Study on Plasma Surface Modification of Hydrophobic Materials

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Abstract. The hydrophobic materials were treated by plasma continual treater to achieve its surface modification and improve its wettability. The influences of treating time, discharge power, working gases and gas pressure on the surface modification of the materials have been investigated. The chemical states and species on the surface of materials have been investigated by some technologies such as contact angles. After plasma surface treatment, the contact angles of PTFE sharply decrease, and the alkali liquid absorption of PE increased to three times of its weight. The contact angles of silicon rubber and polyester decreased remarkably after surface modification. PTFE films were grafted with crylic acid to evaluate the ageing. The effect of vacuum ultraviolet radiation to surface modification was initially described. The results of experiment demonstrate that the better wettability of hydrophobic material can be achieved. The technique and the equipment have the promotional value for industrial application.

Keywords: Materials, Surface, Plasma, Equipment, Glacial Acetic Acid.

1. Introduction

At present, new polymer materials have been widely used, but most of the surfaces of new materials are hydrophobic, which limits their bonding and other applications. Plasma surface modification is to optimize the structure and performance of material surface by plasma glow discharge [1-3], which is a very prospective material surface modification method. Polytetrafluoroethylene (PTFE) has been widely used in industrial applications because of its excellent chemical stability, dielectric properties, very low kinetic friction coefficient, good mechanical workability and flame retardant properties. Diaphragm paper, also known as polyethylene film (PE film), its role in lithium-ion batteries is to isolate the positive and negative materials, and the quality of diaphragm paper directly affects the safety of the battery performance and capacity, so the selection of high quality diaphragm paper is the only way for battery manufacturers; At the same time, silicone rubber with biocompatibility and polyester as a new thermoplastic engineering plastic are widely used. However, due to the defects such as poor surface wettable of this kind of polymer material, its application in some special industrial technology fields such as medical treatment and sanitation is limited [4-6].

In recent years, a large number of researches have been conducted on the surface modification of hydrophobic materials at home and abroad. In order to improve the bonding properties of polymer materials, the current surface activation methods mainly include chemical etching, optical radiation, plasma treatment, ion implantation, surface graft polymerization, etc. [7]. Taking polytetrafluoroethylene (PTFE) as an example, chemical etching (metallic sodium Na) is generally used to achieve surface activation in China, but there are common constraints such as environmental protection and other factors. Plasma surface modification is to optimize the structure of material surface by discharge plasma. Because of its specific environment, cost and other advantages, it has become a commonly used material surface modification method in industry. The key technology of plasma surface modification lies in the design of discharge electrode and the determination of related parameters. In this paper, the effects of RF power, plasma treatment time, pressure and different discharge gases on the surface properties of materials are investigated. Contact Angle measurement, XPS and other analytical techniques have proved that the radio-frequency plasma has carried out ideal chemical modification on the surface of materials.

2. Equipment and Experimental

2.1. Equipment

Conventional plasma power such as DC, low frequency and microwave have disadvantages such as weak discharge, uneven distribution and high power consumption. In this paper, a plasma continuous processor with RF glow discharge (frequency 13.56MHz specified by the equipment console) (developed by Changzhou Ningda Plasma Technology R&D Co., LTD.) and a static plasma processor are adopted. The RF power source is SY type 500W crystal controlled RF power source with frequency 13.56MHz. The output power is continuously adjustable, and the RF power supply is matched with the SP-2 RF matcher to adjust the incident power and reflected power of the RF plasma through the impedance matching network, so that the generator matches the plasma impedance (50Ω). The plasma processor adopts the form of capacitive coupled glow discharge and external electrode discharge. Because the extinguishing time of active particles in the plasma is much longer than the half cycle of excitation under the condition of RF discharge, the plasma formed is uniform, stable and has strong reactivity. Fig. 1 shows the discharge effect diagram of Ar+H2 gas as working gas in the continuous plasma surface treatment reaction chamber. It is obvious that the discharge area presents bright uniform lavender smoke state.

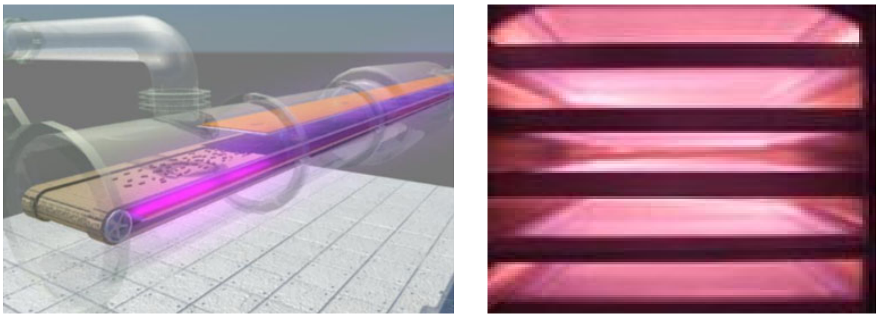


Fig. 1 Diagram of glow discharge with radio frequency plasma

2.2. Experimental

2.2.1 Materials.

PTFE, PE, silicone rubber and polyester, which are strip samples, can be carried out by continuous transmission plasma treatment and ultrasonic cleaning with acetone 20min, and dried to reserve. The purity of the working gas is greater than 99.996%. The samples were cleaned by Ar plasma before treatment, and then modified by plasma surface in related working gas atmosphere.

2.2.2 Experimental Methods

The plasma processor used in this experiment is a capacitive coupled glow discharge, external electrode discharge form. The washed and dry material is placed in the discharge space of the plasma processor and continuously driven at a specific speed. Start the vacuum pump to pump the background vacuum to 1Pa, and inject the working gas Ar+H2 (volume ratio of Ar and H2 is 4:6), N2 or O2 at a certain flow rate. The flow rate is controlled by the rotor flowmeter. When the required air pressure is reached and the air pressure is stable, the discharge power is adjusted and the reflection power is minimized. When the processing reaches the required time, the power supply is turned off (gas phase connection technology can be carried out), the air is passed and the sample is taken out. Contact Angle measurement and XPS and SEM analysis were carried out immediately. After the treatment, the samples were stored in the dryer for a certain period of time, and then taken out to measure the contact Angle to test its timeliness.

2.2.3 Performance Testing

Wettability: The static contact Angle was measured by sessile drop method on the JY-82 contact Angle measuring instrument (ChengDe testing Machine Company). The measurement error was ±0.5°. Water was used as the reference liquid, and the temperature was measured at 24℃. XPS test: ESCALABMKII photoelectron spectrometer (VG) was used to test. MgKa (hn =1253.6eV) excitation source was used for sample analysis. The power was 220W (11kV×20mA). Energy analyzer fixed transmittance of 20eV. And the sweep Angle between the analyzer and the sample was 90°. The etching was observed by GSM5800 microscanning electron microscope.

3. Results and discussion

3.1 The working conditions of the plasma effect on surface wettability

Taking PTFE as a typical case, the influence of plasma working conditions on surface wettability and the timeliness of surface modification were investigated in this paper. The surface modification of PE cell film, silicone rubber and polyester was also analyzed.

3.1.1 Processing time, power and pressure on the surface wettability

In a variety of working gas plasma treatment of PTFE film experiments, it is found that a single Ar, H2 is difficult to achieve a better surface modification effect, and after a single gas treatment generally need to be treated with technology to achieve a better effect. Therefore, this paper mainly conducts comparative experiments on Ar+H2 (volume ratio of Ar and H2 is 4:6), N2 or O2 and other working gases. FIG. 2 shows the influence of plasma treatment time on the contact Angle of PTFE film under the conditions of gas pressure of 25Pa and treatment power of 200W. It can be seen from Fig. 2 that the contact Angle between PTFE and water decreased to different degrees after plasma treatment at different times. The contact Angle of Ar+H2 working gas is obviously smaller than that of other working gas. It can also be seen from Fig. 2 that the hydrophilicity of PTFE can be significantly improved by RF low temperature plasma treatment within a certain time (2min). When the treatment time was longer than 5min, the contact Angle between the sample and water decreased little.

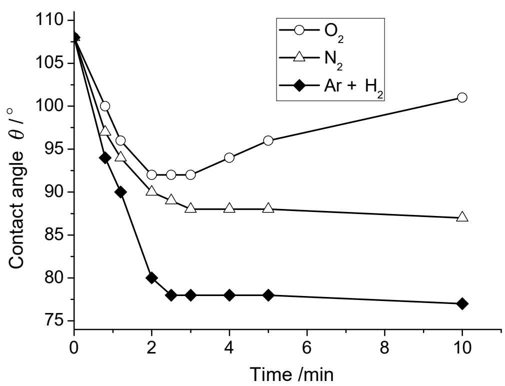


Fig. 2 Influence of contact angle according to the time of plasma treatment

Fig. 3 shows the influence of plasma treatment power on the contact Angle between PTFE film and water under gas pressure of 25Pa and treatment time of 3min. It can be seen from FIG. 3 that the contact Angle of PTFE decreases after being treated by plasma of different power, and the contact Angle tends to stabilize when the power reaches 150W. When the power is the same, the modification effect of plasma is obviously Ar+H2>N2>O2. The increase of power is not conducive to the improvement of the surface hydrophilicity of PTFE samples. This is because at high power, the high energy particles in the plasma increased significantly. Strengthening the impact on the surface of the material will deactivate some of the active groups on the surface and thus reduce the approach of active groups.

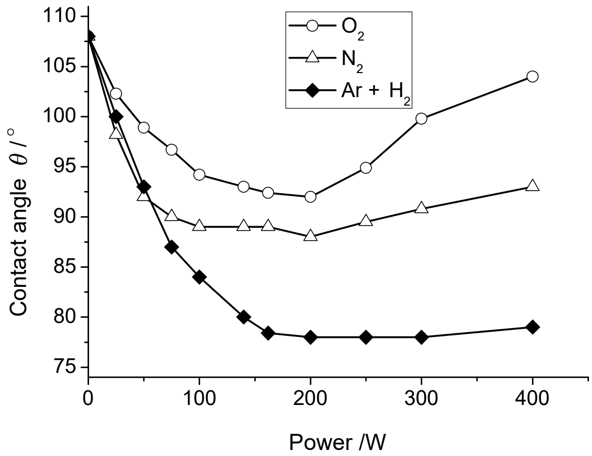


Fig. 3 Influence of contact angle according to the power of plasma treatment

Fig. 4 shows the influence of plasma pressure on the contact Angle between PTFE film and water under the treatment power of 200W and treatment time of 3min. As can be seen from the figure, when the discharge pressure is greater than 10Pa and less than 50Pa, the pressure has no obvious influence on the antenna. However, when the air pressure was greater than 50Pa, the contact Angle increased, which may be due to the high air pressure which makes it difficult for the gas to completely ionize, thus affecting the surface modification of PTFE.

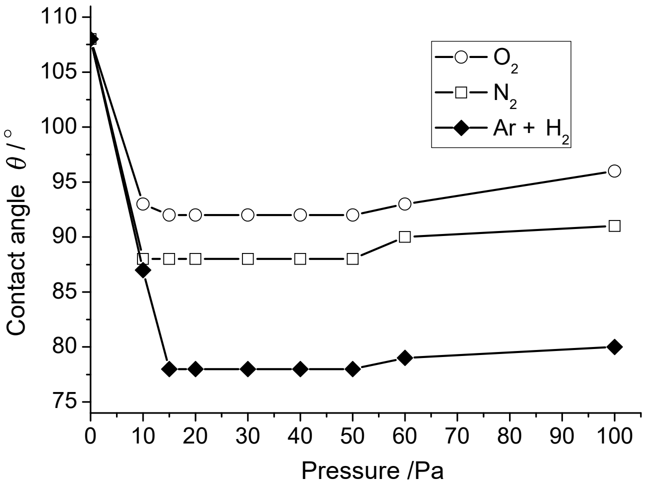


Fig. 4 Influence of contact angle according to the pressure of plasma treatment

3.1.2 PE cell membrane, silicone rubber and polyester surface modification

PE cell diaphragm: Helium, as a working gas, has a radio frequency power of 50W and a working pressure of 25Pa. Before modification, the contact Angle of PE cell diaphragm was close to 160º. After modification, water droplets could be absorbed instantaneously, and the contact Angle was close to 0, which indicated that plasma surface modification played a certain role. After modification, the corresponding performance index has also been significantly improved (alkali absorption rate: 3.5 times of its own weight; climbing rate: nearly 100mm in the initial 3 minutes).

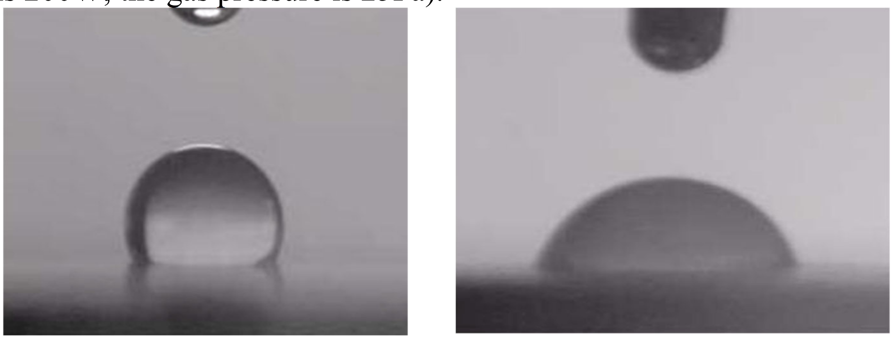
Silicone rubber: Argon is used as the working gas. The RF power is 150W, and the contact Angle is changed from 105º to 30º.

Polyester: With oxygen as the working gas, the RF power is 100W, and the contact Angle is changed from 98º to 15º.

Plasma contains a large number of electrons, ions, excited atoms, molecules, free radicals and other active particles. These active particles and polymer materials interact with the material surface oxidation, reduction, cracking, crosslinking, polymerization of various physical and chemical reactions, so as to optimize the surface properties of materials and increase the surface hygroscopicity (or hydrophobicity), stain, adhesion, antistatic and biocompatibility.

Plasma surface treatment and characterization of surface analysis.

In order to investigate the wettability of each material, the contact Angle was measured. Figure 5 shows the instantaneous droplet variation diagram (distilled water) of contact Angle before and after plasma treatment on PTFE surface (Ar+H2 gas is the working gas; the treatment time is 3min; the discharge power is 200W; the gas pressure is 25Pa).



(a) before treatment (b) after treatment

Fig. 5 Testing of water contact angle for PTFE surface with plasma treatment

In order to analyze the plasma treatment process, XPS element quantitative analysis (Ar+H2, 3min, 200W, 25Pa) was performed on both the original sample and the plasma treated sample. it shows the fact that after plasma treatment of PTFE surface, F1s spectral peak decreases obviously, while C1s and O1s spectral peak gradually strengthen, and N1s peak also appears. The amount of carbon and oxygen increased substantially, while the amount of fluorine decreased correspondingly.

4. Vacuum ultraviolet radiation on the impact of surface modification

When O2 plasma treats PTFE (polytetrafluoroethylene), because the radiation of oxygen at 130.5nm is not absorbed by PTFE, it can not cause photochemical reaction, and the plasma with a shorter wavelength than O2 is needed, such as the radiation of H2 at 121.5nm will be absorbed by PTFE. H2 plasma (radiation wavelength 121.5nm) and Ar plasma (radiation wavelength 104.8nm) are effective for PTFE modification and water contact Angle is significantly reduced. Different proportions of several gas cylinders are necessary for modification equipment. It is generally believed that both plasma bombardment and optical radiation play a certain role in the modification of plasma processing, but the author and other researchers believe that the main role is still optical radiation.

The effect of oxygen plasma on surface treatment is more reflected in the etching effect on material surface, which can be seen from the comparison diagram in Figure 7. However, the etching degree of surface treated by inert gas plasma is lower. Therefore, the hydrophilicity of reactive gas plasma treatment is generally better than that of inert gas plasma treatment. However, since Ar+H2 is used as the working gas, it not only maintains the bombardment effect of inert gas on the material surface, but also utilizes the light radiation of H plasma, so the comprehensive modification effect is better than that of oxygen plasma. This is consistent with the fact that different working gas atmospheres can produce different surface modification effects of materials.

5. Conclusion

The surface modification of polytetrafluoroethylene (PTFE), PE cell membrane, silicone rubber and polyester was realized by plasma using RF discharge technology. Plasma working conditions have a significant effect on the surface hydrophilicity of PTFE. Discharge power, treatment time, gas pressure and other conditions are the main factors affecting response. The surface analysis of PTFE film before and after treatment shows that a large number of polar groups are introduced into the surface of the material after plasma treatment, which is the reason for improving its hydrophilicity. At the same time, the influence of plasma etching on the material surface modification was investigated by SEM analysis. The influence of vacuum ultraviolet radiation on surface modification was preliminarily discussed. This paper has certain guiding significance and practical significance for dynamic continuous production.

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