Study on Performance of Polyvinyl Chloride Treated by Plasma

Runjin Gui and Zhiwen Wang*

Guang Xi University for Nationalities, Nanning 530007 China.
* E-mails: 310484815@qq.com

Abstract. Treating polyvinyl chloride material with plasma, and the contact angle and shear strength, then study the changes of wettability and surface cohesiveness of the polyvinyl chloride material after modification. Measuring the background mass spectrometry and the mass spectrum of the intermediate product in the treatment of PVC, then we investigated the changes in gas composition during plasma treatment of PVC. Based on the analysis of contact angle and we found that the contact angle of PVC treated by plasma changed and the surface wettability was obviously improved. We also found that the shear strength of PVC treated by plasma showed a significant increase in surface bonding performance. The analysis of mass spectrometry shown that the composition of the air after plasma treatment of PVC changed a lot.

1. Introduction

Polyvinyl chloride (PVC) is a high-molecular material, which is a white powder, and its original color is faint yellow, and the degree of transparency is translucent. Because PVC is wear-resistant, flame-retardant, and not easily corroded, and its cost is relatively low compared to other polymer materials, it has been widely used in industry and agriculture [1]. Polyvinyl chloride has poor surface wettability and is hydrophobic and lipophilic, thus limiting its application in oil-water separation membranes, industrial printing and food packaging [2]. In many cases, PVC plastic products need to be subjected to secondary processing such as bonding when applied. Therefore, in many fields, the PVC plastic sheet should be improved as much as possible to make it more firm when bonded. An effective way to improve the surface wettability of PVC [3] and increase the surface roughness [4] is to treat polyvinyl chloride with plasma surface modification technology. The plasma surface treatment does not require wet water treatment, as long as it can be carried out in a dry environment, and there is no need to dry the material during the treatment again. Compared with other materials, the advantages of energy saving and high efficiency, while eliminating the waste water treatment, have protected the environment to a certain extent. The plasma surface treatment is modified only in the range of several nm to several hundred nm on the surface of the material, so that the surface properties of the material are effectively improved while ensuring that the material is not affected. In addition, the plasma surface treatment effect is relatively long-lasting, with simple operation, relatively low cost, and convenient for continuous automated production [5]. Modified surface plasma treatment of chemically inert polymers can lead to chemically reactive groups those result in functionalized polymer surfaces [6]. In this paper, polyvinyl chloride was treated by RF glow discharge plasma to study the change of contact angle of polyvinyl chloride plastic surface after plasma treatment and the bond strength of polyvinyl chloride plastic after adhesive treatment of polyurethane adhesive, and to analyze the reasons for the influence of plasma treatment on the bonding strength of PVC.
2. Experiment and Test

2.1. Specimens and Instruments
Main samples and instruments: polyvinyl chloride plastic sheet, polyurethane adhesive, ultrasonic cleaner, contact angle measuring instrument and HD-2 cold plasma modification equipment.

2.2. Sample Pretreatment
(1) Sanding the edges of the sample to be tested for easy marking and bonding.
(2) Putting the test sample (PVC sheet) in an ultrasonic cleaner for 3 minutes, and then taking out the sample to dry.
(3) Radio frequency glow discharge: A solid glass rod was used as a support part of the sample to be processed in a vacuum chamber.

2.3. Low Temperature Plasma Treatment
The HD-2 cold plasma modification equipment uses a capacitive coupled RF glow discharge plasma device with a frequency of 13.56 MHz. Putting the pretreated PVC plastic sheet in the vacuum chamber of the plasma modification equipment: (1) Evacuating the vacuum chamber to 20 Pa, and plasma discharge treatment was performed on four groups of PVC, the discharge power was 50 W, and the treatment time was 3 min., 5 min, 10 min and 15 min respectively; mass spectrometry was measured simultaneously. (2) The vacuum chamber was evacuated to 20 Pa, and four sets of PVC samples were treated with plasma for 5 min, and the discharge powers were 30 W, 50 W, 100 W and 150 W, respectively.

3. Measurement of Contact Angle of PVC Plastic Sheet
In the measurement experiment of the contact angle, in order to reduce the experimental error, we decide to take four points for each PVC board, and the average of the four points was taken as the value of the last contact angle. The values of the contact angles of PVC (P9, P10) without plasma treatment are shown in Table 1.

| Measuring position | 1  | 2  | 3  | 4  | average value |
|-------------------|----|----|----|----|--------------|
| Contact angle     |    |    |    |    |              |
| Left              | 91 | 87.75 | 85.5 | 87.5 | 87.94        |
| Right             | 89.25 | 85.75 | 85  | 85.25 | 86.31        |

According to the table, the difference in position at the measurement of the contact angle in the table is ±6. The generation of this error may be related to the difference in temperature, the impurities on the surface of PVC sheets and the operation at the time of dropping. Therefore, taking the average value can obtain the value of the contact angle more accurately.

A comparison of the values of the contact angles of plasma treated PVC sheets at the same power (50 W) and at different times is shown in Table 2.

| Processing time | Unprocessed | 3(min) | 5(min) | 10(min) | 15(min) |
|----------------|-------------|--------|--------|---------|---------|
| Contact angle  | Left        | 89.19  | 61.63  | 62.25   | 59.13   | 60.13   |
| Right          | 87.5        | 59.63  | 60.25  | 58      | 57.75   |

A comparison of the values of the contact angles of the plasma treated PVC sheets at different powers at the same time (5 min) is shown in Table 3.
Table 3. Contact of plasma treated PVC sheets at different powers at the same time (5 min)

| Processing power | Unprocessed | 30(W) | 50(W) | 100(W) | 150(W) |
|------------------|-------------|-------|-------|--------|--------|
| Contact angle    |             |       |       |        |        |
| Left             | 87.94       | 57.75 | 58.94 | 57.75  | 58.56  |
| Right            | 86.31       | 55.44 | 56.69 | 55.44  | 56.56  |

Analysis of the above table shows that the PVC surface contact angle changes significantly after plasma treatment of PVC, and the contact angle after treatment is reduced by about 30° than that treatment. The smaller the contact angle is, the better the wettability of the PVC surface is. Therefore, the apparent wetting effect of the PVC surface after plasma treatment is improved, which will help to improve the bonding performance.

Further analysis can also show that the plasma treatment of PVC under the same power, different time, the contact angle have not changed much; plasma treatment of PVC at the same time, under different power effects, the contact angle have not changed much, the difference is Between ±3° and ±2°.

Factors such as temperature, water purity, and adsorption of impurities on the surface of the PVC sheet during the experiment may affect the measured data, but it is in the error range. We can consider that time and power has some effect on the plasma treatment of PVC.

4. Measurement and Data Analysis of Bond Shear Strength

4.1. Test Unit and Test Method
The polyvinyl chloride is bonded using wet-solid one-component polyurethane. Test basis and method: test temperature 20 °C, tensile speed 2 mm/min, clip spacing 91 mm, shear strength = shear force / bonding area, unit MPa, bonding area are 625 mm² (25 mm × 25 mm), calculation results All 3 significant digits are reserved.

4.2. Results
Table 4 is the shear strength data of the bonded body of the PVC sheet after the RF glow discharge plasma treatment, the electric power is 50 W, and the treatment time is 3 min, 5 min, 10 min and 15 min, respectively. We can see that the PVC sheet treated by the nitrogen glow discharge plasma has the best treatment effect when the discharge power is 50W, and the best shear strength after bonding is 1.110MPa.

Table 5 shows the shear strength data of the bonded sheets of the PVC sheets after the RF glow discharge plasma treatment. The treatment time was 5 min, and the discharge powers were 30 W, 50 W, 100 W and 150 W, respectively. We can see that the PVC sheet treated by the nitrogen glow discharge plasma has the best treatment effect when the treatment time is 5 min and the discharge power is 150 W.

Table 4. Maximum shear strength of PVC sheets at different treatment times when the treatment power is 50W

| Processing time/min | Unprocessed | 3(min) | 5(min) | 10(min) | 15(min) |
|--------------------|-------------|--------|--------|---------|---------|
| Maximum shear strength/kN | 0.490       | 0.605  | 0.644  | 0.696   | 0.685   |
| Shear strength/MPa  | 0.780       | 0.970  | 1.030  | 1.110   | 1.100   |

Table 5. Maximum shear strength of PVC sheets at different treatment powers at a treatment time of 5 min

| Processing power | Unprocessed | 30(W) | 50(W) | 100(W) | 150(W) |
|------------------|-------------|-------|-------|--------|--------|
| Maximum shear strength | 0.490       | 0.638 | 0.655 | 0.693  | 0.763  |
| Shear strength    | 0.780       | 1.020 | 1.050 | 1.110  | 1.220  |
5. Mass Spectrometry

In this experiment, we used a quadrupole mass spectrometer to analyze the mass spectrum of the vacuum residual gas, the background mass spectrum of the PVC sample, and the mass spectrum when the PVC sample was discharged. We can determine the composition of the gas qualitatively and semi-quantitatively based on the mass-to-charge ratio and the relative intensity value. According to Fig. 1, among the residual gases, there are: m/e=28 gas such as N₂ or C₂H₄; m/e=16 determines the presence of O₂; m/e=17, 18 determines the presence of H₂O; m/e=44 Gases such as C₃H₆ and CO₂ are present. The components in the air are nitrogen, oxygen, water vapor, carbon dioxide, and other gas components. The gas components obtained from Fig. 2 and Fig. 3 substantially correspond to the air components.

By comparing the mass spectrometer background mass spectrum and the PVC sample outgassing background mass spectrum in the air environment, we can find that when the PVC sample is placed, as shown in Fig. 2, m/e = 14, 16, 28, 32, 40 The relative intensity of the ion peaks is significantly higher, that is, the content of N₂, O₂, Ar, and CO₂ is increased. The reason for this phenomenon is that in the air environment, PVC itself absorbs the components of the gas in the air. When the PVC is placed in a vacuum environment, the air gas absorbed inside is released, so the relative value of each ion peak will be higher. Among them, the existence of Ar came from experimental residue.

By comparing the mass spectrum of the PVC sample treated by discharge (Fig. 3) and the mass spectrum of the PVC sample without discharge (Fig. 2), we can find that when discharging PVC, m/e = 2, 14, 16, 17, 18, 19, 20, 29, 30, 32, 40, 44, and 45The relative intensities of the ion peaks of are significantly higher, that is, the contents of H₂, N₂, CH₄, H₂O, C₂H₆, Ar, and CO₂ increased. The reason may be that when the PVC is discharged, the air gas absorbed inside the PVC is affected by the discharge power and time when released, and is released more than when not discharged, and the release speed is fast.

We can draw conclusion that the discharge treatment can increase the gas released inside the material and improve the treatment effect, especially when the power is large.

![Figure 1. Background spectrum of residual gas in a vacuum chamber](image1)

![Figure 2. Gas output spectrum after placing a PVC sample](image2)
Figure 3. Mass spectrum of discharge treated PVC samples

6. Mechanism Analysis
After the treatment of plasma, the surface energy of the PVC plastic sheet was significantly improved. The contact angle was reduced, while the wettability and hydrophilicity of the plastic surface were greatly improved. When high energy particles in the plasma hit the surface of the material, the electron energy is about 5-10eV, the plasma high-energy particles transfer their energy to the surface molecules, causing the molecular bonds in the polymer to break, and then undergo a series of changes such as etching, cross-linking, and chemical reaction, thereby changing the surface chemical composition and properties of plastic sheet [8].

In addition, when the polymer treated by O\textsubscript{2} and N\textsubscript{2} plasma is in contact with air, the active radicals on the surface of the polymer will bring in oxygen-containing or nitrogen-containing polar group such as \(-\text{COOH}, -\text{OH}, -\text{C=O}\) and \(-\text{NH}_3\) on its surface[3,7]. They have a strong reactive activity, so they can react with other compounds through these groups, and introduce the desired functional groups to functionalize the polymer surface, thereby greatly improving the bonding performance. In addition, after measuring and analyzing the mass spectrum, it is found that the PVC sample adsorbs certain air gas components in the air environment, so when it is in a vacuum environment, the absorbed air gas is released, so that the relative intensity of the ion peak of the gas component is remarkably increased in the background mass spectrum.

7. Conclusion
Polyvinyl chloride has poor wettability and the shear strength when using polyurethane directly for mixing and bonding sometimes fails to meet the requirements of industry and agriculture. In order to make a breakthrough in this respect, this paper uses RF glow discharge plasma to treat the surface of PVC plastic, the surface roughness of plastic increased, and a large number of polar groups were introduced on the surface of plastic. After the plasma treatment, the surface of the plastic is activated, the wettability of the plastic surface is remarkably improved, and the shear strength of the PVC plastic bonded body is remarkably improved. Based on the research of He Yanhe et al., "Adhesive of Polypropylene and Polyethylene Treated by Plasma", we have carried out further research on polyvinyl chloride (PVC) materials. We have found that the shear strength of the bond for PVC is not as high as that of polypropylene (PP) and polyethylene (PE). The reason may be that the hardness of the polyvinyl chloride material is larger than that of polypropylene and polyethylene. The stability is better and the surface energy is relatively smaller, so the shear strength of the bond is not as large as the other two, which requires further research.

Acknowledgement
We are grateful to the project 11300010120001200030006 which have supported us all the time.
References

[1] Yang Liting. Polyvinyl chloride modification and formulation [M]. Beijing: Chemical Industry Press, 2011. P1-P5.

[2] Zuo Xiuqin, Ye Zhiyin, Zhang Baixin, Liu Shuping. Study on Surface Wettability of Rack of Polyvinyl Chloride (RPVC) [J]. Plastic, 2004(06):50-53.

[3] He Yanhe, Li Xuemei, Wang Zhiwen, et al. Bonding of plasma treated polypropylene and polyethylene [J]. Intense Laser and Particle Beams, 2012, 24(9): 2099-2102.

[4] Zhao Huaqiao. Plasma Chemistry and Technology [M]. Beijing: University of Science and Technology of China Press, 1993. P299-P301.

[5] Zhao Qing, Liu Shuzhang, Tong Honghui. Plasma Technology and Application [M]. Beijing: Chemical Industry Press, 2006. P1-P5.

[6] Gui- qiu Ma, Ya-peng Liu, Shu-xian Wei, Jing Sheng, et al. Surface modification of polypropylene by ethylene plasma and its induced β-form in polypropylene. Chinese Journal of Polymer Science, 2015, Vol. 33 (5), pp.669-673

[7] MARYAM A, SIAMAK M, MOJTABA M, et al. investigating the effect of power/time in the wettability of Ar and O2 gas plasma-treated low-density polyethylene. Progress in Organic Coatings, 2009, 64(4): 482-488

[8] Lin Lizhong. Principle and application of plasma surface treatment machine for plastic products [J]. Plastics Industry, 1999 (06): 19 - 21.