

# Synthesis and Leather Application Properties of a Carboxylated Graphene Oxide Modified Waterborne Polyacrylate Leather Finishing Agent

by

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## Abstract

Carboxylated graphene oxide (GO-COOH), prepared by the reaction of bromoacetic acid with the hydroxyl and epoxy groups on the graphene oxide (GO) layers, was blended into a poly(ethyl acrylate) (PEA) emulsion and a PEA emulsion based polyacrylate leather finishing agent respectively, to prepare PEA/GO-COOH composite emulsions and GO-COOH modified waterborne polyacrylate leather finishing agents. The consequence of the amount of GO-COOH on the properties of the PEA film and related leather coatings were systematically investigated. The results indicate that stable GO-COOH dispersed composite emulsions were generated leading to homogeneously dispersed composite films. With an increase in the GO-COOH amount from 0 wt% to 0.5 wt%, the tensile strength increased by 106.2%. Additionally, TGA results demonstrated an improvement of the thermal stability of PEA film after modified with GO-COOH. Most importantly, the folding resistance and rubbing fastness properties of leather finished with GO-COOH modified polyacrylate leather finishing agents were improved proportionate to the GO-COOH amount. Therefore, the GO-COOH modified waterborne polyacrylate leather finishing agent possesses improved performances and likely offers beneficial leather finishing application properties.

## Introduction

Finishing, one of the most important processes in leather production stages, establishes the handle, feeling, fastness, gloss, color and durability characteristics of the leather. The finishing processes include a series of mechanical operations and the application of formulations based on polymeric finishing agents to the surface of leather. With the improvement of environment safeguards and the requirements of leather finishing agents<sup>1</sup>, waterborne polymers have become the research hotspot and have

been developed for leather finishing agents.<sup>2,3</sup> Among various alternatives, waterborne polyacrylate emulsions have been widely used as film forming materials for leather finishing agents because of their attractive properties such as good flexibility, strong adhesion, light fastness, and good compatibility with many additives.<sup>4,5</sup> Nevertheless, the mechanical strength, thermal stability, water resistance and abrasion resistance of the films made from these emulsions often need to be improved for better application performances. To improve the performance properties, it is a common practice to prepare formulations containing additives such as inorganic materials, polyurethane, organic fluorine, etc.<sup>6</sup> Nowadays, the use of inorganic materials as modifiers to improve the properties of waterborne polymers by blending has become a focus because of its ease in manufacture and low cost. Inorganic additives which have been used in the modification of polyacrylate emulsions by physical blending include SiO<sub>2</sub>,<sup>7</sup> TiO<sub>2</sub>,<sup>8</sup> ZnO<sup>9</sup> and so on. One type of additive that has not been studied broadly in leather finishing is graphene oxide (GO).

Graphene oxide (GO), as a nanoscale carbon-based material with exceptional properties, has attracted considerable interest in developing new types of polymer/inorganic composites.<sup>10,11</sup> GO layer contains hydrophilic oxygen-containing groups, which promote the stable dispersion of GO layer in water. Therefore, waterborne polymer/GO composites could also be fabricated through physical blending. However, there are few research examples of waterborne polymer/GO based leather finishing agent, especially on GO modified waterborne polyacrylate leather finishing agents. The weak compatibility of GO with polyacrylate latex particles leads to its aggregation in the prepared polyacrylate composite emulsions/polyacrylate leather finishing agents or in the obtained composite films/leather coatings, which is the main limitation for the application of GO as a potential inorganic additive. As reported in a previous research, polyacrylate/GO and polyacrylate/surfactant-modified

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reduced GO (LAS-rGO) emulsions were prepared to investigate their tribological behaviors on leather substrates.<sup>12</sup> It was found that both GO and LAS-rGO would aggregate in the obtained composite films, and the modification effects of GO and LAS-rGO were weakened by the aggregation since there is no appropriate interaction among GO layers and polyacrylate latex particles to improve their compatibility. To solve this problem, GO needs to be reasonably functionalized to improve its compatibility with latex particles by regulating the hydrogen bonding and electrostatic interactions among the GO layers and the latex particles.<sup>13</sup> Considering that GO layers and polyacrylate latex particles could interact with each other through hydrogen bonding and lead to partial precipitation in the obtained polyacrylate composite emulsion/leather finishing agent, electrostatic repulsions among GO layers and polyacrylate latex particles, which also is a reliable method to keep GO layers stably and homogeneously dispersed, can be considered in the functionalization of GO.<sup>14</sup>

It is well known that the pH value of the obtained polyacrylate emulsion often needs to be adjusted to neutrality or alkalinity to dissociate the carboxyl groups, and the produced negative charges on the latex particles could provide electrostatic repulsions for the emulsion stability.<sup>15</sup> Since the dissociation of carboxyl groups on GO layer also results in increasing hydrophilicity and negative charges, the electrostatic repulsions among GO layers and polyacrylate latex particles can be realized at the same time with increasing pH value to neutrality and alkalinity. However, it is a common opinion that hydroxyl and epoxy are the main groups on the layer of GO whereas the amount of carboxyl group on GO layer is very small.<sup>16</sup> In order to further improve the hydrophilicity and dispersion stability of GO, more carboxyl groups should be grafted onto the GO layer to get adequate electrostatic repulsions among GO layers and polyacrylate latex particles.

The objective of this investigation is to improve the compatibility between GO layers and polyacrylate latex particles by introducing more carboxyl groups on the GO layers to offer enough electrostatic repulsions, and lead to improved stability and optimized homogeneity. By increasing the homogeneity of the dispersed carboxylated graphene oxide layers, it was hypothesized that the coating performance on the leather would improve. Different amounts of GO-COOH were respectively incorporated into PEA emulsion and related PEA emulsion based leather finishing agent by blending to prepare PEA/GO-COOH composite emulsions and GO-COOH modified waterborne polyacrylate leather finishing agents. The dispersion stability of the emulsions was studied followed by the consequence of the GO-COOH incorporation on the mechanical, thermal and water resistance properties. To avoid the precipitation of GO-COOH in the leather finishing agent, the optimized process for preparation of GO-COOH modified

waterborne polyacrylate leather finishing agent was also explored. At last, waterborne polyacrylate finishing agents prepared with different amounts of GO-COOH as modifier were applied in leather finish and the applied properties were determined.

## Materials and Methods

### Materials

Bovine leather was from Zibo Dahuaiju Polygrace Tannery Group Co. Ltd (Shandong, China). Graphite powder (99.95%, 1200 mesh), ethyl acrylate, and  $\alpha$ -methylacrylic acid were purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Concentrated sulphuric acid (96%~98%), hydrogen peroxide (30%), hydrochloric acid (36%~38%), sodium hydroxide, bromoacetic acid, sodium dodecyl benzene sulfonate (SDBS), ammonium persulfate, ammonia, and isopropyl alcohol were obtained from Kelong Chemical Reagent Factory (Chengdu, China). Potassium permanganate was provided by Changlian Chemical Reagent Co., Ltd. (Chengdu, China). TOP-288 (casein), 53A (adhesive resin), 62A (PU resin), and black dye water were supplied by Clariant Chemicals (China) Ltd. (Shanghai, China). Alkylphenol polyoxyethylene (10) ether (OP-10) and TJ-A859 (wax emulsion) were provided by Tingjiang New Material Co., Ltd. (Deyang, China). Black pigment was obtained from Sichuan Dowell Science and Technology Inc. (Chengdu, China).

### Preparation of Poly(Ethyl Acrylate) (PEA) Emulsion

Initially, 0.35 g  $\alpha$ -methylacrylic acid was dissolved with 10 g deionized water, and the pH value of the solution was adjusted to 3.5 with ammonia. Ammonium persulfate aqueous solution was prepared by dissolving 0.1 g ammonium persulfate in 10 g deionized water. At the same time, 0.45 g SDBS, 0.75 g OP-10, and 50 g deionized water were placed in a 200 mL flask equipped with a thermometer, a mechanical stirrer, and a condenser. The equipment was placed in a water bath condition at room temperature and stirred for 15 minutes. Subsequently, 29.25 g ethyl acrylate was slowly dropped into the flask while stirring. Then, the prepared  $\alpha$ -methylacrylic acid and ammonium persulfate aqueous solutions were slowly added to the flask respectively. The temperature of water bath was slowly increased to 80 °C and maintained for 3 hours resulting in a light blue emulsion. The emulsion was then cooled to ambient, filtered, and resulted in a final solids content of approximately 30 wt%. Lastly, the pH was adjusted to 7.8~8.0 with ammonia for subsequent use.

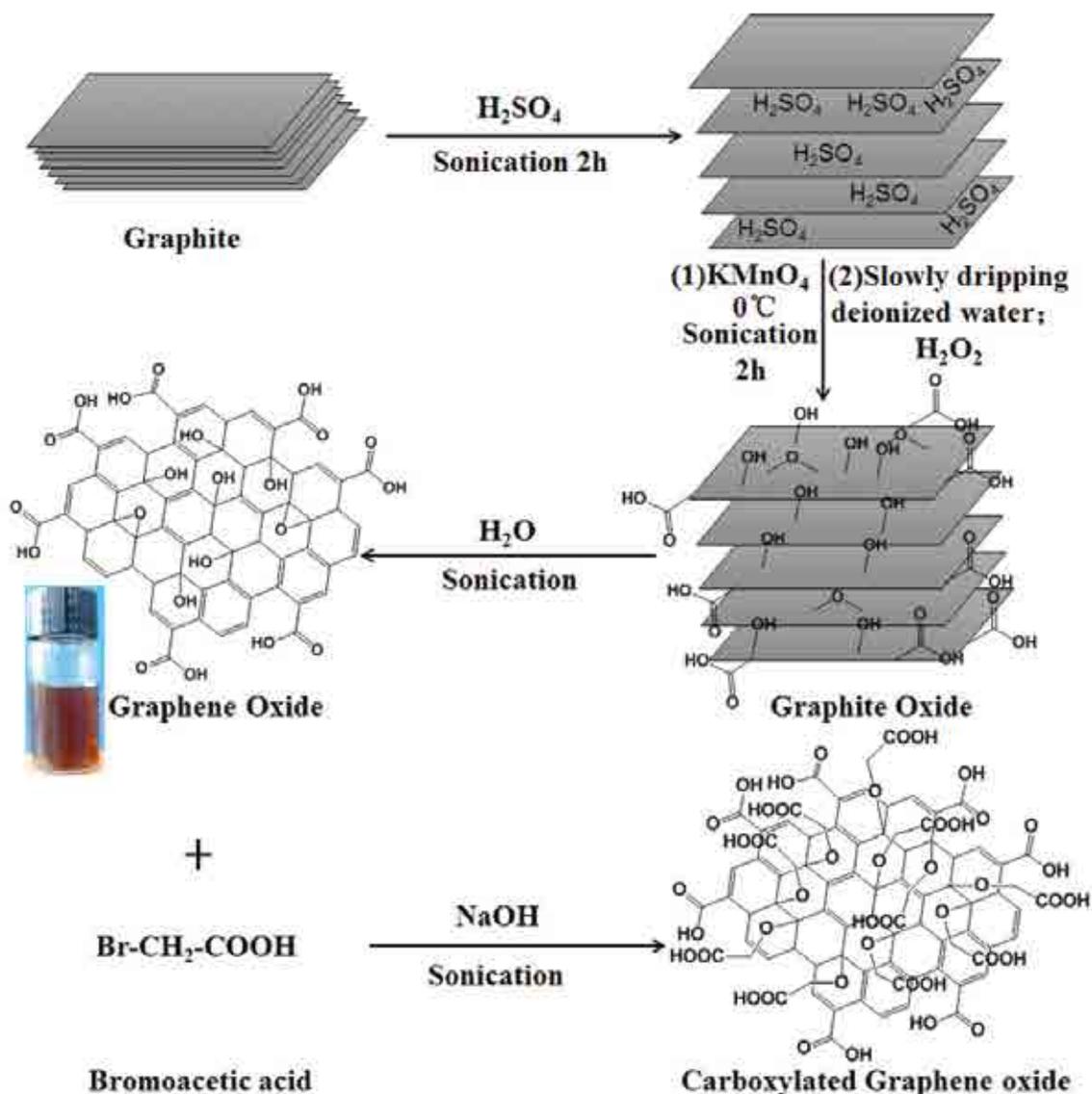
### Synthesis of Graphene Oxide (GO)

In the experiment, a 100 mL flask was charged with 1.0 g graphite and a magnetic stirring bar. After 25 mL concentrated sulphuric acid was added, the equipment was sonicated (120W) for 3 hours. After sonication, the equipment was magnetically

stirred in an ice bath, then potassium permanganate (3.0 g) was slowly added to keep the temperature below 10 °C. Successively, the equipment was transferred to ultrasonic bath again and sonicated for another 3 hours until a slurry mixture formed. Then, 15 mL deionized water was slowly added under magnetic stirring, turning the color of the mixture to brown yellow. Additional 30 mL deionized water was added and followed by addition of 5 mL 30% hydrogen peroxide, turning the color of the mixture to bright yellow. Finally, the product was centrifuged and washed with 1M hydrochloric acid for 3 times. The obtained dispersion was purified by dialysis for one week using a dialysis membrane with a molecular weight cutoff of 5000 Da. Graphite oxide powder was obtained by lyophilization. The aqueous dispersion of GO can be obtained by dispersing the obtained powder in deionized water. The synthesis route is shown in scheme 1.

### Synthesis of Carboxylated Graphene Oxide (GO-COOH)

The synthesis of GO-COOH is also presented in Scheme 1. 30 mg graphite oxide powder was firstly added into a little beaker with 25 mL deionized water. Then, the beaker was placed in an ultrasonic bath (120 W) and sonicated at room temperature for 1 hour to obtain the GO dispersion. Subsequently, 0.3 g sodium hydroxide and 0.6 g bromoacetic acid were added into the little beaker successively under ultrasonic condition. Finally, the reaction system was sonicated at room temperature for another 5 hours to convert the hydroxyl and epoxy groups into -O-CH<sub>2</sub>-COOH moieties, resulting in carboxylated graphene oxide (GO-COOH). The obtained mixture was filtered by a 0.22 μm PTFE membrane and the solid phase was washed over the membrane with deionized water. After washing the solid phase with deionized water for three times, the GO-COOH powder was obtained by lyophilization.



Scheme 1. Synthesis of GO and GO-COOH.

### Preparation of PEA/GO-COOH Composite Emulsions and Films

The amount of GO-COOH in the composite emulsions was controlled at 0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt% respectively according to the weight of the PEA in 20 g emulsion. The calculated GO-COOH was placed into a little beaker with 5 mL deionized water. Then, the aqueous dispersion of GO-COOH was obtained after sonicated (80W) for 1 hour at room temperature. The pH values of the obtained dispersions were adjusted to 7.8~8.0 with ammonia. Subsequently, the obtained GO-COOH dispersions were mixed with 20 g PEA emulsion, respectively. Finally, the mixtures were placed in 50 mL round-bottomed flasks and magnetically stirred for 30 minutes at 50 °C water bath to obtain the PEA/GO-COOH composite emulsions, respectively. The obtained emulsions were then placed into round petri dishes respectively. After drying at 40 °C until constant mass, the composite films containing different amounts of GO-COOH were obtained. All the films were placed in a desiccator before the next procedures to avoid the influence of moisture.

### Application of PEA Emulsion and GO-COOH in Leather Finishing Agent

In this experiment, PEA emulsion and GO-COOH were chosen as the film forming material and inorganic modifier respectively for the manufacture of leather finishing agent. The formulation of the leather finishing agents applied on the leathers is shown in Table I. The amount of GO-COOH (x) was calculated based on the weight of PEA in the used PEA emulsion, which was controlled at 0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt% respectively. The obtained waterborne polyacrylate leather finishing agents with different amounts of GO-COOH were applied in the parallel leather finish experiments. Then, the applied properties of the finishing agents were determined. Operations: bovine leathers were used for leather finishing applications; the leather specimens were cut into squares to ensure a homogenous uptake of finishing agents. The leather specimens were cleaned up by using the mixture of anhydrous ethanol, ammonia, and deionized water in the ratio 3:2:95. The leather specimens were coated once with the prepared finishing agents and allowed to air dry. Next, the same procedure as outlined above was followed two more times.

### Characterization and Performance Measurements

#### Characterization of GO and GO-COOH

Fourier transform infrared (FT-IR) spectra were measured with a NICOLET iS10 spectrometer between 400 and 4000  $\text{cm}^{-1}$ . The powdered samples were mixed with KBr and pressed into thin pellets for FT-IR study. Raman spectra were obtained using a confocal micro-Raman LabRam HR spectrometer at 532.17 nm laser excitation between 500 to 3000  $\text{cm}^{-1}$ . Thermogravimetric analysis (TGA) curves were recorded using a Netzsch TG 209 F1 analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS)

measurements were performed using an ultrahigh vacuum ESCAProbeP spectrometer with a monochromatic Al X-ray radiation source. Wide-scan surveys of all elements were performed, with subsequent high-resolution scans of the C1s peaks. Atomic force microscopy (AFM) measurements were carried out with an SPM-9600 in the tapping mode; the sample dispersion was dropped onto a freshly exfoliated mica substrate. Transmission electron microscopy (TEM) images were acquired using a TecnaiG2F20S-TWIN microscope operated at 100kV. Samples was prepared by evaporating a drop of dilute aqueous dispersion of GO/GO-COOH onto a lacey-carbon copper TEM grid.

### Characterization of PEA/GO-COOH Composite Emulsions

The dispersion stability of the composite emulsions was observed after the emulsions were rested for one month. After diluting the composite emulsions 50 times, the particle size distributions and polydispersity indexes of the emulsions were analyzed by dynamic light scattering (DLS) (Malvern Zetasizer NanoZS), equipped with a monochromatic coherent He-Ne laser (633 nm) as the light source and a detector that detected the scattered light at 25°C at an angle of 90°.

### Characterization of PEA/GO-COOH Composite Films

#### Physical Mechanical Properties

For mechanical tests, the films were cut by a dumbbell-shaped sampler into dumbbell shape of 80×15 mm<sup>2</sup> size. The precise

**Table I**  
**The Formulation of the Leather Finishing Agents**  
**Using PEA Emulsion as Film Forming Material**  
**and GO-COOH as Inorganic Modifier.**

Components	Offer (g)
Deionized water	7
Isopropyl alcohol	2
TOP-288	2
TJ-A859	2
53A	1
62A (pH=7.8~8.0)	3
PEA emulsion	4
Black dye water	1
GO-COOH	x
Black pigment	1

sizes of the sample were measured before carrying out each test; then their tensile strength and elongation at break were measured using an AI-7000S tensile testing machine at 25 °C. Each kind of samples was examined three times.

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) curves were recorded using a Netzsch TG 209 F1 analyzer under nitrogen atmosphere. The films were heated from 50 °C to 600 °C at a heating rate of 10 °C/min.

### Determination of Water Absorption Content

The test to determinate of the water absorption content was based on the immersion of square specimens with a side length of 2 cm into water at room temperature until the weight of the films were constant. The immersed samples were removed from water, and excess water was wiped off with filter paper and then weighed. The water absorption content (W) was determined with the following relationship:

$$W(\%) = \frac{(M - M_0)}{M_0} \times 100$$

Where M and  $M_0$  are the weights of the wet and dry films, respectively.

### Contact Angle Measurements

Film samples were cut into strips and dried in a sealed desiccator, and then attached to a glass slide for contact angle measurements. Images of deionized water droplets on the surfaces of the films were obtained using an OCA20 contact angle goniometer.

### Measurement of Applied Properties

Measurement of gloss of the finished leathers: In accordance with method GB/T 9754-2007. Measurement of folding fastness of the finished leathers: In accordance with method QB/T 3812.9-1999. Measurement of wet and dry rubbing fastness of the finished leathers: In accordance with method QB/T 1327-1991.

## Results and Discussion

### Characterization of GO and GO-COOH

Fig. 1(a) shows the FT-IR spectra of graphite, GO and GO-COOH. In the spectrum of GO, the characteristic features of GO are the peaks corresponding to the C=O stretching at 1724  $\text{cm}^{-1}$ , skeletal ring vibration of the graphitic domain at 1619  $\text{cm}^{-1}$ , the -OH stretching at 3422  $\text{cm}^{-1}$ , the -OH deformation at 1418  $\text{cm}^{-1}$ .<sup>17,18</sup> For GO-COOH, the peaks of -CH<sub>2</sub>- at 2922 and 2851  $\text{cm}^{-1}$  were obviously enhanced, and a strong bending vibration absorption peak of -CH<sub>2</sub>- was also observed at 1380

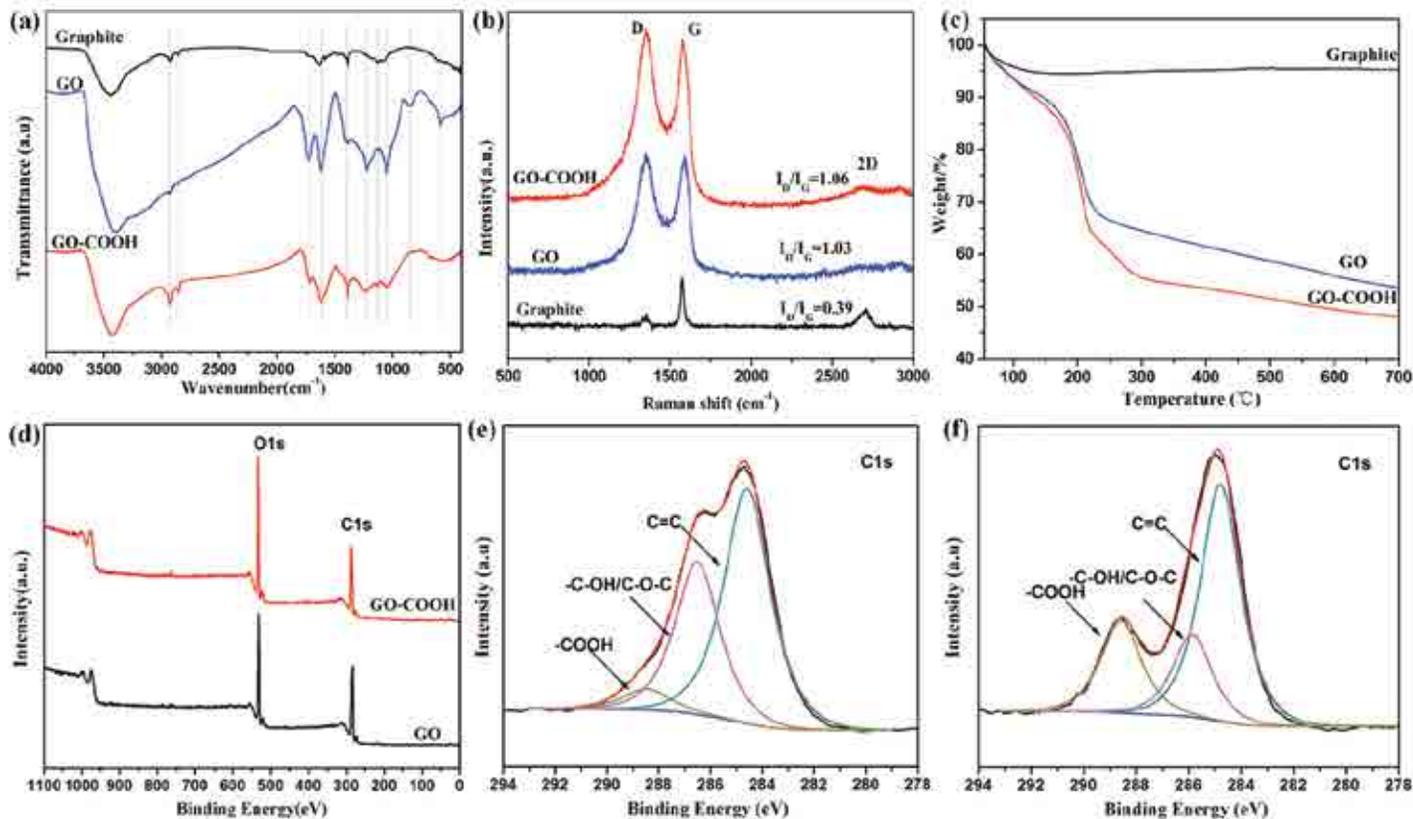


Figure 1. FT-IR spectra (a), Raman spectra (b) and TGA curves (c) of graphite, GO and GO-COOH; XPS survey spectra of GO and GO-COOH (d); high-resolution XPS C1s spectra of GO (e) and GO-COOH (f).

$\text{cm}^{-1}$ . Besides, new peaks of ether bond at  $1240\sim 1045\text{ cm}^{-1}$  can also be found, which demonstrated the formation of the  $-\text{O}-\text{CH}_2-\text{COOH}$  groups as shown in Scheme 1. In Raman spectra (Fig. 1(b)), D and G bands (located at  $1352\text{ cm}^{-1}$  and  $1574\text{ cm}^{-1}$ , respectively) as two main peaks can be seen. The  $I_D/I_G$  value for graphite was 0.39, and the  $I_D/I_G$  values for GO and GO-COOH increased to 1.03 and 1.06, respectively, showing the increased defects.<sup>19</sup> Meanwhile, the 2D band at  $2711\text{ cm}^{-1}$  in the spectra of

**Table II**

**Quantitative Comparison of Different Individual Carbon States in GO and GO-COOH.**

Samples	Relative Atomic Percentage (at%)		
	C=C	-C-OH/C-O-C	-COOH
GO	58.2	36.5	5.3
GO-COOH	57.8	19.7	22.5

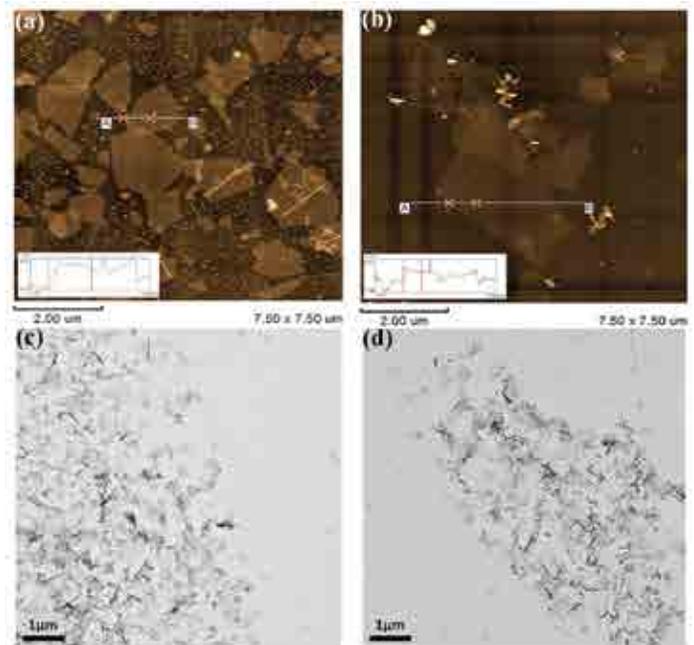


Figure 2. AFM images of GO (a) and GO-COOH (b); TEM images of GO (c) and GO-COOH (d).

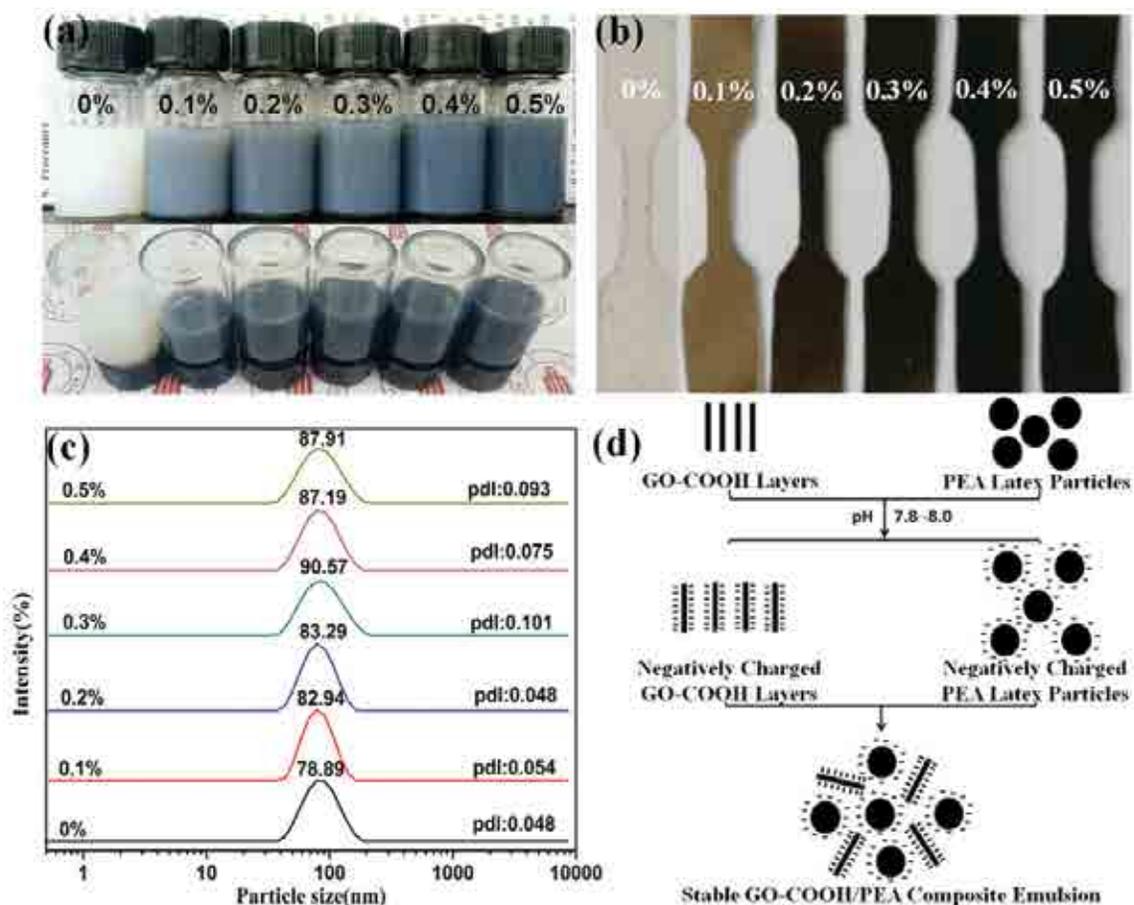


Figure 3. Photograph of the prepared emulsions (a) and the obtained films (b) containing different amounts of GO-COOH; DLS results of the emulsions (c); mechanism of stable dispersion of GO-COOH layers and PEA latex particles in the composite emulsions by electrostatic repulsion under alkaline condition (d).

GO and GO-COOH were almost invisible, indicating that graphene layers in both GO and GO-COOH were well stripped originated from the introduction of oxygen-containing groups on the graphene layers.<sup>20</sup> Moreover, the TGA curves (Fig. 1(c)) show that the elimination of oxygen-containing groups is mainly occurred between 150 and 300 °C.<sup>21,22</sup> In this temperature range, the TGA curve of GO showed significant weight loss of approximately 25 wt%, and the weight loss of GO-COOH increased to about 35 wt%, which demonstrated that the carboxylation of GO was successful because the molecular weight of the introduced -O-CH<sub>2</sub>-COOH group is higher than that of hydroxyl group and epoxy group.

To further evaluate the composition of oxygen-containing groups, XPS characterizations were carried out. As shown in Fig. 1(d), the survey spectra of GO and GO-COOH show the O1s peak at 532.7 eV, and the C1s peak at 284.7 eV. In the C1s spectrum of GO (Fig. 1(e)), the main peak centered at 284.6 eV is originated by the photoelectrons emitted from C=C sp<sup>2</sup> graphitic carbon atoms; peaks centered at 286.5 and 288.4 eV are generated by photoelectrons emitted from carbon atoms belonging to the -C-OH/-C-O-C- and -COOH groups, respectively.<sup>23,24</sup> In the C1s spectrum of GO-COOH (Fig. 1(f)), the intensity of the peak attributed to the signal of -COOH was obviously enhanced, and

the intensity of the peak attributed to -C-OH/-C-O-C- was weakened. This observation further confirmed that the hydroxyl and epoxy groups were consumed, resulting in the formation of the -O-CH<sub>2</sub>-COOH groups. In addition, the relative component concentrations of the different bonding states of carbon in GO and GO-COOH from the detailed XPS C1s deconvolution spectra are also presented in Table II. The results indicated that the amount of carboxyl groups was increased from 5.3 at% to 22.5 at% after carboxylation.

To have a visual impression of the GO and GO-COOH layers, the AFM images of GO and GO-COOH are presented in Fig. 2(a) and Fig. 2(b), respectively. Two-dimension graphene layers with the size ranging from hundreds of nanometers to a few microns could be seen in both the AFM images of GO and GO-COOH, and no agglomeration could be observed. The scanning surface curves across the layers of GO and GO-COOH show that the topographic heights of the layers are about 1 nm, demonstrating that both GO and GO-COOH are monolayer. GO and GO-COOH are also presented as typical two-dimensional layers in TEM images (Fig. 2(c) and 2(d)) but show a curled morphology. As shown in the AFM and TEM images, the skeletal structure of the graphene layer was not changed or destroyed after carboxylation.

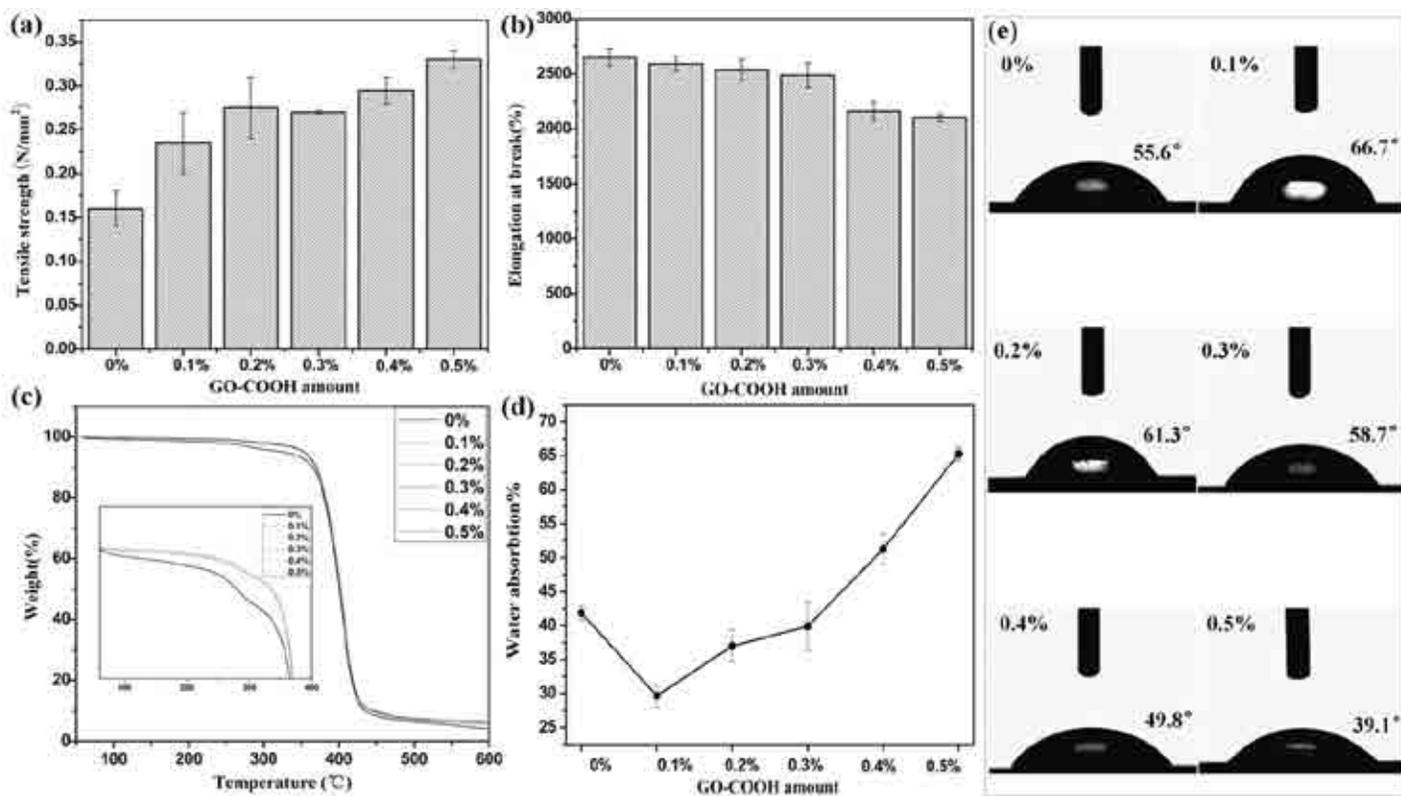


Figure 4. Tensile strength of the films (a); elongation at break of the films (b); TGA curves of the films (c); water absorption of the films (d); photographs of water droplets on the films (e).

### Dispersion Stability of the PEA/GO-COOH Composite Emulsions

The photograph of the prepared emulsions and the obtained films are shown in Fig. 3(a) and Fig. 3(b), respectively. It can be seen that with the increase of the GO-COOH amount, the color of the composite emulsion and the film gradually darkened. The dispersions appearance of all emulsions remains visually stable without precipitates after one month of static placement, indicating that the emulsions exhibit long-term stability. The appearance of the obtained films is also very uniform, indicating that GO-COOH could be homogeneously dispersed in the composite films. To further investigate whether there is any aggregation in the emulsions, the particle size distributions and polydispersity indexes of the emulsions were studied with Dynamic Light Scattering (DLS). As can be seen in Fig. 3(c), the composite emulsions still show a single peak in the DLS spectra after adding different amounts of GO-COOH, and the change of the polydispersity index is not obvious, which proved that

GO-COOH did not aggregate. Considering that the PEA emulsion used in this experiment is in alkaline condition (pH=7.8~8.0), the dissociation of carboxyl groups in the side chains of PEA leads to negative charges on the surface of PEA latex particles and the surface of the GO-COOH layers also contains many negative charges because of the dissociation of carboxyl groups under alkaline condition. Therefore, the composite emulsion can be stabilized by electrostatic repulsion, and the mechanism is shown in Fig. 3(d).

### Properties of the PEA/GO-COOH Composite Films

#### *Effect of the Amount of GO-COOH on Mechanical Properties of the Film*

In order to figure out the effect of GO-COOH on the mechanical properties of PEA film, the tensile strength and the elongation at break of the pure PEA and composite films were measured, and the results are presented in Fig. 4(a) and Fig. 4(b), respectively. The results showed that the tensile strength of the films gradually increased with the increase of the GO-COOH amount. When

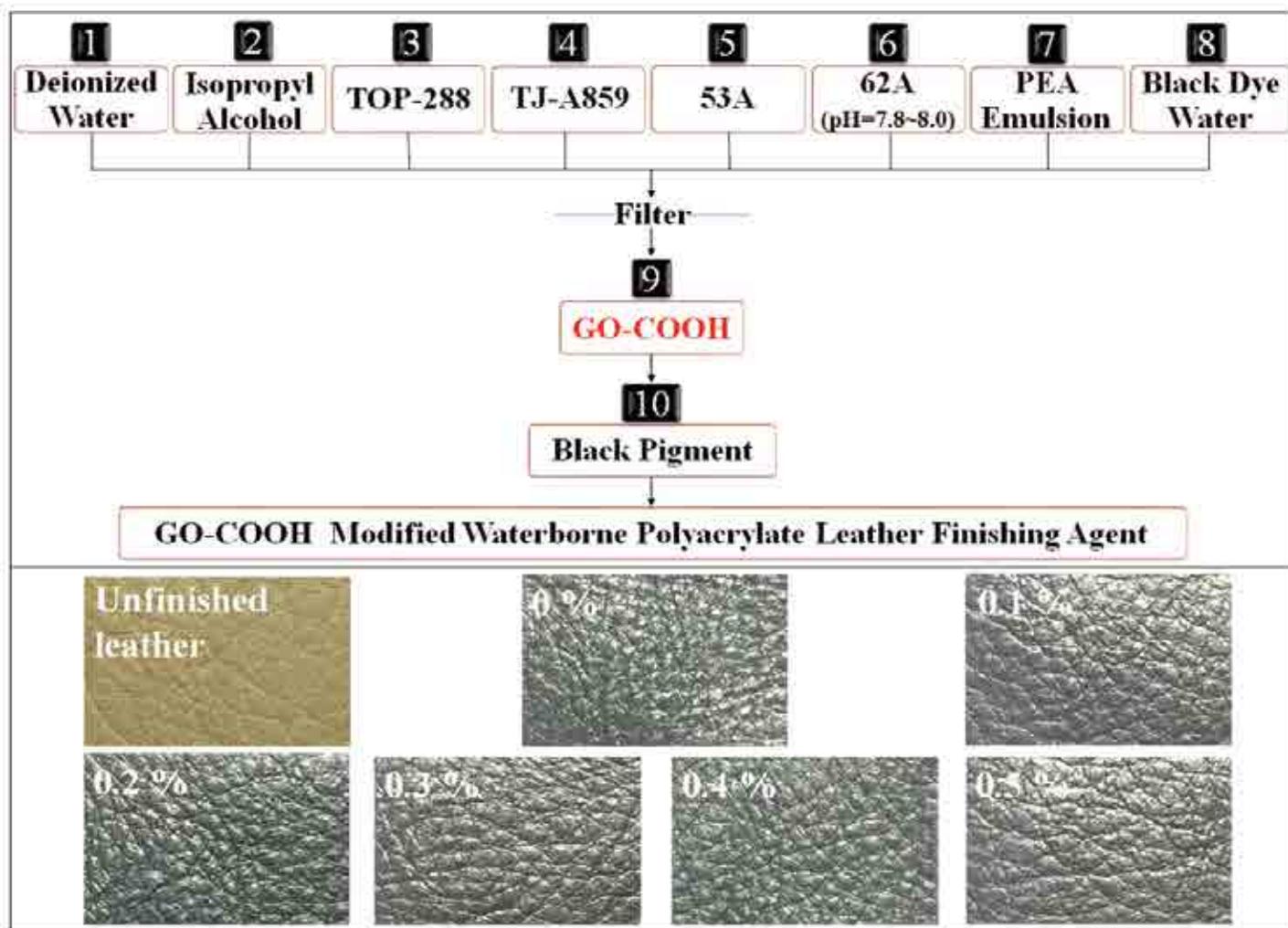


Figure 5. Optimized process for preparation of GO-COOH modified waterborne polyacrylate leather finishing agent; photographs of the surfaces of unfinished and finished leathers.

the amount of GO-COOH was controlled at 0.5 wt%, the tensile strength of PEA/GO-COOH composite film increased to 0.33 N/mm<sup>2</sup>, which is 106.2% higher than that of the pure PEA film. At the same time, with the increase of the GO-COOH amount from 0 wt% to 0.5 wt%, the elongation at break gradually decreased from 2650% to 2100% (decreased by 20.7%). As known, the graphene layer of GO-COOH has a hexagonal honeycomb structure formed by sp<sup>2</sup> hybrid carbon atoms, and the stable conjugate structure makes it a material with excellent mechanical properties.<sup>25,26</sup> As shown in Fig. 3(b), GO-COOH could be homogeneously dispersed in the composite films, which is favorable to the loading transfer from polyacrylate matrix to GO-COOH layers. And homogeneously dispersed GO-COOH layers may serve as physical cross-linking points to prevent mechanical deformation and fracturing of the matrix. Therefore, the tensile strength of the film was enhanced by the incorporation of GO-COOH. However, the incorporation of GO-COOH layers hinders and restricts the extension and slippage of PEA chains to some extent, which leads to the slight decrease of elongation at break.

#### ***Effect of the Amount of GO-COOH on the Thermal Stability of the Film***

To investigate the effect of GO-COOH on the thermal stability of PEA film, TGA studies were carried out. As presented in Fig. 4(c), the weight loss of pure PEA film is about 5 wt% between 50 and 360 °C, but the composite films do not show obvious thermal weight loss in this temperature interval, which proves that the incorporation of GO-COOH can obviously improve the decomposition temperature of the PEA film. The previous studies demonstrated that two-dimensional individual graphene layer shows extremely high thermal conductivity.<sup>27</sup> It is speculated that GO-COOH layers could act as a thermal conductive filler to interact with PEA chains in a way to enhance the thermal stability of PEA matrix. At the same time, the

homogeneously dispersed GO-COOH layers might hinder the flux of degradation products and thereby delay the onset of degradation of the PEA matrix slightly.

#### ***Effect of the Amount of GO-COOH on Water Resistance of the Film***

The water absorption of the films is shown in Fig. 4(d). Interestingly, with the increase of the GO-COOH amount, the water absorption of the film decreased first and then increased. The water absorption of pure PEA film was 41.8%. When the GO-COOH amount reached 0.1 wt%, the water absorption of the film decreased to the minimum value of 29.6%. However, the water absorption increased after the addition amount exceeded 0.3 wt% and reached the maximum value of 65.2% when the GO-COOH amount was controlled at 0.5 wt%. Therefore, the GO-COOH modified composite films have better water resistance property when the GO-COOH amount was controlled at 0.1 wt% to 0.3 wt%. This is due to the incorporation of GO-COOH, which increases the cross-linking degree between PEA chains, and makes water difficult to permeate, thus reducing the water absorption of the film. However, the existence of hydrophilic carboxyl groups on GO-COOH layers will improve the hydrophilicity of the films, especially when the amount of carboxyl groups is large enough.

In addition, contact angle measurements were also carried out to study the water resistance property of the films. As shown in Fig. 4(e), the results of contact angle measurements are consistent with that of water absorption tests. With the increase of the GO-COOH amount, the contact angle increased first and then decreased. The contact angle of the pure PEA film was 55.6°. When the GO-COOH amount was controlled at 0.1 wt%, the contact angle reached 66.7°. Then, the contact angle decreased with the increase of the GO-COOH amount. And the contact angle reached the minimum 39.1° when the amount was

**Table III**  
**Physical Properties of the Leathers Finished with Different Amounts of GO-COOH Modified Waterborne Polyacrylate Leather Finishing Agents.**

Test Items	0 wt%	0.1 wt %	0.2 wt%	0.3 wt%	0.4 wt%	0.5 wt%
Gloss(60°)	5.0	4.5	4.3	5.7	5.3	4.8
Folding resistance*	12 x 10 <sup>4</sup>	12 x10 <sup>4</sup>	13 x 10 <sup>4</sup>	13 x 10 <sup>4</sup>	14 x 10 <sup>4</sup>	15 x 10 <sup>4</sup>
Dry rubbing fastness class	3	4-5	4-5	4-5	5	5
Wet rubbing fastness class	1	1	1	1-2	2	2-3

Note: \*The number of the folding cycles when fine cracks appeared in the folding area of the finished leather.

controlled at 0.5 wt%. The results also indicated that the GO-COOH modified composite films had better water resistance when the GO-COOH amount was controlled at 0.1 wt% to 0.3 wt%.

### Determination of Applied Properties

To investigate the effects of GO-COOH on the properties of the PEA emulsion based polyacrylate leather finishing agent, the formulation for GO-COOH modified waterborne polyacrylate leather finishing agents was designed, as shown in Table I. Initially, a small amount of filter residues was found in the leather finishing agent prepared according to the formulation as shown in Table I, which appeared as granules on the obtained coating. Interactions between polymer molecules, organic dyes and inorganic pigments in waterborne polymer leather finishing agents are very complex. The filter residues may originate from the aggregates produced by the interactions between different components, which will seriously affect the performance of the leather finishing agent. Moreover, considering that the added GO-COOH may interact with the residues and precipitated in the prepared leather finishing agent, a series of exploratory experiments were carried out to optimize the process of preparation of GO-COOH modified waterborne polyacrylate leather finishing agent. Finally, it was found that when GO-COOH was added after the addition of the dye water, no residue was found in the obtained leather finish agent. The optimized process for preparation of GO-COOH modified waterborne polyacrylate leather finishing agent is presented in Fig. 5. The prepared leather finishing agents were applied to the parallel leather finish experiments; and the photographs of the finished leathers are also shown in Fig. 5. From the photographs it can be seen that the leathers were successfully finished and had good surface coverage. The surfaces of the leathers were glossy, and the natural grain pattern of the pristine leathers surfaces was kept. At the same time, no damage was observed on the appearance by GO-COOH usage.

Table III demonstrates that the gloss ( $60^\circ$ ) value of the finished leather did not make much difference after modifying with GO-COOH. Since the amount of GO-COOH used in the leather finishing agent is very small compared to other components, the introduced GO-COOH layers can be homogeneously dispersed without serious aggregation in the obtained coating. Moreover, GO-COOH is transparent thin monolayer as shown in AFM and TEM images (Fig. 2). Therefore, the roughness of the coating surface could not be evidently affected by the introduced GO-COOH layers, which explained why the gloss value of the finished leather has not changed obviously.

Moreover, with the increase of the GO-COOH amount, the number of the folding cycles of the finished leather increased.

Compared with the leather finished with unmodified leather finishing agent, the number of the folding cycles of the leather finished with GO-COOH modified leather finishing agent was increased to  $15 \times 10^4$  when the GO-COOH amount was controlled at 0.5 wt%. The results indicated that the folding resistance of the coating can be improved by the incorporated GO-COOH. The GO-COOH layer is a kind of two-dimensional nanoscale material with high surface area and mechanical properties, the homogeneously dispersed GO-COOH layers can increase intermolecular interaction between PEA chains to improve the strength of the coating and may serve as physical cross-linking points to prevent the coating fracturing (which correlates with the increased tensile strength of the GO-COOH modified PEA films as shown in Fig. 4(a)). Therefore, the folding resistance of the finished leather could be enhanced by the GO-COOH layers.

Compared with the leather finished with unmodified leather finishing agent, the dry rubbing fastness of the leather finished with GO-COOH modified leather finishing agent was improved. The dry rubbing fastness of the finished leather also increased proportionately with the increase of the GO-COOH amount. When the GO-COOH amount was controlled at 0.5 wt%, the dry rubbing fastness of the finished leather increased to 5 units, two units above the leather finished with unmodified leather finishing agent. The strength of the coating could be enhanced by the homogeneously dispersed GO-COOH layers as mentioned above to improve its tribological properties.<sup>12</sup> Therefore, the dry rubbing fastness of the finished leather can be improved by introducing GO-COOH layers.

The results also showed that the wet rubbing fastness of the finished leather increased with the increase of the GO-COOH amount. The wet rubbing fastness of the finished leather increased by 5 units when the GO-COOH amount was controlled at 0.5 wt%. As mentioned in water absorption content and contact angle measurements, the water resistance property of the film first increased and then decreased with the increase of the GO-COOH amount. Therefore, the wet rubbing fastness of the coating should have been increased first and then decreased in theory. However, the results showed that the wet rubbing fastness of the coating increased with the increase of the GO-COOH amount. Maybe it is because the amount of GO-COOH used to modify the coating was relatively small, although there was a certain amount of carboxyl hydrophilic groups on the surface of the GO-COOH layer, which was not sufficient to have a significant effect on the hydrophilicity of the coating. A possible explanation is that due to hydrogen bonding, GO-COOH can form self-lubrication layer to improve its wear resistance, and the coating is not easily destroyed when subjected to wet rubbing.<sup>28,29</sup>

## Conclusions

In this paper, carboxylated graphene oxide used as an inorganic modifier was successfully prepared and applied to modify waterborne polyacrylate leather finishing agent. The results indicated that GO-COOH could be dispersed in the composite emulsions and homogeneously dispersed in the obtained composite films. With the increase of the GO-COOH amount from 0 wt% to 0.5 wt%, the tensile strength of the film was increased by 106.2%, and the elongation at break of the film was decreased by 20.7%. The thermal stability of the PEA film improved by the incorporation of GO-COOH. The composite films have better water resistance when the amount of GO-COOH was controlled at 0.1 wt% and 0.3 wt%. Furthermore, the physical properties of the leather finished with the prepared leather finishing agent indicated that, with the increase of the GO-COOH amount, the folding resistance and the dry and wet rubbing fastnesses of the finished leather were improved. Therefore, GO-COOH is proven to increase the performance of waterborne polyacrylate leather finishing agent as tested and offers application potential in leather finishing industry.

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