Effect of Carboxyl Content on the Performance of Carboxylated Graphene/Chitosan Leather Finishing Agent

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Abstract. Graphene oxide was modified with bromoacetic acid, and then carboxylated graphene was prepared, and its basic structure was characterized by infrared spectroscopy; then chitosan was used as a matrix, carboxylated graphene was used as a filler, and the solution blending method was used to prepare carboxylated graphene/chitosan composite leather finishing agent. The results of this study indicate that the content of carboxyl groups increased with the increase in the amount of bromoacetic acid, so was their stability. The crosslinking degree of carboxylated graphene/chitosan also increased with the increase of carboxyl content. The increase of the carboxyl content also improved the hydrophilicity and solvent resistance of the composite; the carboxylated graphene/chitosan composite with the carboxyl content of 6.48 mmol/L had the best physical and mechanical properties. At the same time, abrasion resistance can be increased to level 4, dry rub resistance to level 5, and wet rub resistance to level 4-5.

1. Introduction
Chitin is widely present in arthropod crustaceans, fungal cell membranes, and higher plant cell walls. Its reserves are the second largest natural polymer after cellulose [1]. The chemical structure of chitin is similar to that of cellulose. The difference is that the C2 position of chitin is acetamido, but cellulose is a hydroxyl group. However, the solubility of chitin in water and organic solvents is extremely poor. Therefore, the N-deacetylation reaction product of chitin, chitosan (CS), is usually studied, that is, part of the acetylamino group at the C2 position of chitin is substituted by amino groups [2]. -NH2 can be protonated to form -NH3+ ions under acidic conditions, so that chitosan can be dissolved in dilute acid solution. Compared with chitin, chitosan is more homogeneous in solution, and easier to modify, activate and couple the active functional groups in the repeating unit, thereby broadening the scope of application [3,4].

Graphene oxide (GO) is a two-dimensional sheet material with multiple active oxygen-containing functional groups -OH, -O- and -COOH. Oxygen-containing functional groups improve the dispersibility, hydrophilicity and compatibility of graphene oxide, and promote the formation of stronger interfacial interactions between GO and polymer materials, thereby improving the overall performance of composite materials [5,6]. There are many reports on GO modified chitosan. Fekry et al.
compounded GO with phosphate functionalized chitosan, which improved the hardness of the composite and gave good corrosion resistance. Luna et al. [8] used glutaraldehyde as a cross-linking agent for GO/CS composites. The results of the study showed that the physical and mechanical properties of the composites have been significantly improved, and the special layer structure of GO can also give the composites certain flame retardant properties. The compatibility of functionalized graphene and the polymer matrix is higher than that of GO. When GO is directly applied to polymer modification, agglomeration often occurs due to excessive interlayer interaction. In order to further improve the dispersion of GO in the CS matrix, carboxylated graphene (GO-COOH) with different carboxyl content was prepared by modifying GO with bromoacetic acid, the basic structure of GO-COOH was characterized by infrared spectroscopy, and the carboxyl content was determined by dialysis. Then composite material were tested the stability, water absorption and solvent resistance, and applied it to the leather finishing section to improve the overall performance of the finished leather.

2. Experimental

2.1. Materials
Chitosan (CS) was purchased from Shanghai Zhanyun Chemical Co., Ltd. Graphene oxide (GO) was obtained from Institute of Graphene Engineering and Industry, Xiamen University. Bromoacetic acid, hydrochloric acid, sodium hydroxide, Tetrahydrofuran were bought from Ron's reagent. Crust leather was supplied by Xingye Leather Technology Co., Ltd.

2.2. Preparation and application of GO-COOH/CS

2.2.1. Preparation of GO-COOH
100 mg graphene oxide and 100 ml deionized water were mixed uniformly under ultrasonic action to obtain graphene oxide suspension, in which the ultrasonic dispersion time was 1 h; the suspension was cooled, 1g NaOH was added, and the ultrasonic was continued for 30 min; Then 1 g, 2 g, 3 g, and 4 g bromoacetic acid were added, ultrasonically dispersed for 15 minutes, and reacted at room temperature for 5 hours to obtain a mixed solution. The carboxylated graphene can be obtained after the mixed solution is centrifuged, washed, filtered, and dried in vacuum.

2.2.2. Preparation of GO-COOH/CS
Disperse 0.01 g of carboxylated graphene ultrasonically in 100 mL of 2% chitosan solution, adjust the pH of the solution to 3, and react at 30 °C for 5 hours to obtain the carboxylated graphene/chitosan finishing agent. They are named GO-COOH/CS 1, GO-COOH/CS 2, GO-COOH/CS 3, GO-COOH/CS 4.

2.2.3. Application of GO-COOH/CS
Adjust the solid content of the carboxylated graphene/chitosan finishing agent to 5%, and use the spray coating method with a coating amount of 20 g/sf²; the coating operation sequence is: Semi-finished leather → spraying the upper finishing agent → ironing → standing → shaking and softening → ironing → finished leather. The ironing temperature is 130°C, the pressure is 30kgf, and the vibration tensile strength is level 6.

2.3. Analysis and test

2.3.1. Carboxyl content test
Dissolve GO-COOH/CS in water, add excess NaOH, and then add them to the dialysis bag. Then change the water every 12 h and collect the exchanged water. The collected water samples were titrated with HCl standard solution, and the content of -COOH was calculated by back titration.
2.3.2. Zeta potential test
The carboxylated graphene/chitosan finishing agent was formulated into an aqueous solution with a conductivity of less than 5 mS/cm for testing. The zeta potential was tested 15 times continuously, and the test results were recorded when the value was stable.

2.3.3. Water absorption and solvent resistance test
Add GO-COOH/CS to phosphate buffer solution with pH 7.4 and tetrahydrofuran, and test the quality of the membrane after water absorption every 10 minutes in an environment with an ambient temperature of 20±2 °C and a relative humidity of 65±4%. According to the quality difference before and after, the water absorption and solvent resistance are calculated.

2.3.4. Physical and mechanical performance test
The test was referred to QB/T 1873-2010 “Shoe upper leather”.

3. Results and discussion

3.1. Mechanism of GO-COOH
GO is a derivative of graphene functionalized with active oxygen-containing functional groups such as hydroxyl, epoxy, carboxyl, etc. The oxidation area at the edge of the sheet is mainly distributed with carboxyl and hydroxyl groups, and the middle of the sheet is distributed with epoxy and hydroxyl groups [9]. Among them, the three-membered ring structure of the epoxy group connects the orbitals of C and O atoms to each other through curved bonds, which prevents them from being fully overlapped. Therefore, the tension in the molecular structure is extremely large and it is easy to react with nucleophiles with electron donating effects [10]. In protic solvents (such as water), bromoacetic acid is extremely nucleophilic. Under alkaline conditions, S_N2 reaction occurs and then the C-O bond is broken, which makes a covalent bond between the nucleophile and the ring carbon atom. In addition, the CO bond in the hydroxyl group is a classic polar covalent bond. Since the electronegativity of the O atom is greater than that of the C, when the nucleophile attacks the positive carbon, the CO bond splits and the hydroxyl group is replaced by the nucleophile, which is the mechanism of the nucleophilic substitution reaction between epoxy and hydroxyl [11]. Taking epoxy as an example, the nucleophilic substitution reaction is shown in Figure 1.

![Fig. 1. Nucleophilic substitution reaction of GO and bromoacetic acid](image)

Figure 2 shows the infrared spectra of GO-COOH with different carboxyl content. The -CH2- absorption peak of -O-CH2-COOH in GO-COOH is around 2950 cm⁻¹ and 2850 cm⁻¹, while the flexural vibration peak of -CH2- is around 1375 cm⁻¹ [12]. This shows that -O-CH2-COOH has been successfully grafted onto the GO sheet. With the increase of the amount of bromoacetic acid, the intensity of the carboxyl vibration peak around 1725 cm⁻¹ gradually increased, indicating that the carboxyl content on the GO-COOH sheet layer gradually increased [13]. And test the carboxyl content by dialysis, the results show that the carboxyl content of GO-COOH/CS 1, GO-COOH/CS 2, GO-COOH/CS 3, GO-COOH/CS 4 is 5.21 mmol/g, 6.48 mmol/g, 7.01 mmol/g, 7.23 mmol/g respectively. When the reaction ratio of GO and bromoacetic acid is 1:30, the increase rate of carboxyl content gradually slows down. When the content of bromoacetic acid is increased, the change of carboxyl group content is not obvious, and it basically stabilizes.
3.2. Stability of GO-COOH/CS

In the GO-COOH/CS composite system, the anionicity of carboxylated graphene is weak. The charge distribution and voltage/electric field establishment of the system mainly depend on the distribution of the -NH₂ and other hydrophilic functional groups of chitosan. For the aqueous dispersion system, when the zeta potential is greater than the maximum energy barrier (30mV), the stability of the system becomes stronger. In a certain pH range, the stability is related to the change trend of the zeta potential [14]. Table 1 shows the change trend of zeta potential of GO-COOH/CS with different carboxyl content.

Table 1. Trend of zeta potential change of GO-COOH/CS with different carboxyl content

| pH value | 1  | 2  | 3  | 4  | 5  |
|----------|----|----|----|----|----|
| GO-COOH/CS 1 [mV] | 34.9 | 47.6 | 61.1 | 32.4 | 24.2 |
| GO-COOH/CS 2 [mV] | 37.5 | 47.0 | 60.8 | 32.2 | 25.0 |
| GO-COOH/CS 3 [mV] | 39.9 | 46.1 | 59.7 | 31.8 | 25.3 |
| GO-COOH/CS 4 [mV] | 40.7 | 45.8 | 58.5 | 30.8 | 26.5 |

When the pH value is 3, the zeta potential of each composite material is the highest, indicating that the system is the most stable at this time. As the content of carboxyl groups increases, the zeta potential becomes lower and lower, this is because the interaction between GO-COOH and chitosan is a nucleophilic reaction [15]. The increase in carboxyl content helps to increase the collision probability of hydroxyl and amino nucleophilic functional groups and protonated carboxyl groups, helps to open the carbon-oxygen π bond in the carboxyl group, forms tetrahedral intermediates, and promotes the departure of water molecules in the molecule. This results in a more stable amide bond (Figure 3) [16]. At the same time, the degree of cross-linking between GO-COOH and CS increases, and the zeta potential decreases. The rigid layer of GO-COOH can overlap the upper layer of the composite material to form a dense insulation layer, which can effectively prevent the infiltration and penetration of acid and alkali to the polymer segment, thereby effectively protecting the polymer segment. With the increase of the carboxyl group content, the degree of crosslinking increases, the zeta potential change becomes smaller, and the composite material becomes more and more stable.
3.3. Water absorption and solvent resistance of GO-COOH/CS

The introduction of GO-COOH changed the distance between chitosan molecular segments. GO-COOH with different carboxyl group content has different hydrophilicity, and the hydrophilicity of the composite membrane is also different. Table 2 shows the test results of water absorption (WA) and solvent resistance (SR) of GO-COOH/CS with different carboxyl content.

Table 2. Test result of WA and SR of GO-COOH/CS with different carboxyl content

| Sample            | WA [%] | SR [%] |
|-------------------|--------|--------|
| GO-COOH/CS 1      | 51.51  | 2.35   |
| GO-COOH/CS 2      | 58.94  | 2.10   |
| GO-COOH/CS 3      | 73.79  | 2.04   |
| GO-COOH/CS 4      | 79.38  | 2.01   |

As the content of GO-COOH carboxyl groups increases, the content of hydrophilic functional groups in the carboxylated graphene sheet increases. When the membrane is immersed in an aqueous solution, the carboxyl groups on the graphene sheet can adsorb water molecules, and the hydrophilicity of the composite membrane is improved [17]. For film-forming agents used in leather finishing, the improvement of hydrophilicity is a double-edged sword [18]. Improving the hydrophilicity can improve the compatibility between the membrane and the membrane, promote the adhesion between different coatings, and also improve the peel resistance of each coating. However, too high hydrophilicity will reduce the waterproof performance and wet rub resistance of the coating. Under normal circumstances, the water absorption rate of leather finishing material will not be higher than 70%. Therefore, GO-COOH/CS 1 and GO-COOH/CS 2 are more conducive to the application in the leather finishing section. From the perspective of the solvent resistance of the composite membrane, the increase of the carboxyl group content can improve the solvent resistance of the membrane, this is because chitosan itself has good solvent resistance [19]. The test results show that the mass loss of chitosan film is less than 5% after soaking in tetrahydrofuran for 2 hours. After the introduction of GO-COOH, the solvent resistance is improved to a certain extent, because the rigid sheet of GO-COOH forms a dense membrane structure that can further reduce the erosion of the chitosan segment by solvent molecules.

3.4. Application of GO-COOH/CS

Taking unpainted crust leather as the blank group, Table 3 shows the test results of the effects of GO-COOH/CS with different carboxyl group content on the physical and mechanical properties of the leather.
Tab. 3. Test result of physical mechanical properties of leather by different finishing agent

| Sample          | Wear resistance [level] | Dry rub resistance [level] | Wet rub resistance [level] |
|-----------------|-------------------------|----------------------------|---------------------------|
| CS              | 3-4                     | 4                          | 2-3                       |
| GO-COOH/CS 1    | 4                       | 4-5                        | 4                         |
| GO-COOH/CS 2    | 4                       | 5                          | 4-5                       |
| GO-COOH/CS 3    | 4                       | 5                          | 4                         |
| GO-COOH/CS 4    | 4                       | 5                          | 4                         |

It can be found from Table 3 that chitosan has excellent film-forming properties and fiber-forming properties. After coating, the abrasion resistance and dry rub resistance have been improved to a certain extent. However, the high degree of deacetylation of chitosan ($\geq 90\%$) results in good water solubility and hygroscopicity. Relevant studies have shown that the moisture absorption rate of chitosan is higher than that of chitin, and it can reach 400-500% [20,21]. So, the chitosan coating has poor moisture resistance. The special $\pi_e^s$ structure of GO-COOH gives it extremely strong physical and mechanical properties. After the introduction of high-efficiency fillers, the physical and mechanical properties of the composite coating have been greatly improved. At the same time, the GO-COOH lamellae are dispersed and penetrated between the chitosan chains and the carboxyl groups at the edge and center of the sheet are cross-linked with the hydroxyl and amino groups on the chitosan segment, which improves the physical and mechanical properties of the coating. In addition, graphene has good thermal conductivity, which can evenly disperse the heat generated when the coating is subjected to external forces to the surroundings, avoiding local damage caused by heat accumulation. Therefore, the wear resistance of the composite coating can be increased to level 4, and the dry rub resistance can be increased to level 4-5 or higher. GO-COOH can also be considered as a crosslinking agent in the chitosan matrix, which can promote chitosan molecules to form a dense crosslinked structure [22]. Therefore, the higher the degree of carboxylation, the better the physical and mechanical properties. The dense membrane structure can better prevent the penetration and erosion of water molecules into the coating to a certain extent. In addition to the conjugated hydrophobic structure in the center of the graphene sheet, the moisture resistance of the composite coating is better than that of the chitosan coating, which has been upgraded from level 2-3 to level 4 or higher [23]. However, when the content of GO-COOH carboxyl group is too high, it will cause the hydrophilicity to become higher, which will make the coating resistance to wet rubbing decrease instead.

In summary, the content of carboxyl groups in carboxylated graphene should not be too high or too low, and 6.48 mmol/g is the best, that is, when the ratio of graphene to bromoacetic acid is 1:20.

4. Conclusion
GO-COOH/CS with different carboxyl content was prepared by solution blending method. The basic structure and carboxyl content of GO-COOH was determined by red light spectroscopy. Stability, water absorption and solvent resistance of GO-COOH/CS were also tested. They can be applied to leather finishing and test the abrasion resistance, dry/wet rub resistance of the coating. The conclusions are as follows:

(1) The carboxyl content of GO-COOH increases with the increase in the amount of bromoacetic acid. When the carboxyl content exceeds 7.01 mmol/g, the increase rate of the carboxyl content gradually slows down.
(2) The performance of GO-COOH/CS is related to the carboxyl content. The higher the carboxyl content there are, the stronger the stability, the stronger the hydrophilicity and the better solvent resistance GO-COOH/CS has.

(3) GO-COOH/CS can effectively improve the physical and mechanical properties of finished leather. The best performance is when the carboxyl content of carboxylated graphene is 6.48 mmol/g. At this time, the abrasion resistance of the finished leather is level 4, dry rub resistance is level 5, and wet rub resistance is level 4 to 5.

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