STUDY OF THE INTERACTIONS BETWEEN PLASMA / POLYSTYRENE AND A NEW APPROACH TO CHARACTERIZE THE MODIFIED SURFACE

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Abstract

A study has been made on the modification of the surface properties of polystyrene by various surface analytical methods including surface energy measurements, XPS analysis, chemical titration and electrokinetic measurements. Besides, the optical emission and mass spectroscopies are employed as diagnostic techniques to examine the plasma composition. All these analyses not only examine the effects of functionalization on the surface of polymers but also serve as the experimental tools to compare with existd theoretical modeling system.

1. Introduction

The surface modification of polymers by cold plasma has drawn a lot of attentions due to the key feature that the modification limited only to the outermost layers (several hundred angstroms) without altering the bulk properties of material. The plasma treatment can modify the properties of surface such as wettability, adhesive, biocompatibility and topography. The plasma treatment is a rapid, clean and non-solvent process which can be used to introduce a specific element or functional groups onto a surface of polymer by selecting a suitable gas[1]. In this work, the surface modification of polystyrene in nitrogen, hydrogen or carbon dioxide plasmas are investigated.

The plasma treatment has been proceeding in a microwave frequent plasma instrument. The parameters (treatment time, input power, gas flow rate and gas composition) of plasma treatment are decided by the studies of degradation and surface energy with respect to both nitrogen and carbon dioxide plasma. In order to identify the variations on surface chemistry resulting from plasma treatment, a number of surface analytical techniques have been employed, these include contact angle measurements, X-ray Photoelectron Spectroscopy (XPS), chemical titration, and zeta potential measurements. Then the interactions of plasma with polymers are examined based on the evolution of reactive species by the analysis of mass and optical emission (OES) spectroscopies.

2. Experimental

Plasma equipment
Th microwave plasma is mainly composed by three compartments: a generator, a quartz cylinder and a pumping system which allow to control the operating parameters as previously described [2]. Moreover, the reactor is in-situ connected with mass (PPM 420 Balzer) spectroscopy and optical emission (HR 320 Jobin Yvon) spectroscopy which are able to examine the compositions of plasma for the active species and the interaction between plasma and materials.

Dielectric analysis

The equipment employed for analyzing the capacitance and zeta potential is composed of a controller (NOVOCONTROL) and an analyzer (WinDETA).

Material

Polystyrene (Mw = 25,000, density = 1.05), the film type samples are prepared by dissolving the polystyrene particles in the THF then allow its total evaporation and then put in the oven for 50°C and 24 hours. PP film, (thickness = 120 μm), films are cleaned by ethanol and distilled water then put in the vacuum container until use. Electrolyte: aqueous KCl in different: 10⁻¹ M, 10⁻² M, 10⁻³ M, 10⁻⁴ M, and 10⁻⁵ M.

Methods

XPS
X-ray photoelectron spectroscopy (XSP) analysis were executed on Leybold LHS 12 at the "Laboratoire de Physics des Couches Minees" at the Université de Nantes.

Surface energy measurement

The surface energy is calculated by measuring the contact angle based on acid-base theory and is measured with 3 liquids: distilled water, diiodomethane, and glycerol. The surface energy is taken averaged by at least 6 measures for each sample.

Chemical titration methods

The newly formed functional groups are examined by Ponceau 2R and thionine acetate solutions as described in previous works[3].

3. Results And Discussion

Plasma treatment of PS in the process gases nitrogen, ammonia, and carbon dioxide proved very effective for surface modification of this normally highly unreactive polymer.

The modification can be observed, first of all, the dramatic change of the surface property from hydrophobic to hydrophilic by the contact angle measurements. The surface energy is measured in function of different parameters of plasma such as exposure time and applied power, (Fig.1). For both of the nitrogen and CO₂ plasma, the total surface energy γ₀ and its acid-base component γ_{AB} increase very rapidly in the first 60 seconds, from 40 to 63 mJ/m², and then approach a constant value with increasing treatment time. On the other hand, the total surface energy γ₀ and its acid-base γ_{AB} component increase very rapidly at applied power of 10-20W (from 43 to 63 mJ/m²), however, the component of Lifschitz-van der Waals γₔ does not vary a lot. Here the increment of γ_{AB} can be considered resulted from the formation of polar groups of the surface[4].

XPS analyses confirmed that the changes in wettability of PS surface are due to chemical changes on the polymer by showing the new peaks which can be assigned to nitrogen and oxygen plasma treatment. The results will be concluded according to the overall spectra and the high resolution C 1s spectra of PS treated by both ammonia and CO₂ plasma (Fig.2). The untreated PS is composed of aromatic carbon-carbon simple bonding (72.31%), aliphatic C-C bonding (23.97%), π-π⁺ shake-up satellite (3.72%) by analyzing the C 1s peak. Moreover, according to the overall spectrum, it shows the presence of oxygen with 3.3% which can be
explained by the absorption of oxygen during the process of preparing the PS film. The effect of plasma treatment on PS was investigated for time period of 10s, 1, 3, and 5 min for both ammonia and CO$_2$ plasma.

For ammonia plasma, the percentage of carbon in the overall composition reaches a steady value after 1 min with a value of 5.5% and the components of C-N (286.1 eV), C=N (287.5 eV), and O=C=N (288.7 eV), increase from 0 to 15.6%, 5.6%, and 3.3% respectively. A remarkable decrease of the main carbon peak is observed by XPS for both ammonia and CO$_2$ plasma. This can be explained by the surface structure of carbon bindings was disrupted by the bombarding species of the plasma. The percentage of oxygen in the overall composition has also been increased to 9% due to the contact with atmosphere right after the plasma treatment.

Furthermore, for the CO$_2$ plasma treatment, the percentage of oxygen reaches a steady value after 1 min with a value of 25.9% and the components of C-O (286.1 eV), C=O (287.5 eV), and O-C=O (288.7 eV), increase from 0 until 15.6%, 6.9%, and 5.9% respectively. Longer exposure time leads to no further change in the surface composition under experimental conditions applied. The results show that the formation of C-N, C-O and C=NC=O groups are proportional with the consumption of the simple carbon bonding for both ammonia and CO$_2$ plasma.

The chemical identity of the nitrogen or oxygen containing groups produced via plasma could not only be clarified from XPS spectra but can also be proved by the chemical titration methods. For amino groups incorporated by nitrogen or ammonia plasma, Ponceau 2R, an aromatic disulfonate which can react with basic functional groups after acidification, is selected. The results (Fig. 3) show that, for the exposure time less than 4 min, the formation of amines is proportional to the treatment time. And the density of amines approaches a constant after 4 min. This can be explained by the saturation of functional groups on the surface. Moreover, the addition of hydrogen in nitrogen plasma can increase the growths of amines. For the applied power, the density of amines increases with the power in the range of 0-60W and then stays at constant for the power exceeds 60W. Then concerning about the carboxylic acid formed via CO$_2$ plasma treatment. The thionine acetate is selected due to its sulfonic groups which can react with carboxylic acid. The results show that the carboxylic acid groups form very rapidly in the first 60 seconds and then reach a constant value afterwards. The applied power has the same influence as nitrogen plasma, that means it favor the formation of functional groups for the applied power is superior 20W and then stays constant for stronger power.

The polymers usually posses considerable surface charge densities in the solid/liquid interface while in contacting with electrolytes due to the dissociation of acidic or basic functions or due to the adsorption of ions from the solution. The surface charge is balanced by countereions in an electrical double layer on the liquid side of the interface which can be characterized by some different kinds of electrokinetic techniques such as streaming potential measurement, electrochemical impedance spectroscopy etc[5, 6]. In this work, the dielectric analysis method is utilized in order to obtain also the electrokinetic properties and then compared with the existed techniques and modeling system.

Under the assumption that there is no specific adsorption for our system, Fig. 4 displays the result ad it shows that the zeta potential, at the first stage, increases with the concentration of functional groups on surface. And then it reaches a steady value and stays constant after some extent of concentration values. This phenomenon can be applied to different concentration of electrolytes. This can be explained, as the chemical titration analysis, by the
possibility that the surface is saturated by the functional groups when the concentration exceeds some values. Moreover, this result can also allow us to compare with our previous work which has set the relationship between zeta potential and concentration of functional groups by the measurement of surface energy[7]. Although the values of the experimental measured zeta potential show some differences with the modeling system, the experimental results do present the same tendency as the theoretical calculated ones. The explanation of this difference can be resulted from the association of functional groups with the electrolyte which formed the electrical double layer is so weak that the interaction can not be evidently measured. On the other hand, the values measured by this dielectric analyses are frequency-dependent, and the frequency taken for the measurements is 1 Hz. Therefore, it exists the possibility to decrease the frequency and obtain a more important value of zeta potential.

The interactions between PS and plasma has been studied by in situ OES and mass spectrosopies which allow to analyze the excited species in the plasma. The evolution of the plasma phases with and without the presence of PS are compared in function of time. The results show, for both nitrogen and CO₂ plasma, the active species of N and O are consumed evidently by the introduction PS in the plasma phase which implies that the interactions are processing. This can be further proved by observing the decreases of those active species in the plasma and the formation of new species by OES. On the other hand, the presence of hydrogen species is observed due to mostly from the degradation of the material.

Fig.1 : results of surface energy measurements
Fig. 2: the results of XPS analyses

Fig. 3: the results of chemical titration
4. Conclusion

The plasma treatment is proved very effective due to it provides a dramatic modification of the wettability of surface in a very short period of time and by a mild applied power. The modifications are resulted from the formation of functional groups on the surface, which can be proved via several analytical methods in this work. The results show some important correlation between different analyses. Furthermore, the experimental results of zeta potential have been proved with the same tendency as the previous established modeling system constructed by surface energy measurement though there exists the difference for the measured and theoretical values. Polystyrene is material widely utilized in biomaterials and its surface properties can be significantly transformed by cold plasma treatment.

References