Preparation and Properties of Inkjet Waterborne Coatings

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Abstract: As an environmentally friendly coating, waterborne coatings have broad application prospects in paper packaging products in food and medicine. In this paper, a waterborne coating is synthesized from epoxy resin, polypropylene glycol diglycidyl ether, acrylic acid, trimellitic anhydride, maleic anhydride, and organic amine by three steps: ring opening reaction, esterification reaction, and neutralization reaction. Using viscosity, particle size, thermal stability, adhesion, and friction resistance as performance evaluation factors, the effects of the ratios of epoxy resin and polypropylene glycol diglycidyl ether in the polymerization system on the performance of synthetic waterborne coatings were discussed. Taking water solubility, water absorption, and water resistance as performance evaluation factors, the effects of the amount of ratio of anhydride groups to hydroxyl groups in the epoxy acrylic resin, which were produced in the second step of the reaction, were considered on the performance of synthetic waterborne coatings. The experimental results showed that when the molar ratio of the epoxy group in the epoxy resin and polypropylene glycol diglycidyl ether was about 1:1, and the molar ratio of anhydride in maleic anhydride to hydroxyl in the epoxy acrylic resin generated in the second step of reaction was about 0.9:1, the performance of the prepared waterborne coatings was comprehensively better. At the same time, the applicability of self-made waterborne coatings was tested. The results showed that when the coating amount was about 3.60 g/m², the properties of the packaging base paper were greatly improved with respect to air resistance, oxygen resistance, oil resistance, and color reproducibility.

Keywords: inkjet; coatings; waterborne; performance

1. Introduction

Packaging paper has the advantages of certain stiffness, good printability, low cost, and environmental friendliness; it is widely used in the fields of food and some specific packaging [1,2]. However, paper also has characteristics of low oil resistance and high air permeability, which will limit its application in some fields [3,4]. In view of the deficiencies of some properties of paper-based materials, impregnation processing, composite technology, coating processing, and other methods are usually used to improve the performance of paper-based materials. For packaging paper-based materials, especially packaging printing paper materials, because the coating process is easy to operate and to combine and or make compatible with other packaging and printing processes, which makes it be a better method to improve the performance of packaging paper [5–9]. Traditional coating methods include roll coating, air knife coating, and blade coating. However, these methods generally have problems, such as difficulty in controlling the coating amount, complicated operation processes, and poor process compatibility [10]. On-demand coating,
a process based on demand as needed, has various advantages—its on-demand nature, timeliness, and individuality—and may be an excellent coating technology for packaging paper coating processing in the future. On-demand coating can use digital printing technology as an application method, which can realize the operation of low coating quantity and on-demand coating to solve the problem of continuous waste of coating materials. At the same time, it can also improve the coating efficiency and optimize the process. Digital inkjet technology can make the coatings spray from the nozzle to the materials, which are then coated under the control of the computer. In addition, it can make the coating by the coating process in the form of fields or graphic shapes. It can be considered a non-pressure and non-contact coating technology [11–18] that can be popularized and used in the field of coating processing. The coating process is accomplished using digital inkjet technology, which requires that the coatings used are suitable for the inkjet process system. Therefore, the preparation of the coatings suitable for inkjet systems is the first step to achieve on-demand coatings. In order to meet the requirements of green environmental protection, waterborne coatings have become the focus of research [19–23]. Among the different types of coatings, waterborne coatings have various characteristics, of non-toxic, low irritation, low volatile organic substances (VOCs), and low cost, which consider to attract increasing attention from manufacturers, consumers, and scholars [24–30].

Among the main raw materials for the preparation of waterborne coatings, this paper intends to explore the effects of the compound ratio of epoxy resin and polypropylene glycol diglycidyl ether in the polymerization system and the compound ratio of anhydride in maleic anhydride and hydroxyl in epoxy acrylic resin on the preparation and properties of waterborne coatings. Through the experimental data, the above two optimal compounding ratios were obtained, which would provide a reference for the preparation and synthesis process of waterborne coatings. In order to ensure that the waterborne coatings prepared in the experiment can be used in the form of spraying, this experiment tested the properties of the waterborne coatings prepared, and adjusted the preparation formula to make it suitable for the inkjet system. In this experiment, the Epson piezoelectric inkjet system was used for the spraying test. In order to test whether the prepared waterborne coatings can meet the requirements of service performance, the related properties of packaging paper before and after coating were also tested, to verify whether the properties of packaging paper were improved after the paper was coated.

The novelty of this study is that viscosity reduction and hydrophilic modification of epoxy resin were performed using new raw materials and new formulas. Finally, a waterborne and environmentally functional coating was prepared, which not only improved the barrier performance of packaging base paper but also improved its printability. In terms of the use of the coating, its performance was able to meet the requirements of the inkjet system. The online coating, printing, and decoration of the packaging base paper could be conducted simultaneously, which would avoid the cumbersome process of coating the base paper first and then changing the machine for decoration and printing.

2. Materials and Methods
2.1. Materials

The waterborne coatings in the experiment were synthesized by epoxy resin (E51), polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether (ED), acrylic acid, triethylamine, trimellitic anhydride, and dimethylaminoethyl methacrylate. The coating base paper in this experiment was packaging paper, of which the gram weight was 50 g/m².

2.2. Equipment

The viscosity of the reactant system was tested by a viscometer (DVS, Brookfield, Middleboro, MA, USA). The particle sizes of the polymer were determined by a Nano-ZS90 particle size analyzer (Malvern, UK). The thermogravimetric analysis of the reactant film was performed using a TGAQ-50 thermogravimetric analyzer (TA Instruments, New Castle,
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DE, USA). Adhesion and friction resistance were tested by QFZ-II paint film adhesion tester and MCJ-01A wear tester, respectively. The morphological changes of the paper surface were determined using Regulus 8220 scanning electron microscope (Hitachi, Tokyo, Japan). The surface roughness of the paper was tested and calculated by the Multimode8 atomic force microscope (Brook company). The absorption of waterborne coatings to packaging paper was tested by a Kruss dsa100s automatic contact angle tester. The air permeability of the paper before and after coating was tested by an SE115 air permeability tester (Lorentzen & Wettre company, Stockholm, Sweden). The oxygen transmittance of the paper was tested by VAC-V1 differential pressure gas permeameter (Jinan Languang Electromechanical Technology Co., Ltd., Jinan, China). The moisture permeability of the paper before and after coating was measured using a W401 moisture permeability tester (Guangzhou Biaoji Packaging Equipment Co., Ltd., Guangzhou, China). The inkjet printing proofs were printed by an L15158 inkjet printer (Epson, Suwa, Japan). The color density of the color sample was measured using an X-rite standard edition spectrodensitometer.

2.3. Sample Preparation

Firstly, bisphenol A epoxy resin (E51) and polyethylene glycol diglycidyl ether (ED) in a certain proportion were subjected to ring opening esterification with acrylic acid. When the acid value of the system decreased to a certain value, the reaction was stopped to obtain epoxy acrylic resin (EB). Then, trimellitic anhydride and maleic anhydride were added for further esterification. Finally, dimethylaminoethyl methacrylate and triethylamine were introduced to neutralize the reaction system, and some deionized water was added to adjust the solid content.

In the experiment, seven groups of epoxy group molar ratios in E51 and ED were selected: 3:1, 2:1, 1.5:1, 1:1, 1:1.5, 1:2, and 1:3. The obtained waterborne coatings were recorded as samples 1 to 7, respectively. The molar ratios of anhydride group to hydroxyl group in EB were 1.2:1, 1.1:1, 1:1, 0.9:1, 0.8:1, 0.7:1, and 0.6:1, respectively, and the obtained waterborne coatings were recorded as samples A–G, respectively.

2.4. Performance Tests

2.4.1. Viscosity

A DVS digital viscometer was used to measure the viscosity of the system at a temperature of 23 ± 0.5 °C. The rotors and speeds were selected, and each sample would be measured at least twice at the same temperature. The average value was calculated as the final viscosity of the system.

2.4.2. Solid Content

The solid content of the sample was tested according to ISO 3251:2003.

2.4.3. Particle Size

The sample was diluted with deionized water to a solution with a mass fraction of 0.5%, and the particle size was tested by a particle size analyzer at room temperature. When three measurements had been made and the obtained values were similar, the average value was calculated to give the final particle size value of the sample.

2.4.4. Thermal Stability

Thermogravimetric analysis was performed on the film of the reaction composition by thermogravimetric analyzer under a nitrogen environment with heating from 15 °C to 600 °C.

2.4.5. Adhesion and Friction Resistance

The adhesion of the coating was tested according to the Chinese national standard GB 9286-98 tape paper method. The abrasion resistance of the coating was tested according to the Chinese national standard GB/T 1768-2006.
2.4.6. Water Solubility

To a certain amount of coating sample, different proportions of distilled water were added in batches and stirred evenly to obtain coating water dispersion. After standing for a period of time, the coating water dispersion was observed to determine whether it had some changes in color, transmittance, stability, or other appearance phenomena; these were taken as the standard to judge the water solubility of the coating.

2.4.7. Water Absorption

The dried curing film was cut into square pieces with a mass of about 0.2000 g. After being weighed accurately \( m_0 \), these square pieces were immersed in distilled water and removed after 24 h. Filter paper was used to remove the water on the surface of the membrane quickly, and the mass of the membrane \( m_1 \) was weighed accurately. The water absorption \( A \) was calculated according to Equation (1).

\[
A = \frac{m_1 - m_0}{m_0} \times 100\% \tag{1}
\]

2.4.8. Water Resistance

The coatings were dried to form a film and soaked in water for 50 min. Pulverization, cracking, light loss, and other phenomena were observed to see if they appeared on the samples. If there were no phenomena as described above, they coatings were judged as qualified.

2.4.9. Absorption of Coatings on Packaging Paper

The absorption of the self-made waterborne coatings on packaging paper was tested. The wetting and spreading process of coating on paper was observed using a contact angle tester, and the corresponding time was recorded simultaneously.

2.4.10. Scanning Electron Microscope (SEM) Analysis

The morphological changes of the paper surface before and after coating were observed by scanning electron microscopy.

2.4.11. Atomic Force Microscopy (AFM) Analysis

The changes of surface flatness and roughness of the paper before and after coating were observed by atomic force microscope, and the mean square roughness of the paper surface was calculated by using the instrument’s own software.

2.4.12. Air Permeability

The air permeability of the paper before and after coating was measured according to the Chinese national standard GB/T 458-2008.

2.4.13. Oxygen Permeability

The oxygen permeability of the paper before and after coating was measured according to the Chinese national standard GB/T 458-2008.

2.4.14. Moisture Permeability

The moisture permeability of paper before and after coating was tested according to the international standard ISO 2528:2017.

2.4.15. Oil Permeability

TAPPI UM 557 Oil Kit Test was used to test the oil resistance of the paper before and after coating.
2.4.16. Color Reproducibility

In order to evaluate the influence of the coatings on the color reproduction performance of paper, the CIE L* a* b* values of uncoated and coated printing samples were measured by a spectrophotometer. According to the measured values, the color gamut map of each printing paper was drawn, and then the color reproducibility of the samples was evaluated.

3. Results and Discussion

3.1. Effect of Different Molar Ratio of Epoxy Groups of E51 and ED

3.1.1. Viscosity

In this experiment, epoxy diluent (ED) and epoxy resin (E51) were used to reduce the viscosity of the initial synthetic system of the prepared coating. The viscosity of the initial reaction system has a direct impact on the viscosity of the final reaction product. The coating system prepared with epoxy resin (E51) as the matrix had high viscosity, which is difficult to use on inkjet equipment with a requirement for low viscosity.

In this experiment, the influence of the diluent on the viscosity of the initial coating reaction system was first tested. Moderate viscosity is conducive to the smooth progress of the reaction. A suitable initial viscosity can ensure that the prepared coating has the performance requirement of low viscosity. The experimental results are shown in Figure 1.

Figure 1. The initial viscosity of the reaction system under different E51 to ED ratios.

As shown in Figure 1, with the increase of ED addition, the viscosity of the initial reaction system became smaller and smaller. The measurements showed that the viscosity of the reaction system without ED was 8326.80 mPa·s. When the molar ratio of the epoxy groups of E51 to ED in the system was 1:1, the viscosity of the initial reaction system decreased greatly: the viscosity of the initial reaction system was 271.15 mPa·s and the viscosity reduction rate reached 96.74%.

In order to verify the effect of the viscosity of the initial reaction system on the viscosity of the final synthetic coatings, eight groups of waterborne coatings with a solid content of 10~80% were prepared using the different proportions of E51 and ED. Their viscosities were tested to examine the effects of different proportions of E51 and ED on the viscosity of the prepared coatings. The results of the test are shown in Figure 2.
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Figure 2. Effect of the E51 to ED ratio on the viscosity of coatings with different solid contents.

According to the experimental data in Figure 2, when the solid content of the prepared coatings increased from 10% to 80%, its viscosities also increased. The viscosities of the samples with the molar ratio of the epoxy groups of E51 to ED of 3:1, 2:1, and 1.5:1 increased rapidly with the increase in solid content. However, when the solid content was greater than 40%, the viscosities of most of the above coatings were greater than 50 mPa·s, which did not meet the viscosity requirements of the inkjet system.

However, in terms of viscosity performance, the prepared coating samples of systems 4–7 were more suitable for inkjet system when the epoxy molar ratio of E51 to ED were 1:1, 1:1.5, 1:2, and 1:3. Samples 1–3 were not suitable for the inkjet system because of their high viscosity.

3.1.2. Particle Size

For the inkjet system, due to the requirements of the precision of the nozzle, the appropriate particle size of the coatings has a great influence on its range of use and performance. In this experiment, particle sizes of the coating samples 1–7 were tested to explore the influence of the ratio of E51 to ED on the particle size of the system. The self-made synthetic coatings were tested to determine whether they could be applied to the inkjet system. The test results of the particle sizes of the coatings are shown in Figures 3–9.

Figure 3. The particle size distribution of the system when the molar ratio of epoxy groups is E51:ED = 3:1.
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Figure 4. The particle size distribution of the system when the molar ratio of epoxy groups is E51:ED = 2:1.

Figure 5. The particle size distribution of the system when the molar ratio of epoxy groups is E51:ED = 1.5:1.

Figure 6. The particle size distribution of the system when the molar ratio of epoxy groups is E51:ED = 1:1.
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Figure 7. The particle size distribution of the system when the molar ratio of epoxy groups is E51:ED = 1:1.5.

Figure 8. The particle size distribution of the system when the molar ratio of epoxy groups is E51:ED = 1:2.

Figure 9. The particle size distribution of the system when the molar ratio of epoxy groups is E51:ED = 1:3.

As can be seen from Figures 3–9, the overall trend of particle sizes of the coatings system prepared in the experiment was getting smaller and smaller with the increase of the...
dosage of ED. The particle sizes of samples 1–3 were about 300–400 nm, and the particle sizes of samples 4 and 5 were about 100–200 nm. The peak heights of samples 1–5 were high and narrow, while the particles of the coatings were uniform in size and concentrated in distribution.

However, the distributions of the particle sizes of samples 6 and 7 were uneven. In this situation, the material structure of the coatings changed during its storage, reducing its service performance. With the increase in ED dosage, the composition of the coatings would become more uneven and unstable. As can be seen from Figures 8 and 9, some particle sizes of samples 6 and 7 were greater than 1 μm, which is not suitable for use in an inkjet printer.

3.1.3. Thermal Stability

The thermogravimetric (TG) curves of films of the waterborne coatings synthesized with different epoxy molar ratios of E51 and ED are shown in Figure 10.

![Figure 10. Thermogravimetric curves of coatings with different epoxy group molar ratios of E51:ED.](image)

It can be seen from Figure 10 that the synthesis had an obvious weight loss step at 330–430 °C, which indicated that the molecular chains in the synthesis had been decomposed at this stage. With the increase in ED ratio, the TG curve shifted to the left, especially for samples 5–7, which meant that its thermal stability performance decreased significantly.

These results are mainly due to the increase in the molar ratio of the epoxy groups of ED:E51, which reduces the proportion of long molecular chains in the composite system. At the same time, the proportion of carbon atoms in the molecule was reduced at the same ratio. Carbon atoms, on the other hand, are larger and more densely packed than hydrogen atoms, which would make themselves less tightly entangled. This may reduce the stability of the composition within a certain range. The composite with a large proportion of E51 should have a stronger network structure after film forming, making its molecular thermal movement unfavorable and the heat hard to release, therefore increasing its thermal stability higher.

3.1.4. Adhesion and Friction Resistance

After the coating film is cured, the tape was stuck on it, pressed tightly, and then torn off. If the film layer were torn off by the tape paper, the adhesion was deemed to be unqualified. If the film were intact, it was regarded as qualified. The friction resistance of the film was tested according to the test standard for the wear resistance of the film. Under the condition of friction pressure of 20 ± 0.3 N, the sample was rubbed 50 times with a friction testing machine. The sample was weighed when the chip was removed, and the weight loss was calculated. The same sample were repeated many times, and the
arithmetic mean value was taken as the result. The above test results for this study are shown in Table 1.

**Table 1. Adhesion and friction resistance of coatings prepared with different epoxy group molar ratio E51: ED.**

| Samples | Performance | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---------|-------------|---|---|---|---|---|---|---|
| Adhesion| Yes         | Yes| Yes| Yes| Yes| No| No|   |
| Friction resistance (g) | 0.0011 | 0.0024 | 0.0031 | 0.0036 | 0.0048 | 0.0072 | 0.0108 |

As can be seen from Table 1, when the amounts of ED were too large, the adhesion of the film formed by coatings was relatively poor. When the epoxy molar ratio of E51 to ED exceeded 1:2, more films would be torn off. The friction resistance of the coatings also decreased with increasing ED content. When the ratio of E51 to ED exceeded 1:1.5, the weight loss increased significantly. The results were also consistent with the thermal stability test results of the coatings. An increase in the amount of ED results in molecular chains of the composite that were not tightly wound and a network structure that was not firm after film formation, which may lead to the decline in its adhesion and friction resistance.

Through the above performance tests and comparison of results, it could be seen that when the molar ratio of epoxy group E51:ED = 1:1, the comprehensive performance of the sample 4 was better.

### 3.2. Effect of Different Molar Ratio of Anhydride and Hydroxyl in EB

As the reaction progressed, the amount of anhydride groups introduced had a deterministic effect on the number of hydrophilic groups in the final synthesis. The water solubility of the synthetic coatings, water absorption, and the water resistance of the coatings after film formation were tested in this experiment, and was used to determine the influence of the ratio of anhydride and hydroxyl in EB on the performance of the coatings. Finally, the optimal proportion was determined.

#### 3.2.1. Water Solubility

The main factor that would affect the water solubility of the coating system was the amount of hydrophilic groups in the system. The amount of hydrophilic groups was determined by the amount of anhydride that was introduced into the reaction system. In this experiment, the waterborne coatings were prepared with seven groups of the molar ratios of anhydride groups to hydroxyl groups in EB. The molar ratios were 1.2:1, 1.1:1, 1:1, 0.9:1, 0.8:1, 0.7:1, and 0.6:1, which were recorded as sample A–G, respectively. The water solubility of each coating group was observed. The experimental results are shown in Table 2.

**Table 2. Effect of the ratio of anhydride and hydroxyl groups in EB on the water solubility of coatings.**

| Samples | Water Solubility | Phenomena          |
|---------|------------------|--------------------|
| A       |                  | Translucent and layered |
| B       |                  | Translucent and layered |
| C       |                  | Transparent        |
| D       |                  | Transparent        |
| E       |                  | Translucent        |
| F       |                  | Opalescent and opaque |
| G       |                  | Opalescent and opaque |

As can be seen from Table 2, both samples A and B were translucent and stratified, perhaps because the excess anhydrides were left in the reaction system without esterification. Moreover, there was the phenomenon of anhydrides crystallized and layered in
samples A and B. Some anhydrides may have reacted with the added organic amines to form some brownish impurities that would make the coating systems turbid and opaque.

When the molar ratios of the anhydride group to the hydroxyl group in EB were less than 0.8:1, the coating solutions appeared turbid until opalescent and opaque. These were because, on the one hand, the reduction of the amount of anhydride decreased the hydrophilic groups of the coating system and the water solubility of the whole system. On the other hand, the decrease in the amount of anhydride caused some EB to remain in the coatings without subsequent reaction, which reduced the water solubility of the coatings system further.

3.2.2. Water Absorption

The prepared coating samples A–G were diluted to different solid contents for drying and curing, and their water absorption was tested. The results are shown in Figure 11.

![Figure 11](image.png)

**Figure 11.** Effect of the ratio of anhydride to hydroxyl groups in EB on the water absorption of coatings after film formation.

It can be seen from Figure 11 that the overall trend in water absorption for samples A–G followed a decrease with the decrease in the ratio of anhydride to hydroxyl groups in EB. When the amount of anhydride was reduced, the hydrophilic group in the final compound molecule was also reduced. The probability of the existence of hydrophilic groups on the surface and in the film layer of the coatings after film formation was reduced, which decreased the water absorption of the coatings after film formation.

With the increase in the solid content, the water absorption of the cured film decreased gradually at solid contents less than 50%. The coatings with high solid content had a relatively high internal crosslinking density, which was not conducive to the penetration of water into the film. However, the number of hydrophilic groups also increased with an increase in solid content, which would increase the water absorption of the cured film when the solid content of the coating was greater than 50%. The experimental results showed that the absorption rate of sample D was 3.9%, and it had the best water resistance performance.

3.2.3. Water Resistance

The waterborne coatings that were prepared in this experiment had many hydrophilic groups, such as hydroxyl, ether, carboxyl, and amino groups, which could make them water soluble. However, for use, a certain water resistance is required after drying. In this experiment, the water resistance of samples A–G with a 50% solid content was tested; the results are shown in Table 3.
As can be seen from Table 3, when the amount of ED was too large, the water resistance of the coating films was affected. The films of samples A and B were cracked and lost light, and sample A was also pulverized. This was attributed to the fact that the excess anhydride material did not participate in the esterification and subsequent neutralization reaction, but remained in the final reaction compounds. After the film formation of the composite, the unreacted material could not form a close cross-linked structure with the main body of the coatings and the water was easily immersed into the interior of the films, which decreased its water resistance.

As the amount of anhydride decreased, the number of hydrophilic groups in the synthetic coatings also decreased and their water solubility became worse. With the increase in immersion time, water became immersed into the film. Due to the existence of water-insoluble substances, the phenomena of pulverization and loss of light all appeared for samples E, F, and G. At the same time, due to the reduction in the amount of acid anhydride, the molecular weight distribution of the final composition may be uneven. After the coatings were formed into films, which had structures that were not uniform and some became less compact, the phenomenon of film cracking occurred. It can be seen from the test results that the water resistance of samples C and D were good, and there were no adverse phenomena.

Through the above performance tests and results, the comparison of the various properties of the coatings, and a consideration of the cost of materials, the molar ratio of anhydride to hydroxyl groups in EB was finally selected as 0.9:1.

### 3.3. Performance of Waterborne Coatings

#### 3.3.1. Absorption of Coatings on Packaging Paper

In order to test whether the prepared coatings could achieve spreading and absorption on the packaging base paper, this experiment tested the wettability of the self-made waterborne coatings in the form of an inkjet, which would help to observe the spreading effect on the paper. In this experiment, the absorption processes of waterborne coatings on packaging paper were tested and recorded by contact angle tester. The absorption process of the coating on the paper is shown in Figure 12.
Figure 12. Spreading process of self-made coating on packaging base paper.

Figure 12 showed that the coating started to spread as soon as it left the nozzle and arrived on the paper. The size of the coating increased by nearly 1/3 in 4 s, and the coating was absorbed and spread on the paper completely in 6 s. The wetting and drying processes of coating on packaging base paper include spreading and infiltration, which take place simultaneously. Therefore, the gram weight of paper and the solid content of coating, which are two important factors, should also be considered when choosing the correct matching paper and coating.

3.3.2. SEM Analysis

In order to observe and analyze the changes of the surface morphology of packaging base paper before and after being coating, four groups of paper samples with coating amounts of 0, 1.51, 2.55 and 3.60 g/m² were used as the test samples. The test results are shown in Figure 13.

Figure 13. SEM views of the uncoated and coated packaging paper. (a) is packaging base paper and the magnification is 200; (b) is the paper with coating amounts of 1.51 g/m² and the magnification is 200; (c) is the paper with coating amounts of 2.55 g/m² and the magnification is 400; (d) is the paper with coating amounts of 3.60 g/m² and the magnification is 400.

As can be seen from Figure 13, the surface of the base paper was rough, and the fiber structure network could be seen clearly. When the coating amount on the paper surface was 1.51 g/m², the grooves on the paper surface were reduced and the paper surface became flat and smooth, indicating that the coatings had filled the pores and bonded with the
fibers. It could be seen that the coatings could greatly improve the surface condition of base paper. However, there were still pores on the surface of the paper at this time, and a continuous coating film layer was not formed. When the coating amount was increased to 2.55 g/m², the pores were filled further, and the smoothness of the paper surface was further improved. The surface of the paper was covered with a uniform and continuous coating film; the fiber structure of the paper was basically completely covered and the fiber network could hardly be seen. The coating film on the paper surface was dense and there were basically no pores when the coating amount was 3.68 g/m². It can be seen that a coating film with a certain thickness could be formed on the paper surface when it was coated with a certain coating amount.

3.3.3. AFM Analysis

In this experiment, four groups of paper samples with coating amounts of 0, 1.51, 2.55, and 3.60 were used as test objects to observe and analyze the changes of surface flatness and roughness of uncoated and coated packaging base paper. The test results are shown in Figures 14–17.

![AFM views of the packaging base paper](image1)

**Figure 14.** AFM views of the packaging base paper.

![AFM views of the coated packaging paper](image2)

**Figure 15.** AFM views of the coated packaging paper (coating amount: 1.51 g/m²).
The left hand images in Figures 14–17 show the base paper surface covered by the coatings. The right hand images in Figures 14–17 show the flatness of the paper surface and the changes in the paper surface after being coated. As can be seen from Figure 14, the surface of the packaging base paper had many pores and was clearly uneven. When the coating amount on the surface of the base paper was 1.51 g/m², as shown in Figure 15, the coating filled the pores of the paper, which effectively improved the roughness of the surface of the coated base paper. However, the surface could not be completely covered by the coating film in some areas of the base paper at this time because of the low coating amount. In addition, the coating thickness on the paper surface was uneven, as shown on the three-dimensional diagram. As can be seen from Figures 16 and 17, when the coating amount increased to 2.55 g/m², the paper surface was covered by a uniform coating and was quite flat. There was no obvious difference between the morphology diagram and three-dimensional diagram obtained by AFM when the coating amount was increased to 3.60 g/m². At this time, the effect of increasing the coating amount was mainly reflected by an increase in the film thickness.

The surface roughness of the paper was calculated by the software of AFM instrument. The calculation results are shown in Table 4.
Table 4. Effect of coating amounts on air permeability of packaging base paper.

| Coating Amount (g/m²) | Root Mean Square Roughness Rq (mL/min) |
|-----------------------|--------------------------------------|
| 0                     | 183.60                               |
| 1.51                  | 87.55                                |
| 2.55                  | 36.92                                |
| 3.60                  | 22.35                                |

As can be seen from Table 4, as the coating amount increased, the roughness of the paper surface decreased significantly and the paper surface became smoother and smoother. However, the speed of this smoothing trend became increasingly smaller. When the pores on the paper surface were filled with the coatings and a uniform coating film had been formed, increasing the coating amount had no obvious effect on improving the smoothness of the paper surface, but only increased the thickness of the coating layer. These results were consistent with the results of the SEM and AFM analyses.

3.3.4. Air Permeability

In this experiment, surface treatment of the packaging base paper with different coating amounts was conducted to test its effect on the air permeability of packaging base paper. The air permeability test results of packing base paper with different coating amounts are shown in Table 5.

Table 5. Effect of coating amounts on air permeability of packaging base paper.

| Coating Amount (g/m²) | Permeation Volume (mL/min) |
|-----------------------|---------------------------|
| 0                     | 115.3                     |
| 1.51                  | 3.52                      |
| 2.02                  | 0.825                     |
| 2.55                  | 0.409                     |
| 3.06                  | 0.268                     |
| 3.60                  | 0.268                     |
| 4.08                  | 0.268                     |
| 4.35                  | 0.268                     |

It can be seen from Table 5 that the air permeability of paper decreased significantly with an increase in coating amounts, which indicated that the coatings prepared in this experiment could effectively reduce the air permeability of the paper. When the base paper was coated, the voids on the surface were closed by the coating film, which reduced the air permeability of the paper.

The air permeability of paper reached the lowest value of 0.268 mL/min when the coating amount was 3.06 g/m², at which time it was considered that the coating had covered the surface pore of the base paper completely and a continuous coating film had formed on the paper surface.

3.3.5. Oxygen Permeability

Packaging materials are required to have a certain oxygen barrier in some applications to prevent the deterioration or damage of the packaged goods caused by aerobic activity. In this experiment, the surface treatment of packaging base paper with different coating amounts was performed to test its effect on the oxygen resistance of the paper. The test results of oxygen permeability of the packaging paper with different coating amounts are shown in Table 6.
Table 6. Oxygen permeability with different coating amounts on packaging base paper.

| Coating Amount (g/m$^2$) | Oxygen Permeance Ratio (cm$^3$/m$^2$·24 h·0.1 MPa) |
|--------------------------|-----------------------------------------------|
| 0                        | >100,000                                      |
| 1.51                     | 26,595.8                                      |
| 2.02                     | 13,320.2                                      |
| 2.55                     | 5230.6                                        |
| 3.06                     | 769.2                                         |
| 3.60                     | 330.9                                         |
| 4.08                     | 328.0                                         |
| 4.35                     | 327.8                                         |

It can be seen from Table 6 that the oxygen permeance rate of the paper samples became increasingly smaller as the coating amount increased. This is likely because when the surface of the packaging base paper was coated, the coatings effectively filled the pores, which were present due to the interweaving fibers in the base paper. At that time, the gas penetration channel had been blocked.

As the coating amount increased, a dense film layer was formed on the surface of the paper, and this played an important role in hindering the passage of gas through the paper samples. The thickness of the film layer was related to the coating amount, and the thickness increased as the coating amount increased.

When the coating amount was 3.60 g/m$^2$, the oxygen permeance rate was reduced to 330.9 cm$^3$/m$^2$·24 h·0.1 MPa, which was 98.7% lower than that of coated paper with a coating amount of 1.51 g/m$^2$. The coated packaging paper obtained better oxygen barrier performance in this experiment.

3.3.6. Moisture Permeability

In a humid environment, water vapor may enter packaging through the packaging materials, which may cause some damage to the quality of packaging products. Therefore, it is very important to test the moisture permeability of the packaging material before use. In this experiment, surface treatment was applied to packaging base paper with different coating amounts to test its effect on the moisture air permeability of packaging base paper. The air permeability test results of packaging paper with different coating amounts are shown in Table 7.

Table 7. Moisture permeability of wrapping paper with different coating amounts.

| Coating Amounts (g/m$^2$) | Water Vapor Transmission Rate (g/m$^2$·24 h) |
|---------------------------|---------------------------------------------|
|                           | 50 ± 2%RH | 75 ± 2%RH                           |
| 0                         | 652.8     | 942.4                                |
| 1.51                      | 612.5     | 952.7                                |
| 2.02                      | 592.2     | 960.5                                |
| 2.55                      | 590.5     | 962.2                                |
| 3.06                      | 581.6     | 966.8                                |
| 3.60                      | 593.7     | 988.7                                |
| 4.08                      | 601.4     | 976.6                                |
| 4.35                      | 607.8     | 965.7                                |

As can be seen from Table 7, as the environmental humidity increased, the water vapor transmission rates of papers with different coating amounts all increased. However, the water vapor transmission rate of the paper decreased with the increase in coating amounts under the condition of 50% relative humidity, but the decrease was not obvious. Under the condition of 70% relative humidity, the water vapor transmission rate did not change significantly with an increase in coating amount, which indicated that the moisture permeability of paper was still not improved significantly.
The moisture permeability of paper was related not only to its surface pores, but also to the surface material’s vapor adsorption. A certain porosity is required for the surface of the packaging base paper, which should reduce the moisture resistance of the paper. For a coated base paper, the porosity should be decreased and the moisture resistance should theoretically also increase, which could, theoretically, occur under the condition of 50% relative humidity and some low coating amounts. However, the effect of the paper surface porosity on its moisture permeability was much smaller than that of the mask layer on the vapor absorption when the coating had formed a closed film on the surface of the base paper with the increase in the amounts of coating.

The waterborne coatings prepared in this experiment contained a high proportion of hydrophilic groups, which caused water vapor to be more easily adsorbed by the coatings, especially under conditions of high relative humidity. Water vapor should be in a state in which it is adsorbed in the coatings and be in another state in which it permeates through the coatings to reach the base paper; however, in a closed barrier, both of these resulted in little changes in the packaging base paper, whether or not it had been coated.

3.3.7. Oil Permeability

According to the experimental method of TAPPI UM 557, the oil prevention grade was divided into 1–12 levels. The higher the test level, the better the oil resistance performance. The test was performed using packaging paper with a coating amount of 1.51 g/m² as an example, and its experimental test samples are shown in Figure 18.

![Figure 18. Oil resistance test of packaging paper with coating amount of 1.51 g/m². (a) is the test of level 1 oil on packaging base paper; (b) is the test of different levels of oil on the paper with coating amount of 1.51 g/m².](image)

As shown in Figure 18, the level 6 test oil had slight traces remaining on the surface of the paper, whereas the level 5 test oil had essentially no traces; thus, it could be judged that the oil prevention level of the paper was level 5.

Following the above method, the oil resistance performances of the papers with different coating amounts were tested, and the test results are shown in Table 8.
Table 8. Oil resistance of packaging paper with different coating amounts.

| Coating Amounts (g/m²) | Oil Prevention (Level) |
|------------------------|------------------------|
| 0                      | <1                     |
| 1.51                   | 5                      |
| 2.02                   | 7                      |
| 2.55                   | 9                      |
| 3.06                   | 11                     |
| 3.60                   | 12                     |
| 4.08                   | 12                     |
| 4.35                   | 12                     |

As shown in Table 8, as the coating amounts increased, the oil prevention level of the paper increased. The oil prevention level of the paper reached a maximum when the coating amount applied reached to 3.6 g/m² or more. The coatings prepared by this experiment contained a large number of non-oily groups, which would restrict the lipid and lipid molecules on the coating surface of paper. Therefore, the coatings could improve the oil resistance of paper and the coated paper could also be used in oil-resistant packaging.

3.3.8. Color Reproducibility

To meet specific requirements, colored images, graphics, or text may sometimes be printed on packaging paper. In order to test whether the coatings synthesized in this experiment had an effect on the color reproduction performance of the packaging base paper, the color gamut before and after coating was calculated and compared in this experiment.

The color gamut of a paper is the range of colors that the paper can express. The larger the paper color gamut area, the better the color reproducibility of the paper. On the contrary, the smaller the paper color gamut area, the narrower the range of color reproducibility of the paper. In this experiment, the square field color blocks of printing sample were designed with yellow (Y), magenta (M), cyan (C), and black (K), as shown in Figure 19.

![Figure 19](image)

Figure 19. Design drawing of color printing sample.

Considering Figure 19 as the original, the pattern samples were printed using papers with different coating amounts. The L* a*b* values of each sample were measured by the color densitometer. According to the measurement data, the a* b* of cyan (C), magenta (M), and yellow (Y) were used as three points to draw the color gamut diagram of each sample. The results are shown in Figure 20.
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Figure 20. Color gamut of paper samples with different coating amounts.

As can be seen from Figure 20, the color gamut of the paper became larger with as the coating amount increased. However, the color gamut area of the paper became narrower when the coating amounts were 3.60 g/m² or more. From the test data, the densities of the color blocks of the printed samples after coating were all increased. This was because that the paper surface became flatter after coating and the ink formed a relatively flat surface after drying, which could give the highest color density of the ink after reflected light. However, the coatings were too thick when the amounts of coating were too large, which would change the optical properties of the printed samples. Consequently, some colors of the ink were dispersed through refraction and projection, which would eventually make the color reproduction ability of the paper poor.

When combining the above tests with the analysis and comparison of the test results, it is indicated that the waterborne coating prepared in this experiment should be used on packaging base paper with a coating amount of 3.60 g/m², and that this could greatly improve the wettability, air resistance, oxygen resistance, oil resistance, and color reproducibility performances of the packaging base paper, and subsequently expand the range of applications for the paper.

4. Conclusions

In this paper, the experimental results showed that the performance of the waterborne coating was better when the epoxy molar ratio of ED and E51 was 1:1 (sample 4), which resulted in a viscosity that was suitable for inkjet printing and an average particle size of less than 0.2 µm. The thermal stability, adhesion, and friction resistance of the films of the coatings were also good. The experimental results showed that when the molar ratio of anhydride to hydroxyl groups in EB was 0.9:1, the waterborne coating had good water solubility, low water absorption, and water resistance performance. At the same time, the packaging base paper displayed great improvements in air resistance, oxygen resistance, oil resistance, and color reproducibility performance when the coating amount was 3.60 g/m². On the whole, the coatings synthesized in the experiment could be coated on the substrate by inkjet printing, which could meet the performance requirements of paper coating. The physical and chemical properties of the prepolymer for waterborne coatings have a decisive impact on the performance of the coating system. However, its properties related to film forming, transparency, and other parameters require further study and improvement. For example, the roundness, volume, speed, tail length, and other properties of the inkjet coating droplets would be influenced by the surface tension of the coatings, and these effects on the quality of coating should also be further studied [31,32]. In addition, a mature and stable synthesis process also needs to be confirmed through refinement experiments.
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References
1. Omobolanle, O.O.; Stella, L. Sustainable Paper-Based Packaging: A Consumer’s Perspective. Foods 2020, 11, 1035. [CrossRef]
2. Zhang, M.; Yang, L.; Deng, P. Sustainable development mode of express packaging based on green concept. Lect. Notes Electr. Eng. 2018, 477, 451–458. [CrossRef]
3. Sheng, J.; Chen, T.; Yang, R.D. A facile method to prepare fluorine-free film transfer paper with excellent oil resistance. Cellulose 2021, 28, 8601–8609. [CrossRef]
4. Sun, Z.X.; Tang, M.; Song, Q.; Yu, J.Y.; Liang, Y.; Hu, J.; Wang, J. Filtration performance of air filter paper containing kapok fibers against oil aerosols. Cellulose 2018, 25, 6719–6729. [CrossRef]
5. Petronela, N.; Mirela, R. Review on Polysaccharides Used in Coatings for Food Packaging Papers. Coatings 2020, 10, 566. [CrossRef]
6. Parvathy, P.A.; Sahoo, S.K. Hydrophobic, moisture resistant and biorenewable paper coating derived from castor oil and renewable diols. Chem. Eng. J. 2022, 433, 134470. [CrossRef]
7. Anca, P.; Leonard, M.C.; Camelia, N.; Anca, M.C.; Robert, A.; Catalina, M.T.; Goran, D.; Antonio, P.; Antonio, J.C.; Franks, K.N.; et al. Morpho-structural and chemical characterization of paper based materials with functionalized surface. Mater. Chem. Phys. 2021, 267, 124693. [CrossRef]
8. Jin, K.Y.; Tang, Y.J.; Liu, J.C.; Wang, J.M.; Ye, C.J. Nanofibrillated cellulose as coating agent for food packaging paper. Int. J. Biol. Macromol. 2021, 168, 331–338. [CrossRef]
9. Song, Z.P.; Tang, J.B.; Wang, H.L.; Guan, F.X.; Wu, Y.Y.; Liu, W.X. Water and Oil Resistance Improvement of Paper Coated with Aqueous Mixture of Hydrophilic and Hydrophobic Cross-Linked Copolymers. BioResources 2020, 15, 3147–3160. [CrossRef]
10. Li, Z.J. Research progress of paper surface finishing technology. China Print. Packag. Res. 2012, 4, 1–8.
11. Hoath, S.D.; Harlen, O.G.; Hutchings, I.M. Jetting behavior of polymer solutions in drop-on-demand inkjet printing. J. Rheol. 2012, 56, 1109–1127. [CrossRef]
12. McIlroy, C.; Harlen, O.G.; Morrison, N.F. Modelling the jetting of dilute polymer solutions in drop-on-demand inkjet printing. J. Non Newton. Fluid Mech. 2013, 201, 17–28. [CrossRef]
13. Daehwan, J.; Dongjo, K.; Jooho, M. Influence of Fluid Physical Properties on Ink-Jet Printability. Langmuir 2009, 25, 2629–2635. [CrossRef]
14. Martin, G.D.; Hoath, S.D.; Hutchings, I.M. Inkjet printing—The physics of manipulating liquid jets and drops. J. Phys. Conf. Ser. 2008, 105, 012001–012014. [CrossRef]
15. Wen, X.; Chen, H.; Lyu, C.; Liu, J. The Key Technology and Achievement of Digital Inkjet Print. Imaging Sci. Photochem. 2019, 37, 227–233. [CrossRef]
16. Chao, J.L.; Shi, R.Z.; Guo, Y.L.; Chu, F.Q.; Deng, Q. Printability of Ink for On-Demand Inkjet Printing on Different Paper. Lect. Notes Electr. Eng. 2021, 754, 334–339. [CrossRef]
17. Katherine, P.; Lisa, P.C.; Margeurite, M. Print-on-demand inkjet digital textile printing technology: An initial understanding of user types and skill levels. Int. J. Fash. Des. Technol. Educ. 2015, 8, 87–96. [CrossRef]
18. Bo, P. Digital printing technology and its application in packaging printing. Int. J. Electr. Eng. Educ. 2021, 1, 1–10. [CrossRef]
19. Lin, D.; Chen, T.; Yang, R.D.; Wang, J.; Yuan, S.C.; Xu, F.; Bao, D.; Wang, H.Y. A robust and eco-friendly waterborne anti-corrosion composite coating with multiple synergistic corrosion protections. Compos. Part B Eng. 2022, 232, 106924. [CrossRef]
20. Zhao, D.D.; Pan, M.W.; Yuan, J.F.; Liu, H.; Song, S.F.; Zhu, L. A waterborne coating for robust superamphiphobic surfaces. Prog. Org. Coat. 2020, 138, 105368. [CrossRef]
21. Yan, H.; Cai, M.; Li, W.; Fan, X.; Zhu, M. Amino-functionalized Ti3C2Tx with anti-corrosive/wear function for waterborne epoxy coating. J. Mater. Sci. Technol. 2020, 54, 144–159. [CrossRef]
22. Sheng, J.; Li, W.; Yang, R.D. A facile method to prepare fluorine-free film transfer paper with excellent oil resistance. Cellulose 2022, 29, 3147–3160. [CrossRef]
23. Yan, X.X.; Wang, L.; Qian, X.Y. Effect of Coating Process on Performance of Reversible Thermochromic Waterborne Coatings for Chinese Fir. *Coatings* 2020, 10, 223. [CrossRef]

24. Liu, S.K.; Zhang, Z.P.; Qi, Y.H. Effect of Emulsifier on the Structure and Properties of Waterborne Silicone Antifouling Coating. *Coatings* 2020, 10, 168. [CrossRef]

25. Zhao, C.C.; Zhou, M.; Yu, H.B. Interfacial combination of Ti3C2Tx MXene with waterborne epoxy anticorrosive coating. *Appl. Surf. Sci.* 2022, 572, 150894. [CrossRef]

26. Pierpaolo, M.; Giuseppe, I.; Giacomo, R.; Andrea, P. Luminescent Solar Concentrators from Waterborne Polymer Coatings. *Coatings* 2020, 10, 655. [CrossRef]

27. Yan, X.X.; Peng, W.W. Preparation of Microcapsules of Urea Formaldehyde Resin Coated Waterborne Coatings and Their Effect on Properties of Wood Crackle Coating. *Coatings* 2020, 10, 764. [CrossRef]

28. Hall, J.L.; Pérez, A.; Kynaston, E.L.; Lindsay, C.; Keddie, J.L. Effects of environmental conditions on the micro-mechanical properties of formulated waterborne coatings. *Prog. Org. Coat.* 2022, 163, 106657. [CrossRef]

29. Ai, D.; Mo, R.; Wang, H.H.; Lai, Y.B.; Jiang, X.; Zhang, X.Y. Preparation of waterborne epoxy dispersion and its application in 2K waterborne epoxy coatings. *Prog. Org. Coat.* 2019, 136, 105258. [CrossRef]

30. Zhang, Z.Z.; Chao, J.L.; Chu, F.Q. Study on the Synthesis and Property of Water-Based UV-Curable Epoxy Acrylate with Low Viscosity. *Adv. Graph. Commun.* 2016, 369, 941–947. [CrossRef]

31. Matyukhin, S.I.; Frolenkov, K.Y. Surface Tension and Adhesion Properties of Films and Coatings. *Inf. Int. Interdiscip. J.* 2017, 20, 5741–5749.

32. Huang, B.Q. Research on the Surface Tension of Water-based Ink-jet Ink. *Appl. Mech. Mater.* 2013, 262, 464–469. [CrossRef]