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Abstract: Gas-sealing coatings on coal mine roadway walls can effectively repress gas emission and are of importance to the safe operation of coal mining. In this study, the performance of coal fly ash (CFA)-based gas-sealing coatings was investigated, including the aspects of drying time, air tightness, impermeability, flame retardancy and antistatic properties. The results show that coating No. 25 with 60 g ultrafine CFA and 50 g emulsion (curing at 22 °C) had the best air tightness, with a permeability coefficient of $2.95 \times 10^{-13}$ cm$^2/(s \cdot Pa)$. The data obtained through the self-developed air tightness test device agreed well with the detection results of the gas permeameter, thus verifying the accuracy and reliability of the device. The impermeability, flame retardancy and antistatic properties of coating No. 25 conformed the requirements of voluntary national standards GB/T 23445-2009 and coal industry standard MT113-1995, respectively. The CFA-based gas-sealing coating in the pilot test reduced the gas emission intensity by 40%–50%. It could have wide applications in coal mine roadway walls.

Keywords: coal fly ash (CFA); gas-sealing coatings; air tightness; gas permeameter

1. Introduction

Most coal mines in China are moderately or highly gassy mines, and gas explosions have resulted in heavy losses to the coal industry and the lives of miners [1]. To reduce the hazards induced by gases, ventilation measures are used in the coal mining process to dilute gas concentrations in roadways (i.e., gases emitted into the air through methane ventilation) [2,3]. However, such measures give rise to serious environmental pollution problems [4]. Another measure used to prevent and control gas disasters is roadway wall blocking, that is, spraying gas-sealing coatings on roadway walls, which blocks the gasses’ leakage through roadway surfaces. Gas (also called coal bed methane) extraction processes on coal mine walls not only prevent gas emission in roadways and ensure safe and high-efficiency underground mining work in coal mines, but also elevate the gas concentration in the coal seam for the sake of extraction and utilization [5,6].

At present, the main sealing materials used to block gases include organic, inorganic, and organic–inorganic composite materials. Underground gas-sealing coatings in non-Chinese coal mines are mostly made up of organic materials, such as polyurethanes, with good sealing effect [7]. However, the extensive application of these organic materials has been restricted to a certain degree due to their high price, poor flame retardation, and possible pollution to air [8]. Inorganic sealing materials with coal fly ash (CFA) in coal mines are more common in China. Inorganic sealing materials have the advantages of being inexpensive, nontoxic, and harmless. However, they generally need to be
very thick, at more than 10 cm. Moreover, they easily crack and fall off [9,10]. Organic and inorganic composite coatings are thus a good choice. The screening of inorganic materials and flame retardants was reported in [11,12]. Their air tightness needs to be improved. Accordingly, there is an urgent need to develop gas-sealing coatings with good air tightness, a low price, and high safety and effectiveness.

Air tightness is a core performance index of gas-sealing coatings [13]. Gas permeability test methods have been developed for materials such as plastic films and rubber sheets. For example, the national standard GB/T7755-2003 [14] included an air tightness determination method and a device applied to vulcanized or thermoplastic rubber. The air tightness detection equipment developed by Shandong Jinan Labthink Technology Company can be used to determine the air tightness parameters of lamellar materials. However, this equipment is of high price and high operational cost. Zhang et al. proposed an air tightness detection method for laboratory detection of composite rubber materials. On the basis of the principle of ISO2782 [15], an air tightness test instrument was developed to realize air tightness detection for rubber materials. However, this instrument cannot obtain a pressure change during gas permeation, and it needs a combination of a hermetically sealed instrument and gas chromatography; thus, its operating procedures are relatively tedious. The mentioned air tightness test methods are not applicable for the air tightness detection of blocking materials under a simulated laboratory gas emission environment on coal walls due to the environmental complexity in underground coal mines. Therefore, a new type of air tightness detection method for gas-sealing coatings, which can simulate the underground gas emission environment in coal mines at a low price and with simple operation, must be developed.

Therefore, this study aimed to explore a kind of CFA-based gas-sealing coating with good air tightness. The influence of an additive amount of ultrafine CFA and temperature on gas-sealing coatings was investigated. The air tightness of sealing coatings was analyzed from the aspects of their internal coating structure and chemical composition. A new type of air tightness detection device made of lamellar materials was self-designed. This device can rapidly and accurately output results by combining a self-compiled software program. With low input and simple operation, this equipment is suitable for simulating the environments of underground gas emissions in coal mine walls and detecting the air tightness of gas-sealing coatings. A pilot experiment was carried out on a coal mine roadway wall, and the results proved that the CFA-based gas-sealing coating is effective and applicable.

2. Materials and Methods

2.1. Experimental Materials

The experimental materials included the following industrial products: styrene acrylic emulsion (BASF-400, BASF, Ludwigshafen, Germany), ultrafine coal fly ash (Shanxi Huatong, Taiyuan, China), and Portland cement (32.5, Taiyuan Cement Company, Taiyuan, China). Aluminum hydroxide, antimonous oxide, 70 chlorinated paraffin, zinc borate, graphite and conductive carbon black were all analytical reagents bought from Tianjin Guangfu Company (China).

2.2. Experimental Methods

The technological preparation process of the coating is shown in Figure 1. On the basis of a certain proportion, 80 g of CFA–cement and 20 g of functional additives were mixed and then added into a beaker filled with 20 or 50 g of emulsion. The procedure and steps are detailed in previous research by the authors [11].
The chemical composition of the CFA was determined using an X-ray fluorescence spectrometer (XRF, S8Tiger, Bruker, Karlsruhe, Germany); the mean size and distribution of the samples were measured using a particle size analyzer (MS3000, Malvern, Melvin City, UK); the coating microstructure was analyzed via a scanning electron microscope (SEM, JSM-6710F, JEOL, Akishima, Japan); the coating compositions after curing were analyzed using an X-ray diffractometer (XRD, D2 PHASER, Bruker, Karlsruhe, Germany).

The ignition loss of the CFA was determined according to the standard for “Fly ash used in cement and concrete” (GB/T 1596-2005) [16]. The weight of the empty porcelain crucible was denoted \( m_0 \), and then the CFA sample to be tested was 1 g and recorded as \( m_1 \). The weighed CFA sample was transferred into the crucible with a constant burned weight. The porcelain crucible was transferred into the muffle furnace and heated at 950 °C for 15 min. The porcelain crucible was then taken out and put into a dryer, cooled to room temperature, and then weighed. When the porcelain crucible was repeatedly burned until the difference in weight between two consecutive times was less than 0.0005 g, it achieved a constant weight and was recorded as \( m_2 \). Then, the burning loss (\( X \)) of the CFA sample to be tested was calculated according to Equation (1):

\[
X = \frac{m_1 + m_0 - m_2}{m_1} \times 100\% \quad (1)
\]

where \( m_0 \) is the mass of the empty porcelain crucible; \( m_1 \) refers to the mass of the sample to be tested; \( m_2 \) is the total mass of the constant weight.

The self-designed and self-prepared air tightness detection device was used to perform air tightness detection on a series of coating specimens. The packaging safety detection center of Shandong Jinan Labthink Technology Company was entrusted to perform synchronous detection using a differential pressure gas permeameter (VAC-V2, Languang, Jinan, China), followed by a comparative validation.

The flame retardancy and static electricity resistance of the coatings were measured with reference to the coal industry standards of the People’s Republic of China—“General test methods and judgment rules for flame retardant and antistatic properties of polymer products used in coal mines” (MT113-1995) [17]. An electric waterproof roll material impermeability tester (DTS-6, Gangyuan, Tianjin, China) was used to test the impermeability of the cured coating. The 0.3-MPa, 30-min impervious index should accord with GB/T 23445-2009 [18]—“polymer cement waterproof coating”.

2.3. Coating Air Tightness Detection Method

A practical air tightness detection device was invented by the authors’ research group [19]. The air tightness detection device shown in Figure 2 could approximately simulate the natural conditions of underground gas leakage. To examine the air tightness of the sealing coating, air was used to replace gas (CH₄) for experiment safety. The main body of the device included an air tightness test barrel, a gas cylinder and a U-shaped tube differential pressure gauge. The air tightness test barrel was filled with coal particles to simulate the underground conditions of coal mines.
The air tightness detection steps of the coating specimens included sample fixation, detection, and calculation. The barrel of the detection device was filled with approximately 1–5 mm coal particles. The surface of the coal particles was kept flat to simulate the natural conditions of a coal mine. A yellow plastic washer was used to prevent air leakage and protect the coating from crushing and rupture. The prepared and dried coating specimen was cut into a circle and then placed on the coal particles. The size of the coating sheet should be slightly larger than the cross-sectional area of the test barrel to prevent air leakage at the edge. A metal plate reserved with an inherent opening area (that is, the air permeation area of the coating sheet) was placed above the coating specimen. The configured flange was covered by the metal plate, such that they could fit well with each other. The flange was then tightly sealed with the barrel using bolts and nuts to prevent air leakage.

The air cylinder and inlet valve were opened, the barrel was rapidly inflated with air until a certain pressure intensity was reached, and then the air cylinder and inlet valve were closed. The gas filling the gaps of coal particles in the barrel was permeated via the cured coating toward the flexible pipe connected to the flange. This approach was performed to simulate the permeation of underground gases via the coating toward the roadway after discharge from the coal wall. After a while, the gas permeability became stable, and the liquid levels in the U-shaped tube differential pressure gauge when the permeation started and when it became stable were recorded. Multiple experimental samples were obtained by measuring multiple times, according to which the gas permeability coefficient of the coal wall coating was calculated.

For easy understanding and calculation, the air tightness detection device was divided into different sections (Figure 3), including the permeation chamber (Zone 0), the left tube of the U-shaped tube (Zone 1) and the right tube of the U-shaped tube (Zone 2).

![Figure 2. The self-designed and self-made detection device for air tightness of sealing coating.](image)

![Figure 3. Schematic diagram of three sections of air tightness detection device related to calculation permeability coefficient of coating.](image)

The calculation method for the permeability coefficient of the coating is as follows. For Zone 2, the air volume and air pressure at the beginning are:

\[ V_2 = H A \]  
\[ P_2 = P_1 \]
After detecting $t$ time, the air volume and air pressure of Zone 2 become:

$$V'_2 = (H - \Delta H)A$$  \hspace{1cm} (4)

$$P'_2 = \frac{P_2 V_2}{V'_2}$$  \hspace{1cm} (5)

where $V_2$ and $P_2$ are the air volume and air pressure at the beginning of the right tube of the U-shaped tube, m$^3$ and Pa; $P_1$ is air pressure at the beginning of the left tube of the U-shaped tube, Pa; $V'_2$ and $P'_2$ are the air volume and air pressure of the right tube of the U-shaped tube after detecting $t$ time, m$^3$ and Pa; $H$ is the gas column height of the right tube of the U-shaped tube, m; $A$ is the cross-sectional area of the U-shaped tube, m$^2$; $\Delta H$ is the descent height of the liquid level in the left tube of the U-shaped tube, m.

For Zone 1, the air volume and air pressure after detecting $t$ time become:

$$V'_1 = V_1 + \Delta H A$$  \hspace{1cm} (6)

$$P'_1 = P'_2 + 2\rho_wg\Delta H$$  \hspace{1cm} (7)

where $V_1$ is the air volume at the beginning of the left tube of the U-shaped tube, m$^3$; $V'_1$ and $P'_1$ are the air volume and air pressure of the left tube of the U-shaped tube after detecting $t$ time, m$^3$ and Pa; $\rho_w$ is the water density, kg/m$^3$; $g$ is the gravitational acceleration, 9.81 m/s$^2$.

From the equation of state of ideal gas (Equation (8)), the mole number and molecular number of permeation-increased air in Zone 1 after $t$ time are:

$$PV = nRT$$  \hspace{1cm} (8)

$$\Delta n = n' - n = \frac{P'_1 V'_1 - P_1 V_1}{RT}$$  \hspace{1cm} (9)

$$N = \Delta n N_A$$  \hspace{1cm} (10)

where $n$ and $n'$ are the mole numbers of Zone 1 before and after detecting, mol; $\Delta n$ is the mole number of permeation-increased air, mol; $R$ is the molar gas constant, 8.31 J/(mol·K); $T$ is the atmospheric temperature, K; $N$ is the molecular number of permeation-increased air; $N_A$ is the Avogadro constant, $6.02 \times 10^{23}$ mol$^{-1}$.

The number of moles in the permeation chamber (Zone 0) decreased, so the air pressure decreased. The air pressure drop and air pressure in zone 0 are:

$$\Delta P = \frac{\Delta nRT}{V_0}$$  \hspace{1cm} (11)

$$P'_0 = P_0 - \Delta P$$  \hspace{1cm} (12)

where $\Delta P$ is the air pressure drop in the permeation chamber, Pa; $P_0$ and $P'_0$ are the air pressures of Zone 0 before and after detecting, Pa; $V_0$ is the air volume of the permeation chamber, m$^3$.

The average pressure difference ($\Delta P_{\text{mean}}$) during the test is:

$$\Delta P_{\text{mean}} = \frac{(P_0 - P_1) + (P'_0 - P'_1)}{2}$$  \hspace{1cm} (13)

The air permeability coefficient of the coating is obtained:

$$k = \frac{\Delta n N_A d}{\Delta P_{\text{mean}} l S}$$  \hspace{1cm} (14)
where $k$ is the permeability coefficient under this temperature, (Pa·m·s)$^{-1}$; $p$ is another form of permeability coefficient after the transformation of the unit, cm$^2$/(s·Pa); $d$ is the thickness of the coating specimen, m; $t$ is the test time, s; $S$ is the gas permeation area of the coating specimen, m$^2$; $M_{air}$ is the air molar mass, g/mol; $\rho_{air}$ is the air density, kg/m$^3$.

The liquid levels $\Delta H$ in the U-shaped tube differential pressure gauge before and after permeation and other related parameters were inputted into the self-designed Excel calculation table (Table S1. Calculation table of permeability coefficient), while the air permeability coefficient of the coating was calculated automatically. It provided a reference for the air tightness evaluation of the coal wall coating under an underground gas emission environment from roadway walls in coal mines.

3. Results and Discussion

3.1. Analysis of Ultrafine CFA

The results of the XRF analysis (Table 1) showed that the main components of the ultrafine CFA were SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$, accounting for more than 86% of the total. The SEM image of the ultrafine CFA (Figure 4a) showed that most of the CFA particles were spherical, with a complete particle shape and a smooth surface. The particle size concentration of the CFA was almost within 10 μm (Figure 4b) and the average particle size was 2.83 μm, classifying it as ultrafine powder (1.3–25 μm). The CFA's loss on ignition was 7.2%, meeting the class II standard (<8%) of the national standard GB/T 1596-2005 [16]—"Fly ash used in cement and concrete". Thus, this type of filler was deemed suitable for coatings.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>SO$_3$</th>
<th>TiO$_2$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>49.48</td>
<td>30.66</td>
<td>6.26</td>
<td>3.87</td>
<td>0.96</td>
<td>0.95</td>
<td>1.03</td>
<td>0.6</td>
<td>6.19</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition analysis of ultrafine CFA.

![Figure 4](image-url) Analysis of ultrafine coal fly ash (CFA): (a) SEM image; (b) particle size analysis.

The utilization of fly ash as a filler for coatings is a topic dealt with by many authors all over the world [20]. CFA has good physical and chemical advantages. The pore structure of porous particles, such as the residual carbon in CFA, is broken in the superfine process, and thus water demand in the coating preparation process is reduced. The gap created in the drying process can be avoided. Most CFA particles are spherical, and they have a favorable morphology and microaggregate effects. In addition, the finer the CFA particle, the better the pozzolanic effect (active effect). The active SiO$_2$ and Al$_2$O$_3$ react with the basic substance of the generated cement to improve the adhesion of coatings.
3.2. The Apparent Performance of Coatings

The most basic performance measure of a coating is that it does not crack after curing. The drying time of the coating, including surface drying time and real drying time, is an important construction performance index. The drying time of the coating is affected by different environmental conditions. In this study, the ratio of emulsion to powder, the ambient temperature of different coatings, and the added amount of different powder particles were investigated. The obtained coating characteristics are shown in Table 2.

**Table 2.** Effect of different factors on apparent performance of coatings. (Factors: ratio of emulsion to powder, temperature, dosage of CFA).

<table>
<thead>
<tr>
<th>Formulation and Factors</th>
<th>The Apparent Performance of Coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFA/g</td>
<td>0 10 20 30 40 50 60 70 80</td>
</tr>
<tr>
<td>Cement/g</td>
<td>80 70 60 50 40 30 20 10 0</td>
</tr>
<tr>
<td>Antistatic agent</td>
<td></td>
</tr>
<tr>
<td>Flame retardants</td>
<td>3 g graphite, 2 g conductive black</td>
</tr>
<tr>
<td></td>
<td>5 g chlorosane, 3 g aluminum hydroxide,</td>
</tr>
<tr>
<td></td>
<td>4 g zinc borate, 3 g antimonous oxide</td>
</tr>
<tr>
<td>~12 °C</td>
<td></td>
</tr>
<tr>
<td>Emulsion/g</td>
<td>No. 1 No. 2 No. 3 No. 4 No. 5</td>
</tr>
<tr>
<td>Surface drying time/min</td>
<td>←20 g →</td>
</tr>
<tr>
<td>Drying time/h</td>
<td>150 150 150 150 150 150 160 160 160</td>
</tr>
<tr>
<td>Apparent performance of coating samples</td>
<td></td>
</tr>
</tbody>
</table>

| No. 6 No. 7 No. 8 No. 9 |

~12 °C
| Emulsion/g | No. 10 No. 11 No. 12 No. 13 No. 14 No. 15 No. 16 No. 17 No. 18 |
| Surface drying time/min | ←50 g → |
| Drying time/h           | 30 32 30 30 31 33 30 34 34 |
| Apparent performance of coating samples |

~12 °C
| No. 19 No. 20 No. 21 No. 22 No. 23 No. 24 No. 25 No. 26 No. 27 |
| Emulsion/g | ←50 g → |
| Surface drying time/min | 8 8 8 9 9 10 10 11 13 |
| Drying time/h           | 6 6 6 6 6.5 7 7 7 7.5 |
| Apparent performance of coating samples |

When the mass ratio of emulsion to powder was 0.2 (20:100 g), the amount of water required in the coating preparation process was between 60 and 70 g. This was not conducive to the formation and drying of the coating at the low temperature of 12 °C. In addition, more than 150 min was needed to achieve surface drying at such a low temperature, resulting in the deposition of powder particles and uneven emulsion distribution. Thus, almost all samples at 12 °C (No. 1–9) cracked.

When the ratio of emulsion to powder increased to 0.5, the water demand decreased with the increase in emulsion. The adhesive states of this series of coatings (No. 10–18) were better, and drying times were significantly reduced. The apparent performance of these coatings was greatly improved...
after drying, except that the surface of No. 17–18 had obvious cracks and No. 10–11 had some scratches. The rest of the coating surfaces (No. 12–16) were smooth and intact, but some coating surfaces had an obvious emulsion halo. This means that the emulsion dispersion in these coatings was not very good.

When the mass ratio of emulsion to powder was 1:2 (50:100 g) and the temperature was 22 °C, the drying times of all coatings (No. 19–27) with different additive amounts of CFA decreased. Surface drying and real drying were achieved only within 8–13 min and 6–7.5 h, respectively. As shown in Table 2, the coating specimens that contained pure cement (No. 19) had scratches but no cracks. The appearances of coating specimens No. 20–25 containing 10–60 g CFA were uniform and flat. As the additive amount of CFA continued to increase to 70 g and 80 g, obvious cracks appeared on coating specimens No. 26–27, without the most fundamental properties of sealing coatings. Thus, the air tightness test was conducted only for coating specimens No. 19–25.

3.3. Air Tightness Detection of Coating Specimens with Different Additive Amounts of CFA

The air tightness detection of coating specimens No. 19–25 (with 0–60 g CFA) was implemented using the self-developed air tightness detection device. On the basis of the thickness \( d \) of the coating specimen, permeation balance time \( t \), and descent height \( \Delta H \) of the liquid level in the left tube of the U-shaped tube differential pressure gauge, the air permeability coefficients of coating specimens could be obtained using the self-designed Excel calculation table (Table S1. Calculation table of permeability coefficient). Taking coating specimen No. 25 as an example, permeation became stable when \( t \) was 900 s, \( \Delta H \) was 0.24 m, and the coating thickness was 0.0028 m. The air permeability coefficient \( p \) of this coating was obtained as \( 2.95 \times 10^{-13} \text{ cm}^2/(\text{s·Pa}) \).

To verify the accuracy of the air tightness data obtained through this device, the packaging safety detection center of Shandong Jinan Labthink Technology Company was entrusted to perform the synchronous detection of air tightness of the series of coating specimens using a differential pressure gas permeameter. The air tightness data obtained through the two test methods are shown in Figure 5, where the blue dots represent the experimental data obtained through the device in this study, and the red triangles represent the detection data obtained through the gas permeameter. The two groups of data basically accorded with each other, and overall laws could be clearly observed. As the additive amount of CFA (0–60 g, No. 19–25) gradually increased, the permeability coefficient of the corresponding coating specimen was gradually reduced. That is, air tightness was gradually improved, which indicated that CFA contributed to the enhancement of the air tightness of the coating. The permeability coefficient of the coating specimen containing 60% CFA (No. 25) was \( 2.95 \times 10^{-13} \text{ cm}^2/(\text{s·Pa}) \). After this coating was sprayed on the underground wall of the coal mine, the gases before and after spraying were monitored [21]. It was possible to reduce the gas emission by over 60%, which is higher than the 40% mentioned in the related literature [22]. Thus, coating specimen No. 25 would block the gas flow passage in the coal wall, increase the mass transfer resistance in the roadway wall, and repress the mass transfer process of gases to effectively prevent gas emission. The detection data of the gas permeameter verified the accuracy and reliability of the device and its test method. In comparison with the precise gas permeameter, this device reduced the detection expense to a great degree and with excellent flexibility, and it could simulate the environment of coatings to refit the test barrel, thereby improving the applicability and reasonability of the test device.
Thus, a good pore structure is of great importance to the gas-sealing performance of materials. In this study, the microstructures of specimens No. 19 and No. 25 were analyzed via SEM, as shown in Figure 6a,b. The pores in specimen No. 19 were large with obvious cracks, whereas coating specimen No. 25 had uniform and compact internal structures with only a few micropores. The ultrafine CFA formed a reasonable particle size grading in the coating, which exerted a secondary sealing effect, and prevented cracks from forming in the coating. Therefore, as a type of powder filler, the CFA had a dual function, not only exerting morphological and microaggregate effects but also effectively improving the pozzolanic reaction intensity, optimizing internal structures of coatings, and practically improving their compactness. Hence, the organic and inorganic particles in the coating realized effective gelatinization bonding, thus forming a compact structure that prevents the formation of cracks and pores and improves air tightness.

![Figure 5](image.png)

**Figure 5.** Permeability coefficients of coating specimens No. 19–25 obtained through self-developed device and through gas permeameter.

The internal pore structure of a coating material will have a direct influence on its gas permeability. Thus, a good pore structure is of great importance to the gas-sealing performance of materials. In this study, the microstructures of specimens No. 19 and No. 25 were analyzed via SEM, as shown in Figure 6a,b. The pores in specimen No. 19 were large with obvious cracks, whereas coating specimen No. 25 had uniform and compact internal structures with only a few micropores. The ultrafine CFA consisted of almost spherical particles with smooth surfaces and regular shapes, and its average particle size was about 2–3 μm, whereas that of ordinary cement was approximately 15–20 μm; thus, the two formed a reasonable particle size grading in the coating, which effectively prevented pore formation inside the coating. In addition, the CFA effectively promoted the formation of hydrate gelatinization products due to its large specific surface area and high pozzolanic activity. New hydrate gelatinization substances were generated after the coating was cured. It further filled the pores between particles, exerted a secondary sealing effect, and prevented cracks from forming in the coating. Therefore, as a type of powder filler, the CFA had a dual function, not only exerting morphological and microaggregate effects but also effectively improving the pozzolanic reaction intensity, optimizing internal structures of coatings, and practically improving their compactness. Hence, the organic and inorganic particles in the coating realized effective gelatinization bonding, thus forming a compact structure that prevents the formation of cracks and pores and improves air tightness.

![Figure 6](image.png)

**Figure 6.** Comparison of SEM graphs of coating specimens (a) No. 19 and (b) No. 25, and (c) XRD patterns of different coating specimens.

XRD analysis was performed to further explore the influence mechanism of CFA on the coatings’ air tightness, as shown in Figure 6c. Calcium silicate hydrate gelatinization products appeared in
coating specimens No. 19 and 25, and water-containing aluminosilicate was also generated in the latter. Formed by Al, Ca, H, O, and Si, this newly generated substance was a type of Ca–Al–Si–O macromolecular hydration product with a dense matrix [23]. Thus, the gelatinization cohesiveness of this coating was high, with an improved air tightness.

3.4. Impermeability Test of Coatings

According to the GB/T 23445-2009 standard of “Polymer cement waterproof coating”, the impermeability of coatings No. 19 and 25 were tested using an electric impermeability tester. Both met the impermeability requirements at 0.3 MPa in 30 min. However, after the completion of the permeability experiment, the partial magnification image of specimen No. 19 (Figure 7a) showed a rough and porous surface, whereas specimen No. 25 (Figure 7b) had a smooth and fine surface. Thus, specimen No. 25 had a better sealing effect.

![Impermeability test of (a) coating No. 19 and (b) coating No. 25.](image)

**Figure 7.** Impermeability test of (a) coating No. 19 and (b) coating No. 25.

3.5. Flame-Retardant and Static Electricity Test

The gas-sealing materials used in underground coal mines must have a good flame-retardant performance. In organic–inorganic polymer coatings, the emulsion content is the main factor affecting the flame retardancy of the coatings. According to the requirement of MT113-1995, the flame retardancy of coatings No. 19 and 25 were tested by the alcohol lamp method. The distance between the test piece and the alcohol lamp was 19 mm. After burning for 90 s, the alcohol lamp was removed and the data shown in Table 3 were recorded. The flame retardancy of both coatings met the requirements of the coal industry standard MT113-1995. However, specimen No. 25 had a shorter flame extension length. In addition, a bulge appeared on specimen No. 19 after the burning test, which might be because the emulsion was not dispersed as well in the coating and therefore the emulsion expanded during the burning process. As for specimen No. 25, it showed a burn mark and no deformation. Thus, coating No. 25 had a better flame-retardant performance and was more suitable for use in coal mines to ensure safety.
Table 3. Flame retardancy tests of coating specimens No. 19 and 25.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Flame Retardancy Tests</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Burning Time with Fire/s</td>
<td>Burning Time without Fire/s</td>
</tr>
<tr>
<td>No. 19</td>
<td>2</td>
<td>9.8</td>
</tr>
<tr>
<td>No. 25</td>
<td>2.1</td>
<td>8</td>
</tr>
<tr>
<td>MT113</td>
<td>≤6</td>
<td>≤20</td>
</tr>
</tbody>
</table>

Static electricity is a great threat to underground safety and mining work. Fires and explosions caused by static electricity often happen in underground coal mines. According to the requirements (<3 × 10^8 Ω) in MT113-1995, specimens No. 19 and 25 were tested for upper and lower surface resistance at a nominal constant load voltage of 500 V, as shown in Table 4. The upper and lower surface resistance of specimen No. 19 were 7.8 × 10^4 and 3.2 × 10^4 Ω, respectively, and those of specimen No. 25 were 6.1 × 10^3 and 1.3 × 10^4 Ω, respectively. Thus, they were all well qualified. This showed that No. 25 had excellent antistatic properties and met the requirements of underground materials in coal mines.

Table 4. Antistatic resistance properties of coating specimens No. 19 and 25.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Antistatic Resistance Tests</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specimen Pictures</td>
<td>Upper Surface Resistance/Ω</td>
</tr>
<tr>
<td>No. 19</td>
<td>7.8 × 10^4</td>
<td>3.2 × 10^4</td>
</tr>
<tr>
<td>No. 25</td>
<td>6.1 × 10^3</td>
<td>1.3 × 10^4</td>
</tr>
</tbody>
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3.6. Application of CFA-Based Gas-Sealing Coating

In order to investigate the application of gas-sealing coating No. 25, pilot spraying tests were carried out on an underground tunnel wall in Shanxi Huashengrong coal mine, China. A screw grouting pump for coal mines (LZBQ-2/1.4, Gu’ante, Binzhou, China) was used to stir the materials of formula No. 25. Then, the spray gun was turned on, and the tunnel’s side and roof were sprayed in the wind direction of the roadway. Detection points were set up in the roadway to detect the gas volume fraction before and after spraying and to evaluate the sealing effect of the solidified sealing materials [24].

Figure 8 shows images of the spraying process and the coal mine wall with the coating, and compares the gas emission rate before and after spraying. There was a reduction of about 40%–50% in the gas emission rate after spraying. The cured gas-sealing coating solidified on the coal wall surface and formed a dense protective layer. It reduced the permeability coefficient around the roadway and delayed the gas migration to the roadway space. In addition, the gas emission rate decreased as the distance from the fully machined mining face increased. This is because the longer the distance from the fully mechanized working face, the longer the coal wall exposure time, and the gas emission rate gradually decreases. In summary, the results showed that the gas-sealing coating based on CFA with a dense structure could seal small cracks in the surface of the coal mine wall, which effectively delayed gas gushing.

![Figure 8](image_url)

**Figure 8.** Pilot spraying tests on the underground tunnel wall. (a) Spraying process picture; (b) coal wall after spraying coating; (c) gas emission rate before and after spraying.

4. Conclusions

Gas-sealing coatings are important for underground coal mines. CFA-based gas-sealing coatings were explored in this study. A pilot test was carried out to verify the application of this coating. The addition of CFA in the coating generated new hydrate gelatinization substances, which optimized the internal structures and improved the compactness of the coating. The appropriate dosage of CFA was 60 g with 20 g of cement and 50 g of emulsion. This coating, No. 25, had the best air tightness with a permeability coefficient of $2.95 \times 10^{-13}$ cm$^2$/(s·Pa). This self-designed air tightness detection device is characterized by its low equipment input, low detection cost, simple operation, and reliable measured data. It is suitable for laboratory simulation tests of gas-sealing coatings for underground roadway walls in coal mines. Coating No. 25 met the impermeability requirement at 0.3 MPa in 30 min (GB/T 23445-2009). Both the flame retardancy and antistatic properties of this coating met the requirements of underground materials in coal mines (MT113-1995). The pilot application test proved that this CFA-based gas-sealing coating hindered gas emission from the coal wall to the roadway, and the gas emission intensity was reduced by 40%–50%. It is thus beneficial to underground safety and mining work. In addition, our CFA-based gas-sealing coating is inexpensive. It has good prospects for industrial applications in coal mine roadways.
Supplementary Materials: The following are available online at http://www.mdpi.com/2079-6412/10/9/863/s1, Table S1: Calculation table of permeability coefficient.

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