1. Introduction

Chitosan, (1, 4) - 2 - amino - 2 - β - deoxy-D-glucose, is the most abundant natural polymer except cellulose. It is the deacetylated product of chitin, the only basic polysaccharide in nature. It has good biocompatibility, biodegradation, adsorption, antibacterial ability and film-forming properties. So the application areas of chitosan [1‒3] are expanding because of its excellent properties. The demand for chitosan is continuously increasing.

However, due to the hydrogen bonds between molecules and high crystallinity of chitosan, it is not dissolve in common organic solvents, which greatly limits the application of chitosan. Chitosan is only dissolving in some acidic aqueous solutions, including sulphuric acid, acetic acid, formic acid, and hydrofluoric acid. Knowing the disadvantages of environmentally-unfriendly, separation and recovery of these solutions, it is highly desirable to seek a green solvent of chitosan.

Dielectric barrier discharge (DBD) of water produces a large number of oxygen based species. The reaction of these plasma species with water forms a hydrated proton (H₃O⁺). The obtained H₃O⁺ has acidity. The concept of plasma acid was initially presented by Liu and Zou for the hydrolysis of starch catalyzed by DBD plasma [4]. Plasma acid has a great advantage over some frequently used inorganic acids, such as sulphuric acid, hydrochloric acid, phosphoric acid, etc. It can be obtained and separated more easily than them, because of coming from water.

Graphene oxide (GO) is the precursor of graphene prepared by chemical method. GO is one of the important graphene derivatives. It has many oxygen-containing functional groups, such as hydroxyl, carboxyl and epoxy group. It is a kind of good active material [5]. For these reactive groups amenable for chemical modifications, GO is tailored for a range of biomedical and other applications [6‒8]. For the GO/chitosan composite material, the molecular structure of chitosan contains amino groups, which can react with carboxyl groups in GO to form -NHCO- bond [9], chitosan and GO are closely connected together to form a composite material, showed some special properties.
The mechanical properties and heat resistance of pure chitosan membrane have a limitation, which greatly limits the scope of application of this material. Therefore, in this work plasma acid was prepared and used as the solvent of chitosan. Then GO was added into the chitosan solution. A GO/chitosan composite solution was made and then GO/chitosan composite membrane was made. The groups of GO can improve the interfacial interaction between GO and matrix materials, and improve the properties of nanocomposites [10]. Then the mechanical properties, thermal stability and crystallization of composite membrane were analyzed through mechanical testing, thermal-gravimetric (TG), scanning electron microscope (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

2. Experimental

2.1 Materials

Chitosan (DAC ≥ 85%) was purchased from Jinan Haidebei Marine Biological Engineering Co., Ltd (China). GO (purity ≥ 99%) was purchased from Tangshan Jianhua Technology Development Co., Ltd (China). NaOH was purchased from Tianjin Kermel Chemical Reagent Co., Ltd (China).

2.2 Preparation of plasma acid

The plasma treatment equipment, CTP-2000 K low temperature plasma power, made by Nanjing Suman Electronics Co., Ltd (China). It was used to produce plasma acid. Before the plasma discharging, 5ml of distilled water was placed on the surface of the quartz electrode. Then, it was treated by plasma at discharge power of 125 W and discharge gap of 8 mm. After plasma treatment, the plasma acid was obtained and used to prepare chitosan/plasma acid solution immediately.

2.3 Effect of discharge time on the pH of plasma acid

5ml of distilled water was put into the plasma reaction vessel. Under the experimental conditions of 2.2, plasma acid with acidic characteristics was prepared. Then the plasma acid was sucked out by pipette and diluted by adding a proper amount of distilled water and diluted for 10 times. The pH value was measured by pH meter PHSJ-4 A, made by Shanghai Electrical Apparatus Science Instrument Co., Ltd (China). Then, according to the measured data and dilution relationships, the curve between discharge time and pH value was drawn, in which the horizontal coordinate was the discharge time (s) and the ordinate was the pH of plasma acid. The experimental scheme was shown in Table 1.

The pH value of plasma acid was tested every 2 h, and a timeliness curve of plasma acid was obtained.

2.4 Preparation of chitosan/plasma acid solution

The 1% and 1.5% chitosan powders were added into 5 ml plasma acid respectively. The solutions were sealed and placed on the magnetic stirrer to prepare chitosan/plasma acid solution at the temperature of 25°C. The stirring time was about 3-4 h on the magnetic stirrer, RT 10 power mixer, made by IKA (Germany). The conductivity and surface tension of chitosan/plasma solution were determined by DDS-307 conductivity meter, made by Shanghai Electrical Apparatus Science Instrument Limited Co., Ltd (China), and the K100C automatic surface tension meter, made by KRUS GmbH (Germany).

2.5 Preparation of GO/chitosan composite solution

The 0.5% GO was added into the chitosan/plasma acid solution to prepare GO/chitosan composite solution at the temperature of 25°C. The stirring time was 4 h.

2.6 Preparation of GO/chitosan composite membrane

Chitosan/plasma acid solution and GO/chitosan

| Number | Power (W) | Discharge gap (mm) | Time (s) |
|--------|-----------|--------------------|----------|
| 1      | 125       | 8                  | 10       |
| 2      | 125       | 8                  | 30       |
| 3      | 125       | 8                  | 60       |
| 4      | 125       | 8                  | 180      |
| 5      | 125       | 8                  | 300      |
| 6      | 125       | 8                  | 420      |
| 7      | 125       | 8                  | 600      |
| 8      | 125       | 8                  | 900      |
composite solution were de-bubbled in the vacuum oven, DZF-6020 vacuum drying oven, made by Shanghai Yiheng Scientific Instrument Co., Ltd (China). Then the solution was put on a clean ceramic plate using the method of tape casting to prepare the membrane. A glass rod was used to control the thickness of the liquid membrane. Finally, place the membrane in a vacuum drying oven. The drying time was 15 h at room temperature.

After drying, 1% NaOH solution was added to neutralize the plasma acid on the surface of the membrane. Then it was washed and dried for 15-20 minutes at room temperature for further measurements.

2.7 TEM analysis

A small amount of GO was dissolved in ethanol solution and dispersed by ultrasonic wave. Eventually it was fully dissolved and dispersed in solvent ethanol. The microstructure of GO was analyzed by JEM-2100 (UHR) transmission electron microscopy, made by Japan Electronic Co., Ltd. Technical parameters and indicators were as follows: point resolution was 0.19 nm, line resolution was 0.14 nm, acceleration voltage was 200 kV and magnification was 50~1,500,000.

2.8 XPS analysis

The oxygen content of GO was tested by XPS instrument, made by Thermo ESCALAB 250 Xi (America). Test conditions are as follows, monochrome Al Kaa (hvn=1486.6 eV), Power was 150 W, beam spot was 500 μm, analyzer fixed penetration energy was 30 eV.

2.9 FTIR analysis

The FTIR analyzer was made by American Perkin Elmer Co., Ltd. The chitosan membranes were tested in the range from 450–4000 cm⁻¹.

2.10 XRD analysis

The D/max-3B type X-ray crystal diffraction, made by Japan Science Co., Ltd, was used to analyze samples under radiation of Cu with the tube, tube voltage of 40.0 kV and tube current of 30.0 mA. The scanning range was 5°–55°, and the scanning speed was 5°/min.

2.11 SEM analysis

SEM, JSM-5600 LV scanning electron microscope, made by Japan Electronic Co., Ltd, was used to observe the surface morphology of the membranes. The images were collected at different magnification.

2.12 TG analysis

The chitosan membranes were cut into powders and TG was used to test thermal stability of the membranes. The HCT microcomputer differential thermal balance was made by Beijing Permanent Scientific Instrument Factory (China). Conditions were as follows: the nitrogen atmosphere, start quality of about 5 mg, the initial temperature of 35°C, the termination temperature of 400°C and heating rate of 10°C/min.

2.13 Mechanical property analysis

The digital fabric thickness instrument YG141LA, made by Laizhou Electronic Instrument Co., Ltd (China), was used to determine thickness of two kinds of membrane. Its accuracy was 0.001 mm. Each membrane was tested three times as follows and average value was obtained.

The membrane was cut to 5 cm × 1 cm. The LLY-06 E electronic single fibre tensile strength tester, made by Laizhou Electronic Instrument Co., Ltd (China), was used to test the tensile strength. Each membrane was tested three times and the average value was obtained, according to the following equation (I) to calculate the tensile strength of the membrane:

\[ \sigma = F / (100 \times H \times d) \]  \hspace{1cm} (1)

where \( \sigma \) was the tensile breaking strength (MPa), \( F \) was the fracture force of specimen (cN), \( H \) was the width of specimen (mm), and \( D \) was the thickness of specimen (mm).

3. Results and discussion

3.1 The solution of chitosan in the plasma acid

Previous reports [11‒12] have shown that a large amount of oxygen species, including O atoms, OH radicals and HO₂⁻ radicals, were produced during the reaction of producing plasma species.

The following equation(2) illustrates the interaction of HO₂⁻ radicals with water, which is in agreement with the literature [13] showing that the HO₂⁻ radicals are a better proton donor but a weaker proton accepter in water. It is clear that this reaction resulted in the formation of a hydrated proton H3O⁺. It is the plasma product in the liquid water that originally presented a strongly acidic feature. The pH of plasma acid varies with the discharge conditions.

\[ \text{HO}_2^- + \text{H}_2\text{O} \rightarrow [\text{O}_2^-\text{H-OH}_2^-] \rightarrow \text{O}_2^- + \text{H}_3\text{O}^+ \] \hspace{1cm} (2)
The above analysis showed that the plasma acid has a potential ability to dissolve the chitosan. Then the chitosan was dissolved in the plasma acid.

3.2 Effect of discharge time on the pH of plasma acid

Figure 1 was the variation curve of plasma acid with discharge time. As can be seen from the figure, when the distilled water was treated of 10 s, its pH value was 6.53. The water became neutral to acidic. In the initial stage of discharge (10‒60 s), the change of pH value of plasma was largely reduced from 6.53 to 3.38, which showed that the discharge time has a great influence on the pH value of plasma acid in the initial stage of discharge. With the prolonging of discharge time (60‒420 s), the pH value of plasma acid continued to decrease acidity, reduced from 3.38 to 1.52. During this period, the H₃O⁺ of plasma acid continued to increase, but the change was smaller than the initial stage of 10-60 s. This result showed that the influence of discharge time on the acidity of the plasma became smaller. In the later stage of discharge (600-900 s), the pH value of plasma acid changed from 1.25 to 1.17. At this stage, the change in pH value of the plasma acid was the smallest, which indicated that the pH value of plasma acid was stable, and it had small dependence on the discharge time. Therefore, by combining the time efficiency, the plasma discharge treatment of distilled water was determined. The best discharge time to obtain plasma acid was 600 s, which was 10 minutes. The pH was 1.25.

In our experiments, 1% and 1.5% chitosan solution were prepared by the plasma acid at pH of 1.25. The results showed that 1% chitosan could be dissolved in the plasma acid and a transparent solution could be obtained. However, 1.5% chitosan could not be dissolved completely, and some sediment at the bottom of bottle appeared. Then 1% chitosan solutions were used in the following experiments. The electrical conductivity of 1% chitosan solution was 4.62 ms/cm, and the surface tension was 43.09 mN/m.

Therefore, the conditions for the preparation of the membrane were as follows, 1% chitosan, the discharge power of 125 W and the discharge time of 10 minutes.

3.3 Determination of timeliness of plasma acid

The timeliness of plasma acid of pH=1.25 was determined every 2 h. The pH-Time relation curve was obtained and shown in Fig. 2. Seen from the chart, the initial pH value of plasma acid was 1.25. After standing for 4 h, the pH became to 1.65. The value of plasma acid was relatively stable. The pH change rate of per unit time (/h) was small. In the 4-8 h period, the acidity of plasma acid was unstable, changing from 1.65 to 4.06. The change rate was larger. After 4 h, it was shown that the acidity of the solvent varied greatly. In the 8-12 h period, the pH value was changed from 4.06 to 6.84, and finally the plasma acid gradually became neutral.

In our experiment, the chitosan/plasma acid solution was prepared about 3-4 h, which was made in a relatively stable period of plasma acid. This result also illustrated that plasma acid is a green solvent, for it will become neutral after 12 h. It needs no post-treatment of solvent.

3.4 Properties of GO by XPS and TEM analysis

As shown in Fig. 3, the TEM image of GO with different magnification was obtained at an accelerating voltage of 200 kV. As can be seen from the pictures, the GO has good dispersion, the surface

![Fig. 2](image-url)  
**Fig. 2** The variation of pH value of plasma acid with time

![Fig. 3](image-url)  
**Fig. 3** The pH of plasma acid changed with discharge time
was smooth and transparent, and a large number of folds were appeared in the edge of the structure. It was shown that the GO membrane was very thin, at the same time, and it was also proved to have a monolayer molecular structure of GO. XPS spectrum scanning of GO showed that C 1 s was 68.2% and O 1 s was 31.7%. The O/C atomic ratio was calculated to be 0.46.

3.5 FTIR analysis of chitosan membrane

Figure 4 was the FTIR of chitosan and GO/chitosan composite membrane. For the FTIR curve of chitosan, the peak at 3362.25 cm⁻¹ was the overlap band of -OH stretching vibration and -NH stretching vibration, the peak at 2882.33 cm⁻¹ was the absorption band of C-H stretching vibration, the peak at 1656.19 cm⁻¹ was the absorption band of amide, the peak at 1379.21 cm⁻¹ was the -CH₃ symmetric vibration absorption band, and the peak at 1060.29 cm⁻¹ was the vibrational absorption band of C-C skeleton.

However, compared with chitosan membrane, there were no new peaks appeared in GO/chitosan composite membrane. The main component was chitosan after adding GO. Because of the low content of GO, the peaks which belongs of GO could not be seen in FTIR.

3.6 XRD analysis of chitosan membrane

Figure 5 was the XRD spectra of GO and GO/chitosan composite membranes. From GO spectrum, there was a strong diffraction peak appearing at 2θ=11.3°. For GO/chitosan composite membrane spectrum, two diffraction peaks of chitosan appeared at 2θ=20.62° and 2θ=10.32°. They were the peaks of chitosan. But there was no characteristic diffraction peaks of GO. Therefore, from the disappearing of GO peaks in composite, it was indicated that the GO was uniformly distributed in the chitosan without agglomeration. The ordered structure of GO was formed in the chitosan matrix.
Membranes | Elongation (%) | Strength (MPa)  
--- | --- | ---  
Chitosan membrane | 8.2±0.2 | 0.61±0.03  
GO/chitosan composite membrane | 4.2±0.3 | 1.48±0.12  

3.7 SEM analysis of chitosan membrane  
The surface morphology of chitosan membrane and GO/chitosan composite membrane were observed by the SEM and shown in Fig. 6. Without adding the GO, the surface of chitosan membrane had many strips. They were mainly caused by the polysaccharide chains of chitosan. After adding the GO, the surface of GO/chitosan composite membrane became smooth. It was due to the well dispersion of GO in chitosan coming from the interaction between the hydroxyl groups in chitosan and the oxygen containing groups in GO. Therefore, the surface of GO/chitosan composite membrane was smooth compared with the chitosan membrane.

3.8 TG analysis of chitosan membrane  
Figure 7 was the TG curves of chitosan membrane and GO/chitosan composite membrane. The addition of GO increased the thermal stability of the chitosan membrane. In the curve of chitosan membrane, the first weightlessness at 100°C was due to the evaporation of the water contained in the membrane. The second weightlessness at 250°C was due to the thermal degradation of a large number of chitosan molecules. However, for the GO/chitosan composite membrane, the second weightlessness appeared at 270°C. This result illustrated that the thermal stability of chitosan membrane was increased after adding GO.

3.9 Mechanical property analysis of chitosan membrane  
Chitosan membranes need to have a good mechanical strength. Its breaking strength and breaking elongation were shown in Table 2.  
When the GO added, the strength of GO/chitosan composite membrane was enhanced from 0.61 MPa to 1.48 MPa, increased by 143%. But its elongation was decreased from 8.2% to 4.2%. It may be due to the strong interfacial interaction between the homogeneously of dispersed GO and the chitosan matrix, which limited the movement and deformation of the molecular chain, thus increasing the strength of the composite membrane. However, the elongation
was decreased from 8.2% to 4.2%, the material exhibited brittle, possibly due to the interfacial interaction was too strong between GO and chitosan matrix. At present, the brittleness mechanism of this kind of composite material was not very clear, so it was necessary to study further.

4. Conclusions

In this paper, plasma acid was used as a green solvent to prepare chitosan membrane and GO/chitosan composite membrane. After adding GO, the properties of the membrane were changed. FTIR showed that there were no new peaks appeared in GO/chitosan composite membrane, its main component was still chitosan. XRD showed that the diffraction peaks of chitosan was appeared at 2θ= 20.62° and 2θ=10.32°, without characteristic diffraction peaks of GO, it was illustrated that GO dispersed uniformly in the chitosan matrix. Due to the interaction between the hydroxyl groups in chitosan and the oxidation groups in GO, the surface of GO/chitosan composite membrane became smooth and the thermal stability of GO/chitosan composite membrane was increased. Besides, it also had good mechanical properties. Therefore, plasma acid was used as a green and environmentally-friendly solvent, it would have extensive applications.

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