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Acrylic Resin Coating Agent Modified by Cellulose Nanofibers

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Abstract

Acrylic resin is commonly used in leather finishing process, but it has some problems such as poor mechanical properties. Cellulose nanofibers are a kind of biomass material with excellent mechanical properties and are often used as reinforcement materials. In this paper, high strength acrylic resin coating agent was prepared by cellulose nanofibers and acrylic resin. The micro morphology and properties of acrylic resin before and after modification were characterized by scanning electron microscope, tensile testing machine, rotary viscometer, etc. The use performance of finished leather coated with acrylic resin was evaluated by fabric moisture permeability tester, and rubbing color fastness tester, and the effects of different modification conditions and cellulose nanofiber content on the performance of acrylic resin finishing agent were explored. The results showed that when 0.3% cellulose nanofiber was added, the mechanical properties of acrylic resin finishing agent were greatly improved. The tensile strength was up to 7.43 N/mm^2, increased by 111.68%. The tear intensity was 17.61 N/mm and the elongation at break was 653%. Compared with the unmodified acrylic resin, the tear strength and elongation at break were increased by 32.61% and 31.92%. In addition, the modified acrylic resin was used as a finishing material to improve the performance of finished leather.

Keywords: cellulose nanofiber, acrylic resin, leather finishing, mechanical property

1. Introduction

Acrylic resin finishing agent is a layer of treatment agent applied on the surface of leather. It is composed of acrylic resin, colorants, and various functional additives in a certain proportion [1-2]. Acrylic resin finishing agents have been favored by the leather industry and rapidly developed due to their excellent film-forming properties, strong adhesion, simple production process, and low cost [3-5].

The common acrylic resin has some shortcomings, such as "hot viscosity and cold brittleness", poor mechanical properties, and solvent resistance. These is limited in leather finishing applications [6]. At present, various materials are blended with acrylic resin to improve the comprehensive performance of finishing agents and effectively expand the application field of acrylic resin. Carbon nanotubes effectively improves the wear resistance and tensile strength of the resin. Organic montmorillonite can significantly improve the tensile strength and thermal stability of polyurethane resin. However, these materials can only improve 1-2 mechanical properties of the coating agent [7-10]. In practical production and application, higher requirements have been put forward for the tensile strength, tear strength, and elongation at break of acrylic finishing agents. It is important to develop a simple and efficient technology that can simultaneously improve various mechanical properties of acrylic resin.

Cellulose nanofibers are prepared from natural cellulose fibers and have high strength and modulus, large specific surface area, and high aspect ratio, making them excellent reinforcement materials. Cellulose nanofibers contain numerous active functional groups that can form hydrogen bonds and molecular chain entanglements with various polymers, improving their performance [11-13]. This article improves the compatibility between cellulose nanofibers and acrylic resin by modifying them, and then blends them with acrylic resin to obtain high-strength acrylic resin finishing agents.

2. Material and Methods

Material:

Cellulose nanofibers (MFC-F, solid content 2.6%, diameter 20 nm), self-made; Potassium persulfate, industrial grade, Shandong Jining Hongming Chemical Co., Ltd; Sodium dodecyl sulfate (K-12), industrial grade, Shandong Jining Hongming Chemical Co., Ltd; Methyl acrylate, industrial grade, Shandong Jining Hongming Chemical Co., Ltd; Ethyl acrylate, industrial grade, Shandong Jining Hongming Chemical Co., Ltd; Acrylic acid, industrial grade, Shandong Jining Hongming Chemical Co., Ltd; Acrylamide, industrial grade, Shandong Jining Hongming Chemical Co., Ltd; Tween-80, industrial grade, Shandong Jining Hongming Chemical Co., Ltd.

Methods:

Acrylic resin synthesis: Add 100 g of deionized water to a three necked bottle, heat to 70 ℃, and add 1.5 g of sodium dodecyl sulfate emulsifier. Continue to heat up, and when the internal temperature rises to 95 ℃, add 1 g of acrylic acid and acrylamide, as well as 3 g of methyl acrylate and ethyl acrylate, and then add 0.67 g of potassium persulfate. React at 90 ℃ for 15 minutes and quickly cool to 85 ℃. When the temperature stabilizes at 85 ℃, add the remaining 5 g of methyl acrylate and ethyl acrylate, 15 g of acrylic acid and acrylamide, and 0.33 g of potassium persulfate dropwise at a uniform feeding rate. The dripping time should be controlled between 2 and 2.5 hours. After the dripping is completed, raise the temperature to 90 ℃ and keep it warm for 2.5 hours. Lower the temperature to 60 ℃, add 0.78 g of Tween-80, stir for 10 minutes, let stand for 10 minutes, filter and discharge to obtain acrylic resin.

Modification method of acrylic resin: Weigh cellulose nanofibers of different qualities and mix them evenly with an equal amount of emulsifier. During the acrylic resin synthesis process, when the temperature reaches 95 ℃, mix the cellulose nanofibers with aqueous monomers and add them together.

Determination of properties of acrylic resin finishing agent emulsion: Evaluate the appearance, solid content, pH value and emulsion viscosity of the prepared acrylic resin before and after modification. Refer to the national standard GB/T 2223-1996 Test Methods of Acrylic Resin emulsion for Leather Making for specific methods.

Acrylic resin finishing agents - Determination of film properties: The acrylic resin before and after modification shall be filmed with reference to the national standard GB/T 2223-1996 Test Methods of Acrylic Resin emulsion for Tanning, and the tensile strength, elongation at break, water absorption and chemical stability of the resin film shall be measured. Observation of cellulose nanofibers in the cross-section of acrylic resin film using Hitachi S-3400N scanning electron microscope.

Determination of application performance of acrylic resin finishing agents: Mix the acrylic resin coating agent before and after modification with functional additives (color paste, wax agent, and hand feeling agent) used for leather coating in a mass ratio of leather coating agent: water: pigment paste: hand feeling agent: wax agent=6:5:2:1.5:1. After coating the two leather embryos, determine the application performance of the leather.

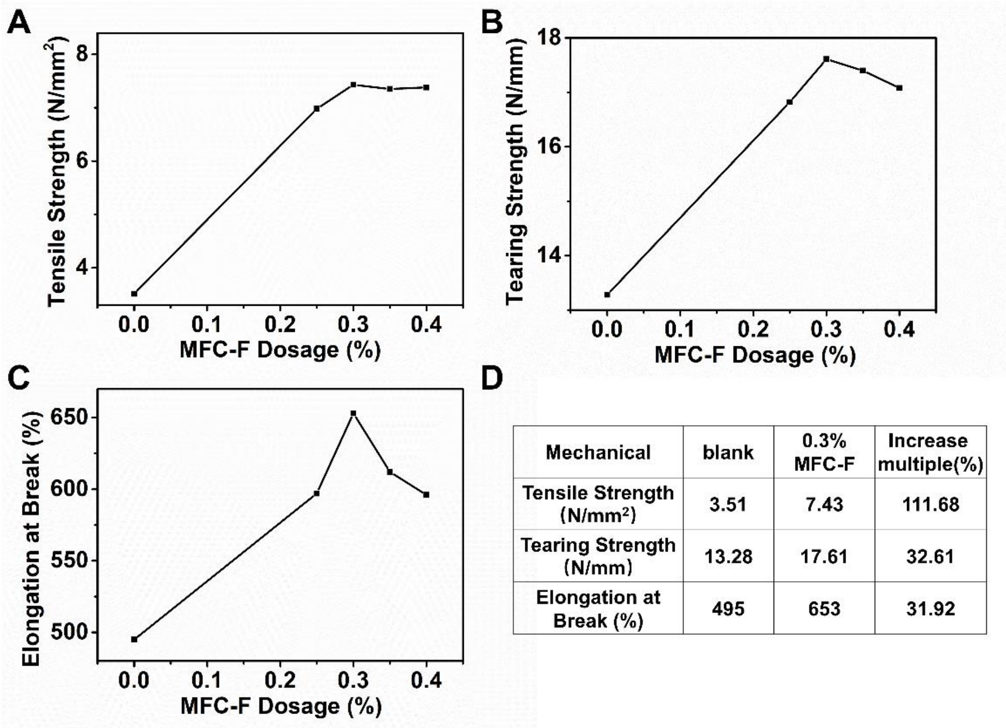
3. Results and Discussion

Properties of acrylic resin emulsion and film modified by cellulose nanofibers: Cellulose nanofibers were added into acrylic resin, and the effect of the amount of cellulose nanofibers on the properties of acrylic resin emulsion and film was investigated. The emulsion performance of cellulose nanofiber modified acrylic resin with different dosage was tested, and the results are shown in Table 1. It can be seen from Table 1 that the appearance, solid content and pH value of the modified acrylic resin emulsion have little influence, but have great influence on the viscosity of the acrylic resin emulsion. With the increase of the amount of cellulose nanofibers added, the viscosity of acrylic resin emulsion will increase significantly from 16.2 mPa · s to 41.1~49.0 mPa · s, but its use performance will not be greatly affected.

Table 1 Effect of cellulose nanofiber content on the performance of acrylic resin emulsion

MFC-F dosage （%）	Appearance	Solid content （%）	pH value	Viscosity (mPa·s)
0	Milky white liquid	34.82	6.7	16.2
0.25	Milky white liquid	33.71	6.7	41.1
0.30	Milky white liquid	33.36	6.6	46.3
0.35	Milky white liquid	33.18	6.7	46.4
0.40	Milky white liquid	33.05	6.6	49.0

The mechanical properties of acrylic resin film modified with different amounts of cellulose nanofibers were tested, and the results are shown in Figure 1. From Figure 1, it can be seen that the amount of cellulose nanofibers has a significant impact on the mechanical properties of the modified acrylic resin film. As the amount of cellulose nanofibers increases, the mechanical properties (tensile strength, tear strength, and elongation at break) of the adhesive film increase significantly. When the dosage of cellulose nanofibers is 0.30%, the mechanical properties of the acrylic resin film, such as tensile strength, tear strength, and elongation at break, all reach their maximum values. The tensile strength is as high as 7.43N/mm^2, the tearing strength is 17.61N/mm, and the elongation at break is 653%. Compared with unmodified acrylic resin, the tensile strength is increased by 111.68%, the tearing strength is increased by 32.61%, and the elongation at break is increased by 31.92%. This may be because the addition of high-strength cellulose nanofibers to acrylic resin enhances its strength. However, as the content of cellulose nanofibers increases, the original regularity of acrylic resin is gradually disrupted, leading to a decrease in strength. Therefore, it is best to modify acrylic resin by adding 0.3% cellulose nanofibers, with a focus on studying the addition of 0.3% cellulose nanofibers to acrylic resin.



Mechanical	blank	0.3% MFC-F	Increase multiple(%)
Tensile Strength (N/mm^2)	3.51	7.43	111.68
Tearing Strength (N/mm)	13.28	17.61	32.61
Elongation at Break (%)	495	653	31.92

Figure 1 A) The variation of the tensile strength of acrylic resin modified by the amount of MFC-F; B) The variation of the tearing strength of acrylic resin modified by the amount of MFC-F; C) The variation of the elongation at break of acrylic resin modified by the amount of MFC-F; D) Changes in mechanical properties before and after modification of acrylic resin.

Stability of cellulose nanofiber modified acrylic resin adhesive film: Test the swelling rate of acrylic resin film modified with cellulose nanofibers in different solvents. From Table 2, it can be seen that after modification, the swelling rate of the acrylic resin film in 5% H_2SO_4 decreased from 3.87% to 3.68%, and the swelling rate in 5% Na_2SO_4 decreased from 5.01% to 4.57%. The swelling rate in ethanol decreased from 58.03% to 50.30%, and it changed from a dissolved state to a partially dissolved state in acetone solvent. The swelling rate in water increased from 6.73% to 7.86%, and the swelling rate in 5% NaOH increased from 32.51% to 34.91%. This proves that the acid resistance, electrolyte resistance, and solvent resistance of the acrylic resin film have been improved to a certain extent after the modified by cellulose nanofibers, but the water resistance and alkali resistance have slightly decreased. This may be due to the stronger water affinity of cellulose nanofibers as a natural bio based material.

Table 2 Swelling rate of cellulose nanofiber modified acrylic resin film in different solvents before and after modification

MFC-F dosage （%）	Deionized Water	5%Na_2SO_4	5%H_2SO_4	5%NaOH	Ethanol	Acetone
0	6.73	5.01	3.87	32.51	58.03	Dissolve
0.30	7.86	4.57	3.68	34.91	50.70	Partial dissolution

Microscopic morphology of acrylic resin film modified by cellulose nanofibers: The microstructure of the acrylic resin film cross-section before and after modification with cellulose nanofibers was observed using SEM, and the results are shown in Figure 2. From Figure 2, it can be seen that compared to acrylic resin without cellulose nanofiber modification, cellulose nanofiber modified acrylic resin can clearly observe the structure of cellulose nanofibers, and the cellulose nanofibers are uniformly dispersed in the acrylic resin.

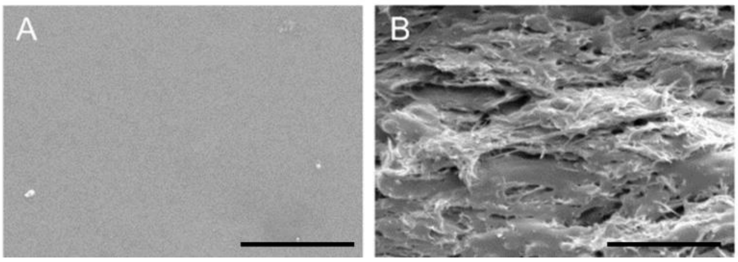


Figure 2 SEM scanning electron microscope of acrylic resin film before and after modification A) Before modification B) After modification, (Scale bar: 20 μm)

Application performance of cellulose nanofiber modified acrylic resin finishing agent: During the experiment, cellulose nanofibers (0.30% in absolute dry weight) were used to modify acrylic resin and mix it with commonly used paint paste and other finishing aids for leather finishing. Sheep garment leather was treated and the comprehensive properties of the leather coating, including adhesion fastness and vapor permeability, were tested and analyzed. The results are shown in Table 3.

From Table 3, it can be seen that the adhesion fastness (N/mm) of the resin before and after modification has increased from 4.46 to 5.42, the vapor permeability ($mg/10cm^2 \cdot 24h$) of the finished leather coating has increased from 317 times to 343, and the wet scratch resistance (grade) of the bottom layer of the finished leather has increased from 2.0 to 2.5. Therefore, cellulose nanofibers modified acrylic resin can significantly improve the comprehensive performance of finished leather coatings.

Table 3 Performance analysis of cellulose nanofiber modified acrylic resin finished leather coating

	Adhesion Fastness (N/mm)	Vapor Permeability ($mg/10cm^2 \cdot 24h$)	Dry/Wet Scratch Resistance (grade)	
			Bottom Coating	Finished Leather
Blank	4.46	317	4.0/2.0	4.5/4.5
Modified Acrylic Resin	5.42	343	4.0/2.5	4.5/4.5

Exploration of Enhancement Mechanism: Cellulose nanofibers is a semi rigid linear polymer compound with a large number of hydroxyl groups between molecules. There are hydrogen bonding interactions within and between molecular chains, causing them to aggregate and form crystalline regions, which typically have high strength. When high crystallinity cellulose nanofibers are uniformly dispersed in the polymer matrix, they can act as nucleating agents, limiting the movement of polymer chains, and providing nucleation sites to promote crystallization, increasing the crystallinity of the composite material, thereby improving the strength of the composite material. Cellulose nanofibers can entangle with polymer chains, forming a stable three-dimensional network structure, improving the impact resistance and toughness of composite materials [14-15]. The strengthening mechanism of cellulose nanofibers on acrylic resin adhesive film is shown in Figure 3. There are hydrogen bonds and molecular chain entanglement between acrylic resin molecular chains, and the addition of cellulose nanofibers forms hydrogen bonds and molecular chain entanglement between cellulose nanofibers and acrylic resin molecular chains, forming a more complex network structure and improving the strength and function of composite materials.

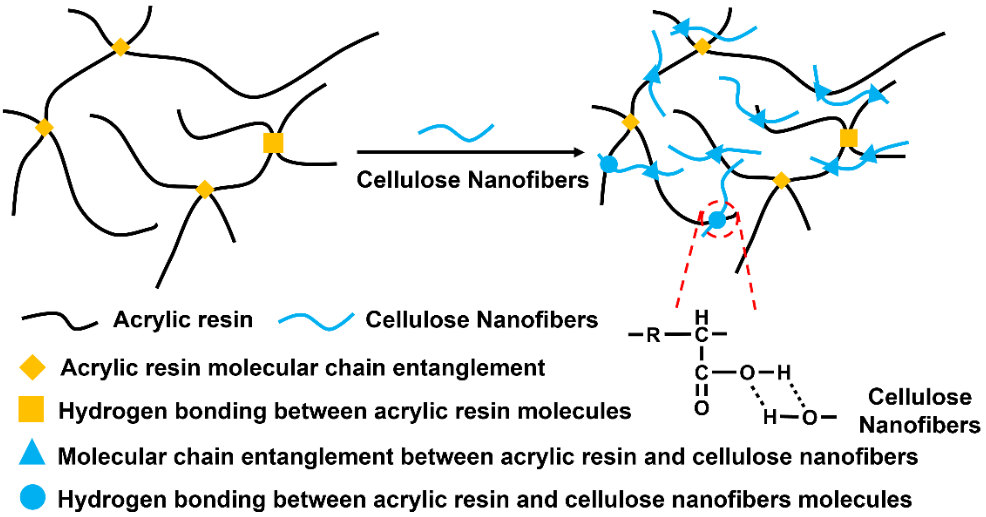


Figure 3 Schematic diagram of the reinforcement mechanism of cellulose nanofibers in acrylic resin.

4. Conclusion

A high-strength acrylic resin finishing agent was synthesized using cellulose nanofibers, with the best performance achieved when the addition amount of cellulose nanofibers was 0.3%. The mechanical properties of acrylic resin modified with cellulose nanofibers have been significantly improved, with a tensile strength of up to 7.43 N/mm2, a tear strength of 17.61 N/mm, and an elongation at break of 653%. Compared with unmodified acrylic resin, the tensile strength has increased by 111.68%, tear strength has increased by 32.61%, and elongation at break has increased by 31.92%. Cellulose nanofiber modified acrylic resin can significantly improve the comprehensive performance of the finished leather coating. The adhesion fastness of the finished leather coating has increased from 4.46 N/mm to 5.42 N/mm, and the vapor permeability of the finished leather coating (mg/10 cm^2 · 24h) has increased from 317 times to 343 times. Therefore, cellulose nanofibers, as a reinforcing material, can simultaneously improve the tensile strength, tear strength, and elongation at break of acrylic resin, significantly improving the performance of acrylic resin, and expanding the practical scenarios and fields of acrylic resin.

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