipment (plastic parts of disposable syringes are pre-treated before they are glued to the barrel of the needle and polystyrene containers used in biomedical research are hydrophilised to facilitate wettability by liquids).

3.2. Selective etching

The idea behind selective etching is that different materials have different erosion yields under the same plasma conditions [13]. Therefore, in the case of a two-component material in principle it should be possible to find such conditions for which one of the components is eroded by the plasma atoms while another one is not. Whether a component of the material will be etched depends solely on the chemical properties of the component. In the case of inorganic particles in a polymer matrix, it is possible to achieve a perfect selectivity. Also, since the neutral atoms are propagated through space only by diffusion, such etching is isotropic, meaning that even surfaces with complex shapes will be etched (almost) as well as perfectly flat surfaces.

3.2.1. Study of pigment dispersion in powder coatings. Powder coating (PC) is a method of applying coatings to surfaces without using solvents. The coating is applied as a free flowing powder and heated to cause it to flow and adhere to the surface. The powder may be a thermoplastic or a thermoset polymer. It is normally used to create a hard finish on metals. Powder coating is mainly used for coating metals, such as "white goods", aluminium extrusions, and automobiles, although some other materials (like MDF – medium-density fibreboard) also can be coated in this way.
The most common polymers used are polyester, polyester-epoxy (known as hybrid), fusion-bonded epoxy, and acrylics. The majority compound of a powder coating mixture is the binder polymer, which amounts to around 70 mass %. The pigment particles typically represent from 0.1 to 10 mass %. The rest is the filler (usually salts such as CaCO$_3$ or BaSO$_4$), which amounts from 10 to 20 mass % depending on how many different pigments are used.

Powder coating is popular because compared to other coating technologies (procedures) the emission of volatile organic compounds is much smaller, making it an environmentally much friendlier and more acceptable technology.

One of the technological issues of powder coating is the dispersion of the pigment particles. When they are not dispersed well enough – meaning that they form relatively large clusters – the visual properties of the coating are affected (reduced gloss and increased haze values) as well as the viscosity of the final PC system. Needless to say that a good pigment dispersion is desired.

The dispersion of a pigment in powder coatings is usually incomplete. It is influenced by the properties of the pigment itself, by the binder and, to a large extent, by the extrusion process. Several properties of the coating formulation influence the dispersing process, namely the viscosity of the binder, its ability to wet the pigment surface, the attractive forces between the primary particles and the production process, i.e., pre-mixing, extrusion, and grinding. Sufficient pre-mixing of the ingredients is especially important for materials that are used in small quantities. Pigment particles are broken down to primary particles during the extrusion process, which typically lasts for 20 – 30 s. Differences in the extrusion equipment and extrusion shear force also influence the final state of the pigment.

In the past years different approaches for improving the dispersion have been used, which include the use of pigment predispersion in the coating formulation, different additives to improve wetting of the pigment surface, and modifications in equipment design. However, for a truly successful improvement of pigment dispersion, an effective method of analysis of dispersion in needed. Unlike classical coatings where the degree of dispersion can be easily observed in situ, the degree of pigment dispersion in powder coatings can only be evaluated at the end of the extrusion process or at the end of manufacture of the powder coatings [14].

While there are certain indirect methods for evaluating the state of the pigment (using colorimetry, etc.) a direct, quantitative method would be preferred.

One of the few suitable methods for quantitative determination of the state of pigment dispersion in powder coatings is the use of scanning electron microscopy (SEM). However, a scanning electron microscope by itself is not enough. Since the microscope makes only an image of the surface, that would not reveal any appreciable information of the degree of dispersion. As mentioned, the pigment particles amount to only a few mass percent of the powder coating, so there are obviously very few visible at the surface that is mostly represented by the polymer binder. Therefore, before the SEM can be used, the pigment particles must be exposed. That means that the binder must be removed from the surface.

A very efficient way of removing the binder and thus exposing the pigment particles is by etching with weakly ionized oxygen plasma. The oxygen atoms etch away the surface layers of the binder while leaving the pigment particles intact. This happens because the binder is made of polymers that oxygen atoms easily transform to volatile products while pigments are mostly metal oxides and as such do not react with oxygen [15].

3.2.2. Metallization of a graphite grain – polymer composite. A less studious and a more applicable use of selective etching can be found in the metallization of composite materials [16]. Currently metal-coated parts made of polymer and graphite grain composite are being used as a replacement for metal commutators in electric motor industry. Such parts are lighter than metal ones; also they are chemically more resistive to certain compounds, which make electric motors built with composite parts more suitable for use in environments where aggressive chemicals are present, e.g. gasoline.
pumps in automobile motors where the gasoline corrodes the copper that is used for conventional commutators.

The standard metallization procedure consists of etching with ultrasound and NaOH, surface activation with palladium, and chemical deposition of nickel. Only then the galvanic deposition of nickel is possible. While galvanic deposition is a fairly inexpensive and efficient process, the chemical deposition and palladium activation are not. Weakly ionized oxygen plasmas successfully replace the classical procedure. The oxygen atoms not only etch the polymer matrix as seen on figure 1, which replaces the NaOH etching, but also activate the carbon particles, hence eliminating the need for palladium baths. Thus weakly ionized plasma technology offers an environmentally friendlier and a less expensive alternative to the classical procedure.

![Figure 1. Selective plasma etching of a powder coating (epoxy polymer) sample by weakly ionized, highly dissociated oxygen plasma. The SEM images represent samples (from left to right):) untreated, plasma treated for 60 s, and plasma treated for 400 s.](image)

3.3. Surface cleaning
In terms of plasma processing, cleaning can mean both the removal of organic impurities (greases, oils, waxes, and solvents) by oxygen plasmas or the removal of corrosion products (such as oxide layers) by hydrogen plasmas. The first process is not much different from etching, as described in the previous section. Oxygen atoms transform organic molecules on the surface into volatile compounds such as H₂O, CO, etc, which detach from the surface and are pumped away. This procedure is widely used in electronics industry where organic residues on metal surfaces strongly hinder the mechanic and electric properties of joints created on those surfaces.

Hydrogen cleaning is employed in order to remove corrosion products from metal surfaces. H atoms form products such as H₂O, H₂S, HCl, etc, which are desorbed from the surface and are pumped away [17]. This procedure is also widely used in industry [18,19], but also in other applications such as the treatment of archaeological artifacts [20–22]. Figure 2 shows Auger electron spectroscopy depth profiles of a copper surface prior to cleaning, after wet chemical treatment, and after combined oxygen and hydrogen plasma treatment.

3.4. Ashing
Ashing is a procedure used prior to analysis such as atomic adsorption spectroscopy (AAS) which is used to test organic matrices for traces of inorganic compounds. As concentrations of said inorganic compounds can be below the level of detection, the organic matrix has to be removed until so little material remains that the concentration of inorganic compounds is high enough for a reliable detection [23].
Figure 2. Selective etching of a polymer-graphite composite. SEM images of: a) untreated sample; b) weakly treated sample; c) heavily treated sample. In the first picture it is apparent that the surface consists mostly of the polymer matrix (smooth edges) while on the right hand picture we can see by the increased presence of sharp edges that the carbon particles have been revealed.

Figure 3. Green leaf before (left) and after (right) ashing in oxygen plasma. During the ashing all of the water and the organic matter has been removed yet the structure of the leaf has been very well preserved.

In ashing by oxygen plasma oxygen atoms from the plasma react with the surface material, transforming the organic matrix into volatile molecules (H2O, CO, etc). Unlike wet ashing, which utilises acids, not only does ashing by plasma cause less damage to the environment but it also eliminates the danger of introduction of other elements into the analysed material during the process of ashing.

4. Conclusion
We have presented weakly ionised plasma as a tool in surface engineering technologies. Due to its high concentration of neutral atoms it is a chemically reactive medium that can be used to induce chemical changes on the surface of the processed material without causing any changes in the bulk of the material. We have presented examples of surface engineering technologies in which plasma processing can offer an alternative to traditional, wet cleaning methods. As plasma treatment eliminates the need of aggressive chemicals, it is an environmentally less damaging procedure.

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