# PREPARATION AND CHARACTERIZATION OF EPOXY/REDUCED GRAPHENE OXIDE NANOCOMPOSITES AS LEATHER FINISHING AGENT

**Hasibur Rahaman Santo, Sabbir Islam Showrov, Shazneen Chowdhury and Md Elias Uddin***

*Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna 9203,*
*Bangladesh, e-mail:* *santohasib79@gmail.com;* *e-mail:* *sabsabbir01@gmail.com*;
shazneeng786@gmail.com **Corresponding author: Dr. Md. Elias Uddin;*
*e-mail:* eliasuddin@le.kuet.ac.bd

***Corresponding Author**

## ABSTRACT

The effective fabrication of a novel nanocomposite leather-finishing agent (referred to as Epoxy/rGO) made of epoxy as the matrix and reduced graphene oxide nanoparticles as the nano-additives. Modified Hummers method are used to create Graphene oxide from graphite, then used to hydrazine hydrate with graphene oxide to produce reduced graphene oxide (rGO) . Epoxy/rGO nano composites are then created by mixing epoxy resin and reduced graphene oxide (rGO) in dimethylformamide solvents. The surface of the leather was covered with various ratios of these nanoparticles mixed with epoxy. SEM and Fourier transform infrared spectra was used to analyze the morphology and structure of different samples. Correct rGO dispersion in epoxy resin was demonstrated by the SEM picture of the films, and hydrogen or other types of bonds between rGO and epoxy were detected by the FTIR. UV-vis absorption spectra of different samples was assessed. The coated leather's mechanical, physical, and thermal properties were evaluated, and its morphology was examined using scanning electron microscopy. In compared to traditional, the nanocomposites coated leather sample's strength and water vapor permeability increased to 12% and 8.5% respectively. The experimental findings shows that, in comparison to conventional finishing, the nanocomposite leather-finishing agent not only has great transparency but also gives leather improved weather resistance, thermal stability, hydrophobicity, and mechanical properties.

***Keywords:*** *Leather Finishing, Nanocomposites, Mechanical properties, Thermal stability, Fastness*

## 1. INTRODUCTION

The set of procedures used to enhance the surface qualities and look of leather is referred to as finishing. Leather is finished to give it a well-filled appearance and great flaw covering. Leather finishing is one of the most important processes in the production of leather. It enhances the leather's look, adds value, and specifies the final functionality that end consumers need from the products. The coating process is done mostly for aesthetic reasons, while it also affects the physical characteristics of leathers. Leather finishing uses solution or suspension of synthetic or natural polymers which may incorporate dyes, pigments or other additives [1]. We all know that the most popular film-forming agents for leather finishing are materials for film formation, particularly acrylic resin, urethane, and its derivatives. However, the film-forming agents in bare acrylic resin and urethane have poor weatherability, wear resistance, and are not resistant to organic solvents. These polymer binders only display essential functionality, such as an adhesive property. These benefits are unquestionably necessary for regular leather items, but they are by no means sufficient to satisfy customers' rising expectations for product quality and functionality, including look, durability, flame retardancy, wear comfort, and hygienic properties. Epoxy compounds are now available to improve the finishing properties. Epoxies are the most commonly used matrix material in structural composites of lightweight polymer-matrix. Epoxy resin is a thermoset polymer that has garnered significant interest as a film-forming material for primer coatings because of its superior physical and shielding barrier qualities [2-4]. Epoxy resins, they are used in this research due to their diverse characteristics, such as high strength, good stiffness, good thermal stability, antibacterial properties, low contractibility, and strong adherence chemical resistance. The speed reached after 31 days using 30 g/kg of epoxy resin is rather good for finishing when working with chrome leather. Prior to 31 days after introducing epoxy to leather, epoxy exhibit extremely poor fastness and mechanical properties [5]. Also in an outdoor setting, epoxy can absorb ultraviolet (UV) light and deteriorate, which will harm the coating or perhaps lead it to fail entirely [6]. It has been discovered that the typical finishing agents' mechanical strength, weatherability, and thermal insulation can all be successfully enhanced by adding nanoparticles to an epoxy polymer matrix to create organic–inorganic nanocomposite coatings. A few polymer-based nanocomposites incorporating zero-dimensional or two-dimensional nanomaterials, such as silicon oxide, silver, titanium dioxide, zinc oxide nanoparticles, clay , or graphene nanosheets  have been conceived and created by researchers in recent years [7]. Depending on the application, certain parameters such as structure, size, size distribution, and elemental composition of the nanomaterials as additives in polymer matrix play a more important role for their applications in leather finishing. As a nanomaterial, reduced graphene oxide (rGO) exhibits high specific surface area, high aspect ratio, outstanding thermal conductivity, and great electrical mobility. Reduced graphene oxide is typically mixed with epoxy resin, and the two materials interact through hydrogen bonds or other kinds of interactions [8]. Epoxy and reduced graphene oxide work together to improve physical properties such as adhesion, fastness, and mechanical property etc. Additionally, adding a small amount of reduced graphene oxide into epoxy improves the characteristics of the composite [9].

The present study has two main goals: (a) to prepare chemically reduced graphene oxide (rGO) due to its scalability and high yield, (b) to create a novel nanocomposite leather-finishing agent, rGO nanosheets were simultaneously incorporated into the matrix (epoxy) as nano-additives. The dispersion of rGO nanosheets is crucial, as opposed to rGO aggregates. Depending on the amount of epoxy resin, dispersing the rGO at a low weight fraction of 2% [10]. An innovative concept and technique for enhancing the characteristics of conventional leather finishing agents through the application of nanomaterials and nanotechnology is presented by the combined action of rGO and epoxy, which endows the goat skin with outstanding finishing effects.

## 2. METHODOLOGY

### 2.1 Materials and Characterization

The following items were bought: hydrazine monohydrate, sulfuric acid, dmf solvents, hydrogen peroxide, hydrochloric acid, and natural flake graphite. Epoxy resin and hardener was purchased from Azad chemical company, Bangladesh. Crust leather was purchased from Savar tannery, Bangladesh. Red pigment, wax, silicone, nitrocellular lacquer was collected.

Using KBr pellets in the 4000–500 cm-1 range, Fourier transform infrared spectra (FTIR) were obtained using a Bruker Vertex70 FTIR spectrometer (Perkin Elmer). Using a JSM-7610F scanning electron microscope (SEM), the various samples' morphologies were examined.

The UV-2600 spectrophotometer, which uses a quartz cell with a path length of 1 mm, was used to record the absorption spectra of ultraviolet-visible light.

In compliance with the specifications of different leather performance tests in the Analysis and Inspection of Leather Products. A universal testing equipment was used to assess the samples' tensile strength and elongation at break. A leather fastness testing machine was used to measure the dyeing and finishing fastness of the leather samples. The volume of air permeated by the leather sample per unit area, under specific pressure, and for a specific amount of time is referred to as the leather's air permeability. Measurements were taken using the leather tester. A static approach was used to measure the membrane's water vapour permeability. 30 mL of distilled water should be measured precisely into a sample dish. The sample dish should then be placed in a desiccator with strong sulfuric acid and left for 24 hours. The leather sample's water vapour permeability (M) was ascertained. Shrinkage temperature of finished leather was also measured by shrinkage tester machine.

#### 2.1.1 Preparation Of Nanocomposites As Leather Finishing Agents:

GO was created by employing a modified Hummers technique to oxidize natural graphite flakes [11]. A round-bottom flask was filled with 46 mL of concentrated H2SO4 (95%) in this standard preparation procedure. The flask was then submerged in an ice bath to keep the reaction temperature at 0-5°C. The spherical bottom flake was then gradually filled with 2 g of graphite flake while being constantly stirred. After then, the reaction mixture received a very gradual addition of 6 g of potassium permanganate. After adding KMnO4, the liquid was taken out of the ice bath and agitated for six hours at 35 degrees Celsius. The reaction mixture gradually turned from black to light brown and solidified into a thick paste. After that, 92 mL of water was added gradually, which caused the reaction mixture's temperature to rise quickly. A brown to pale yellow hue shift resulted from the addition of 10 mL of 30% H2O2 to the reaction mixture. Using 5% HCl, centrifugation was used to purify the GO. Ultimately, centrifugation and repeated re-dispersion in water were used to produce GO, which was then collected by drying the pellet under vacuum following centrifugation.

A uniform brown solution was created by dispersing 0.1 g of GO powder in 150 mL of water and sonicating it for 30 minutes. Subsequently, 1 mL of hydrazine monohydrate was gradually added to this aqueous GO solution, which was submerged in an oil bath at 80°C. After then, the reaction mixture was left to agitate for a full day. The solution turned from brown to black in a matter of minutes, and black particles started to separate out of it. Following vacuum filtering, the resultant black powder was collected and dried for 24 hours at 60 degrees Celsius in a vacuum oven.

Three different types of materials were used in this work to create the composites: hardener, reduced graphene oxide, and epoxy resins. First, dmf solvents were used to sonicate reduced graphene oxide. The concentration of rGO is controllable depends on amout of epoxy resins. Added 2%, and 3% of rGO based on epoxy weight for find out the optimal dispersion of rGO in epoxy. Next, dmf solvents were employed with epoxy resin and hardener. It took 30 minutes of sonication to fully disperse rGO into epoxy. After that, the mixture was continuously stirred while being maintained at 65 degrees Celsius. The mixture was then sprayed onto the crust leather's surface. In the end, the samples were dried for 5 h at 60°C.

The recipe in Table 1 was followed to prepare the leather finishing agent. Spraying on the purchased blanks required adjusting the spray gun's discharge quantity using the high pressure, airless spraying method. Following the technique, leather samples were dried for ten minutes at 60 degrees Celsius. The entire procedure was carried out twice. To achieve a final leather sample, the ironing machine polished it twice.

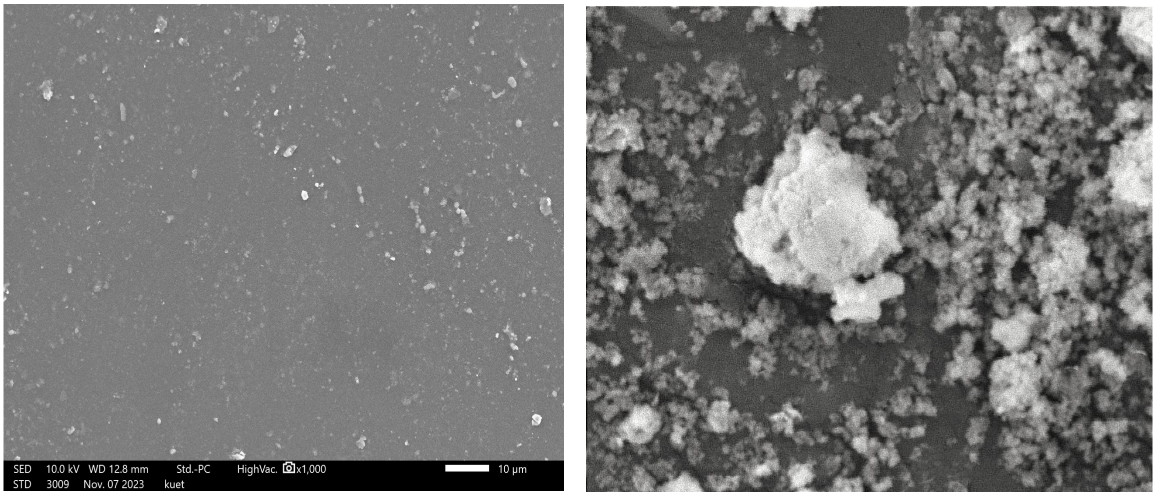
Table 1: Formulation of leather Finishing

| Composition | Content (g) |
|---|---|
| *Red Pigment* | 30 |
| *Epoxy/rGO* | 10 |
| *Water* | 500 |
| *Wax* | 2 |
| *Filling Agent* | 12 |

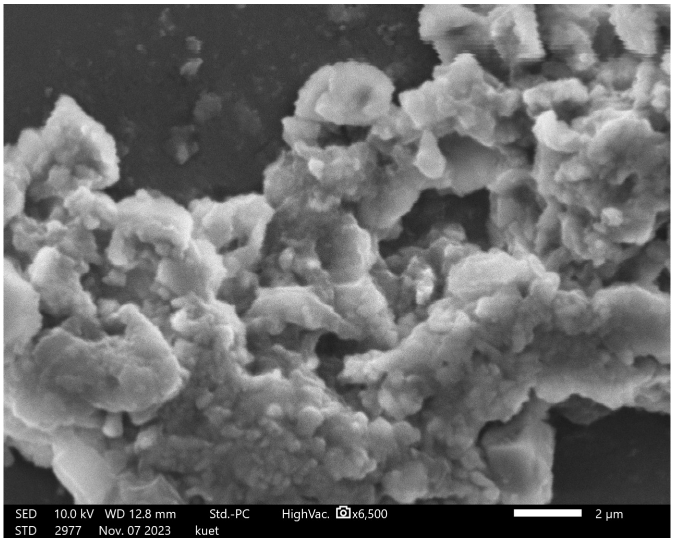
## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of composite films

Figure 1 a–c displays the structural and morphological results of scanning electron microscopy (SEM) for the epoxy and the rGO/cured epoxy composites at varying rGO loadings (2% and 3% rGO). The epoxy resin and hardener SEM images are shown in Fig. 1a. Figure 1b, 1c displays a SEM image of a cured epoxy composite with rGO to help explain the dispersion of rGO in the epoxy matrix. Figure 1b, 1c demonstrates how the rGO powder was distributed throughout the epoxy resin. Large-sized merged particles of the rGO powder were distributed throughout the epoxy resin, as seen in Figure 1b. Figure 1c demonstrates how the rGO powder was distributed as agglomerates in the epoxy resin. According to the morphology figures, the cured epoxy and 2% rGO particles have indeed reacted to form the appropriate rGO/cured epoxy composites.



(a) (b)



(c)

Figure 1: The sem micrograph of the a. Epoxy, b. 2% rGO loading Epoxy c. 3% rGO loading Epoxy

Using Fourier-transform infrared (FT-IR) spectroscopy, the types of functional groups in the surface of the 2% rGO/cured epoxy composites, produced epoxy and rGO were identified. The typical FT-IR spectra of the rGO, epoxy and rGO/cured epoxy composites are shown in Figure 2. Absorption bands are depicted in Figure 2 in relation to the following: the absorption bands in Figure 2 correspond to the stretching vibrations of C–O at 1089 cm−1, C=C at 1638 cm−1, and O–H at 3435 cm−1. These characteristics unequivocally demonstrate that the rGO flakes' surface contains carboxyl and carbonyl functional groups [12].

Additionally, Figure 2 displays absorption bands for epoxy resin, that correspond to the following: aromatic C–C stretching at 1477 cm−1, C–O–C stretching at 1242 cm−1, C–O stretching at 1077 cm−1, C–H of CH2 stretching at 2883 cm−1, C=C stretching at 1602 cm−1, and rocking CH2 at 551 cm-1.

Conversely, the presence of distinctive absorption peaks verified the generated rGO/Epoxy hardener composites at 2 % of rGO filler component. Strong absorption bands can be seen in the IR spectrum of the rGO/cured epoxy composites at 2 weight %. These bands correspond to the following: aromatic C–C stretching at 1472 cm−1, C–O–C stretching at 1235 cm−1, C–O stretching of ethers at 1077 cm−1, C–O–C stretching of the oxirane group at 809 cm−1, and rocking CH2 at 544 cm−1. When their blends have a strong connection, such hydrogen bonding or any other bonding, the IR spectra show a shifting of the peaks and an increase in peak strength. The synthesis of the composite of rGO and epoxy is identified by these IR spectra.

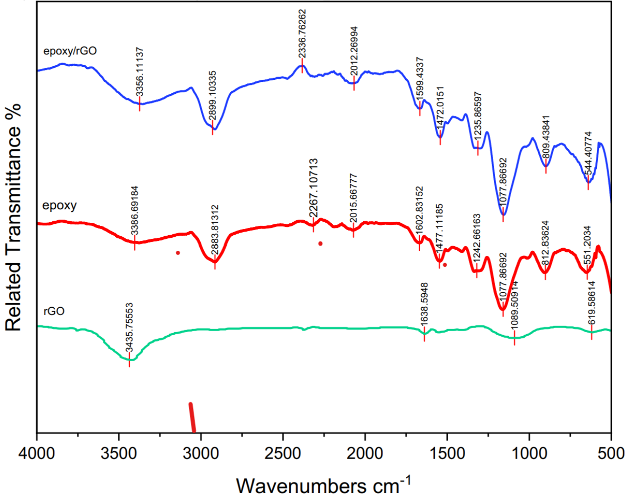


Figure 2: FTIR Spectra of the rGO, epoxy & 2% loading rGO/epoxy

We prepared the samples for the UV-Vis absorption test by taking several emulsions, each of which had a volume of 2 milliliters and a solid content of 30%, and spreading them equally on the slides using a glue homogenizer. According to Figure 3, the addition of rGO to the epoxy polymer greatly increases the matrix's UV absorption. As a two-dimensional nanomaterial with a high aspect ratio, high specific surface area, great thermal conductivity, and high electrical mobility, reduced graphene can be used as an epoxy sensitizer [13] The aqueous rGO/epoxy compound has the strongest UV absorption because of the synergistic effects between the rGO nanoparticles and epoxy, which can also effectively increase the compound finishing agent's weatherability.

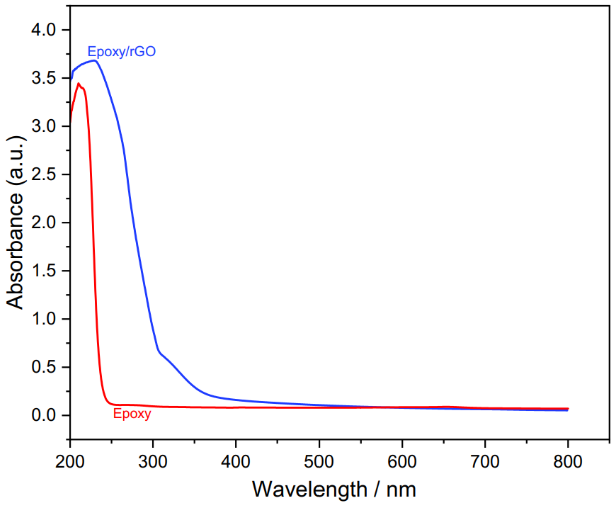


Figure 3: Ultraviolate absorption spectra of epoxy & 2% loading rGO/epoxy

The thermal stability of film samples is displayed by thermogravimetric analysis (TGA). Fig. 4 displays the curves derived for the original samples. The thermal decomposition trend of both films (Fig. 4) indicates that the main thermogravimetric stage of the thin film is between 270 to 395 ° C, during which the polymer chain segments undergo thermal degradation [14]. The rGO/Epoxy composite film is determined to have the best thermal stability at this stage due to its high initial decomposition temperature and slow rate of decomposition. The primary cause of this is the abundance of organic rGO components in the epoxy polymer and their dense distribution on the latex film surface, which may impede heat transfer. Prior research has demonstrated that adding organic particles to the polymer matrix can generally increase heat stability by acting as a barrier to volatile compounds generated during decomposition. Thus, rGO/epoxy resin performs better than epoxy resin in terms of the heat resistance of films. The findings indicate that applying rGO particles to epoxy resin's surface improved the films' ability to withstand heat.

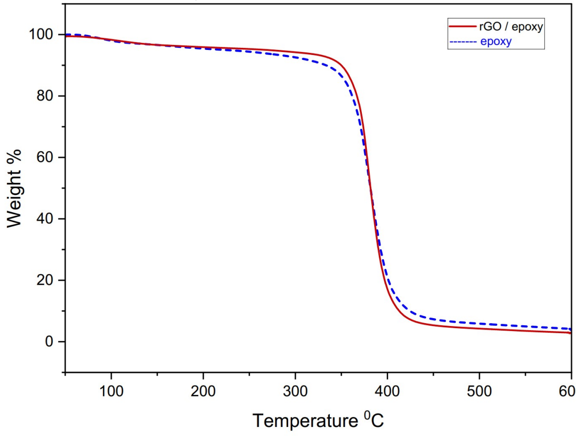


Figure 4: TGA curve of epoxy and rGO/epoxy

## 3.2 The application results of leather finishing

### 3.2.1 The measurement results of physical and mechanical properties

Table 2 shows the tensile strength and elongation at break values. Following the application of the composite coating, the leather samples' tensile strength increased and elongation at break was essentially unchanged. The leather samples' tensile strength is higher than it is with traditional treatment. The force of interaction between collagen fibers is mostly reflected in the tensile strength of leather samples. The application of the composite resulted in the rGO particles becoming partially embedded in the collagen fibers between the epidermis and cross-linked with the polymer matrix. This improved the force of interaction between the collagen fibers and raised the tensile strength of the leather samples.

Table 2: Tensile Strength and elongation at break of leather sample

| **Sample** | **Tensile strength (MPa)** | **Elongation at break %** |
|---|---|---|
| Conventional | 25±0.5 | 55.2 |
| Epoxy/rGO Coated L/R | 28±0.2 | 55 |

### 3.2.2 The measurement results of dry and wet rubbing

The degree of discoloration of a leather sample caused by external elements like water, sweat, and friction is known as dry and wet rubbing fastness. When used or processed, it serves as a crucial indicator of the quality of the leather covering. The results of the leather samples' wet and dry rubbing fastness are displayed in Table 3. The key reason why the rGO/epoxy composite was able to improve the leather sample's wet rub resistance when compared to the pure polyacrylate emulsion is because the addition of hydrophobic rGO particles helped to increase the coating layer's water repellency. Wet rub fastness was improved by one level, while dry rub fastness was improved by half a grade. When determining dry and wet rubbing resistance, reduced graphene oxide particles may create a rough surface structure on the film that would effectively prevent the sample and coated pigment from coming into contact.

Table 3: Dry and Wet rub fastness of finished Leather

| **Sample** | **Dry rub fastness** | **Wet rub fastness** |
|---|---|---|
| Conventional | 4/5 | ¾ |
| Epoxy/rGO Coated L/R | 5 | 4/5 |

### 3.3.3 The measurement results of breathability and water vapor permeability

Table 4 displays the water vapor permeability and breathability of the leather samples**.** The rGO/epoxy composite emulsion with hydrophobic nanoparticles has somewhat improved the sample's breathability as compared to pure polyacrylate emulsion. Furthermore, rGO's production of mesopores—pores bigger than water vapor but much smaller than water droplets—led to an increase in WVP

Table 4: Breathability and water vapor permeability of finished leather

| **Sample** | **Breathability(mL/cm2 h)** | **WVP (mg/cm2 h)** |
|---|---|---|
| Conventional | 38 | 656.5 |
| Epoxy/rGO Coated L/R | 41.2 | 712.0 |

### 3.3.4 Measurement of shrinkage temperature

Table 5 displays the shrinkage temperature of conventional and rGO/epoxy finshed leather. Shrinkage temperature is higher in case of rGO/epoxy finished leather compare to the conventional. This is due to the Nanocomposites filling up the interwoven collagen and hair holes follicle of leather fibers and the inorganic net of nanoparticles restricted the movement.

Table 1: Shrinkage Temperature of leather Finishing

| Sample | Shrinkage Temperature °C |
|---|---|
| Conventional | 118.6 |
| Epoxy/rGO Coated L/R | 119.2 |

### 3.3.5 SEM images of finished leather

The SEM morphologies of leather that have been treated with rGO/epoxy nanocomposite finishing agents are displayed in Figure 5. The finished leather surface becomes flat and fine after finishing, as shown in Figure 5.

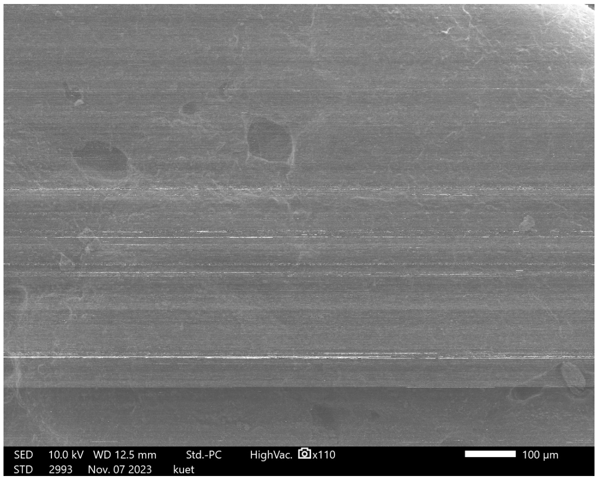


Figure 5: SEM Images of Epoxy/rGO

## 4. CONCLUSIONS

It was possible to create a unique nanocomposite leather finishing agent by using rGO nanoparticles as the nano-additive and epoxy resin as the matrix. In addition to providing the nanocomposite coating's tensile strength (28 Mpa) and shrinkage temperature (Ts) of final leather, which are 119.2°C. Additionally, the finished leather has a smooth, flat surface and high breathability. These properties are likely considerably enhanced by the rGO nanoparticles, which also contribute to the coating's good dry and wet rub resistance and water vapour permeability property. In conclusion, we determined the influence rule of composite morphology on the properties of leather samples after coating by comparing the film-forming and coating properties of composite with morphologies. There is some significance to this research for the future design and manufacturing of leather finishing agents. This paper offers a novel approach to using nanoparticles and nanotechnology to enhance leather finishing performance.

## ACKNOWLEDGEMENTS

"We extend our sincere gratitude to the collaborative efforts of the Common Lab, Testing Lab, and Manufacturing Lab Centre of Excellence at KUET. Their invaluable support and resources have significantly contributed to the success of this research paper.

## REFERENCES

[1] Mohamed, O., Elsayed, H., Attia, R., Haroun, A. and El-Sayed, N., 2018. Preparation of acrylic silicon dioxide nanoparticles as a binder for leather finishing. *Advances in Polymer Technology*, *37*(8), pp.3276-3286.

[2] Liu, C., Du, P., Zhao, H. and Wang, L., 2018. Synthesis of l-histidine-attached graphene nanomaterials and their application for steel protection. *ACS Applied Nano Materials*, *1*(3), pp.1385-1395.

[3] Ghosal, A. and Ahmad, S., 2017. High performance anti-corrosive epoxy–titania hybrid nanocomposite coatings. *New Journal of Chemistry*, *41*(11), pp.4599-4610.

[4] Morozov, Y., Calado, L.M., Shakoor, R.A., Raj, R., Kahraman, R., Taryba, M.G. and Montemor, M.F., 2019. Epoxy coatings modified with a new cerium phosphate inhibitor for smart corrosion protection of steel. *Corrosion Science*, *159*, p.108128.

[5] Bacardit, A., Shendrik, A., Combalia, F., Jorge, J. and Ollé, L., 2016. Study of cross-linking reactions on butadiene binders in aqueous finishing. *Journal of the Society of Leather Technologists and Chemists*, *94*(6), p.248.

[6] Malshe, V.C. and Waghoo, G., 2004. Weathering study of epoxy paints. *Progress in organic coatings*, *51*(4), pp.267-272.

[7] Nan, D., Li, X., Liu, Q., Wang, B., Gao, X., He, N., Xu, Y. and Liu, J., 2023. Epoxy primer topcoat syncretic coating prepared by using modified graphene oxide incorporated with TiO2 nanoparticles. *Materials Today Sustainability*, *21*, p.100282.

[8] Ahmad, A.F., Ab Aziz, S., Abbas, Z., Obaiys, S.J., Khamis, A.M., Hussain, I.R. and Zaid, M.H.M., 2018. Preparation of a chemically reduced graphene oxide reinforced epoxy resin polymer as a composite for electromagnetic interference shielding and microwave-absorbing applications. *Polymers*, *10*(11), p.1180.

[9] Nan, D., Li, X., Li, D., Liu, Q., Wang, B., Gao, X., Ma, T., He, N., Xu, Y. and Dong, J., 2022. Preparation and Anticorrosive Performance of Waterborne Epoxy Resin Composite Coating with Amino-Modified Graphene Oxide. *Polymers*, *15*(1), p.27.

[10] Yu, Z., Di, H., Ma, Y., He, Y., Liang, L., Lv, L., Ran, X., Pan, Y. and Luo, Z., 2015. Preparation of graphene oxide modified by titanium dioxide to enhance the anti-corrosion performance of epoxy coatings. *Surface and Coatings Technology*, *276*, pp.471-478.

[11] Hummers Jr, W.S. and Offeman, R.E., 1958. Preparation of graphitic oxide. *Journal of the American chemical society*, *80*(6), pp.1339-1339.

[12] Kamatchi, R., Venkatachalapathy, S. and Srinivas, B.A., 2015. Synthesis, stability, transport properties, and surface wettability of reduced graphene oxide/water nanofluids. *International Journal of Thermal Sciences*, *97*, pp.17-25.

[13] Wei, L., Ma, J., Zhang, W., Liu, C. and Bao, Y., 2018. The tribological behaviors of polyacrylate/graphene oxide and polyacrylate/surfactant-modified reduced graphene oxide composite coatings on flexible leather substrates. *Progress in Organic Coatings*, *122*, pp.64-71.

[14] Gao, D., Chang, R., Lyu, B., Ma, J. and Duan, X., 2018. Preparation of epoxy-acrylate copolymer/nano-silica via Pickering emulsion polymerization and its application as printing binder. *Applied Surface Science*, *435*, pp.195-202.