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Atmospheric-Pressure Non-thermal Plasma-JET effects on PS and PE surfaces

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Abstract. The Atmospheric-Pressure Non-Thermal Plasma (APNTP) has become a topic of a great interested for a wide spectrum of applications in different industry branches, including the surface of treatment processes. In this work we evaluate the effect of an argon APNTP exposure to determine changes suffered by a polystyrene (PS) nd polyethylene (PE) polymer surface through RAMAN spectroscopy and SEM. It was determined that the hydrophilic change in energetic terms, i.e. surface activation in the PS and PE polymers is addition of oxygen by surface activation when the samples with jet plasma are exposed with the inert argon gas. It was possible to characterize the hydrophilic shift based on the change in intensity of the spectra.

Introduction

Recently Atmospheric-Pressure Non-Thermal plasmas (APNTP) have become a topic of great interest for a wide range of applications in different branches of industry. In these plasmas the electron temperature is far higher than the temperature of the heavy particles [1]; elastic collisions of the electrons are not effective in terms of it not having a large impact on heavy particles surrounding however electrons can transfer energy to other processes such as ionization, activation or dissociation of molecules.

For over two decades there is a growing interest in the development of devices for the application of this type of plasma discharges in many industrial processes, it is well known also that there is now a wide variety of commercial options to apply treatments of surface activation in different materials with the aim of improving the adhesion properties of certain surfaces.

In the Biomedical field for example, the establishment and quantification of the atomic additions in surfaces (which are carried by the action of the plasma) is very important for the adequate interaction of the cellular matrices in implants and medical devices. In fact, the modification of the original surface through the ion bombardment, corona discharge in air, plasma (nitrogen, argon, axygen), gamma or beta radiation and pre-absorbed surfactants with work gas discharge, is one of the most used methods for the superficial modification of polymeric biomaterials without significantly changing the physicochemical properties and their mechanics [2]

The fundamental physical function of the discharge and the knowledge of basic plasma parameters have been analyzed in several studies. The objective of many studies is to determine the temperature and the concentration of electrons in particular in the active discharge area, however, the chemical dynamics of the process is unknown or has not been extensively studied.

Recently an Atmospheric-Pressure Non-Thermal Plasma-Jet for biomedical and industrial applications has been developed in our laboratory, we evaluate the effect of an argon plasma using this device on a polystyrene (PS) and polyethylene (PE) samples to determine changes suffered in the surface. Some tests RAMAN spectroscopy were performed. It was showed an increase in the intensity of the peaks, which shows a higher surface energy per atom detachment due to exposure to plasma. Furthermore, micofibers in SEM were captured to observe the surface changes of the macro and micro order.

2. Methodology.

2.1. Materials & Experimental Set-Up

Comercial samples of polystyrene and high density polyethylene were used, these samples did not receive any pretreatment prior to application of the plasma discharge. Eight samples of 1 cm^2 area were used for each polymer, two unexposed sample was left as a standard, and the others are grouped in pairs that were treated for 1, 2 and 3 minutes.

Figure 1 shows configuration of reactor, this set-up allows the device work in two working modes depending if plume enters or not in contact with an object, the configuration corresponds to a model developed in our laboratory previously [4]



To generate the plasma discharge is used argon as working gas adjusting a flow of 5 l/min, the central electrode of the device is made of copper and glass as dielectric with an aperture of 4.5mm. Using an AC Power Supply set to 25kHz, 300V and a duty cycle of 50%

2.2. RAMAN Spectroscopy.

Raman spectroscopy is obtained by irradiating a sample with a powerful source of visible or infrared laser monochromatic radiation. During irradiation, the spectrum of radiation is scattered at an angle (90 °) anging from 0 to 100 on the intensity of the source is recorded. In these cases, they are useful for the detection of functional groups and fingerprint regions to detect and identify specific compound. Reading the spectrum is done with Weighted intensities for each atomic bond.

2.3. Scanning electron microscope.

It is used as one of the most versatile techniques in the study and analysis of the microscopic characteristics and structural of the solid objects. It works as a superficial study since it does not have a high penetration depth, which is adequate for the surface study.

3. Results

3.1. RAMAN Spectroscopy.

The Raman study is sensible to nanoscale change levels and the addition of functional groups or energy increase in the bound displacement, so it is very important for the analysis of the surface changes, (B. Welt, 2009).

As it is shown in the Figures 3 and 4, in the case of polystyrene, the oxygen addition or interaction by energy changes determine waves between 1300 to 3000, when as showed increase of intensity in spectrum. It is extremely low and does not show a dependence with the time. In the case of polyethylene, it is shown an increase in this intensity and a clear dependence is shown with the exposure time



Illustration 2. Graph polystyrene exposed to plasma-jet at different times, (1 min–Blue, 2min-Purpule, 3 min-Green and 4min-Red).



Illustration 3. Graph polyehtylene exposed to plasma-jet at different times, (1 min–Blue, 2min-Purpule, 3 min-Green and 4min-Red).

3.2 SEM

As the Raman analysis also detects changes in roughness it is important to determine every surface change at the macro level [greater than 100 nm], polystyrene was examined only for simplicity and it is observed as shown in Figures 6 and 7 do not change. It can be clearly seen that the same increase in the same area before and after its exposure there are no detectable changes in the microscope



Illustration 4.Control test of polystyrene



Illustration 5. Polystyrene statement 3 minutes

3.4 Analysis of the results.

The characterizations of the samples were focused in two directions. The analysis macro and micro surface after being exposed to the plasma for 0, 1, 2 and 3 min. The macro-level analysis is the SEM, we can see in Figure 4 and 5, if we compare the polystyrene with the sample exposed for 3 minutes there is change in roughness, which can be seen at 500X. Therefore it can be mentioned that the change in properties of the surface, in this case, the interaction with aqueous or oily solutions, is due to a chemical change in the first layer of atoms, because the Raman study showed an increase in intensity in the peak. The micro-level study confirmed the previous idea, the use of RAMAN spectroscopy could characterize the addition of atomic oxygen to the polymers, and however, it could not quantify the amount of reactant molecules[2]. The theory states that in the range between 1300 and 3000 wave number we found the presence of oxygen in their various functional groups and link availability[3]. In Figure 2, the spectrum [intensity versus wave number] of the polystyrene is observed, we can observe that the increase over time in the range of 1300-3000 was not high enough, and it is held stationary at the time, this is because the energy of benzene is almost saturate, it requires more energy than other functional group because the phenyl structure has a high molecular stability[3]. In the case of Figure 3, we can see peaks in this range because the polyethylene is a simple hydrocarbon chain with one sigma bond if there is a dependence on the exposure time. This is because depending on how much energy the system is submitted, more and more carbon will adhere radicals. in the two spectrums denote increase of intensity in the peaks but not changes in the form. This point showed that materials of this study don't change your chemical structure, but this energy provide the change of relation with the water.

4. Conclusions

1) The hydrophilic chemical aspect is not physical because no physical, n terms of macrostructure, since evidence was found in the SEM micrograph obtained

2) The results from the RAMAN studies show that the surface changes are product of adittion of more superficial energy ince there is an increase of intensity in the wave numbers between 1300 y 3000. Which is equivalent to the C-O and C=O bonds because this bonds are the most chemically energizable in the molecule. Furthermore, it is seen that the time dependence is only shown with the polyethylene since it lacks the stable and hard to energise since this have one steady state phenyl groups (such in polystyrene). It also contains anoxidizable lineal chain along its structure.

5. References.

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