Study of inorganic powders used for preparation of waterproof coating to coal mine roadways

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Abstract: The new coatings based on styrene-acrylate copolymer with solid powder additives were prepared. Solid additives were one of three types of adhesives (white cement, Portland cement, and alumina cement) and one of four inorganic fillers (quartz powder, talcum powder, calcium carbonate powder, and fly ash). The coatings were tested by determination of surface drying time, hard drying time, tensile strength, and elongation at break. The ratio of water absorption after 7 days was also measured. The results showed that white cement was the best inorganic adhesive with optimal amount of 40–50 wt % in solid powder part. Quartz powder served as better inorganic filler compared with talcum powder and calcium carbonate powder. Fly ash could also be used as good inorganic filler but in amount lower than 10 wt %. Thus prepared coatings satisfy requirements for class III according to GB/T 23445-2009 standard.

Keywords: waterproof coating, coal mine roadway, adhesive, inorganic filler.

Badanie proszków nieorganicznych stosowanych do przygotowania wodoodpornych powłok jezdni w kopalniach węgla

Streszczenie: Przygotowano nowe powłoki na bazie kopolimeru styren-akrylan z dodatkiem proszków stałych. Dodatki stałe stanowiły jeden z trzech rodzajów spoiwa (cement biały, cement portlandzki i cement glinowy) oraz jeden z czterech napełniaczy nieorganicznych (kwarc w postaci proszku, talk, sproszkowany węglan wapnia oraz popiół lotny). Powłoki badano przez określanie czasu suszenia powierzchni, czasu całkowitego suszenia, wytrzymałości na rozciąganie i wydłużenia przy zerwaniu. Wyznaczano również współczynnik absorpcji wody po 7 dniach. Badania wykazały, że najlepszym spoiwem nieorganicznym jest cement biały w ilości 40–50 % mas. Proszek kwarcowy jest lepszym napełniaczem nieorganicznym niż talk lub sproszkowany węglan wapnia. Stwierdzono również, że dobrym napełniaczem nieorganicznym są popioły lotne, ale mogą być stosowane tylko w ilości mniejszej niż 10 % mas. Tak przygotowane powłoki spełniają wymagania klasy III według normy GB/T 23445-2009.

Słowa kluczowe: powłoka wodoodporna, jezdnia w kopalni węgla, spoiwo, napełniacz nieorganiczny.

Gas explosion disasters are the major safety concerns in coal mining in China due to poor natural conditions and complex geological and hydrogeological conditions of coal mines [1, 2]. Some state-owned large coal mines use spray-applied functional materials of high polymer content to prevent gas disasters and water seepage [3, 4]. After spraying, these functional materials solidify and form a waterproof layer on the bare coal-rock masses. The materials adhere tightly to the coal rocks with high elasticity and sealing performance. Thus the gas leakage through coal-rock masses can be prevented and the gas concentration can be reduced. Moreover, the materials also have waterproofing effect and reduce the seepage and leakage through the walls [5].

Polyurethanes and urea-formaldehyde resins and other high molecular foaming materials are the most commonly used waterproof materials for underground coal mines. But these materials are expensive and have poor flame retardation. Spraying of these substances involves emission of pungent and toxic gases, causing damage to the environment and the health of the workers [6, 7]. It is very urgent to develop cheaper and environmental friendly waterproof materials with excellent fire retardation and resistance to static electricity for coal mines. Polymer cements such as polyurethane (PUR), epoxy-PUR, and polyacrylate cement display good adhesiveness, air tightness, flexibility, weatherability, and waterproof performance [8, 9]. Moreover, the use of cement and inorganic fillers greatly reduces the cost. These features

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make such cement materials highly suitable as a waterproof material in underground coal mines [10].

Different types of cement may be used as inorganic adhesives in polymer cements with varying physical and chemical performance. The choice of cement usually depends on such parameters as: fineness, consistency, curing time, stability, strength, and hydration heat. These parameters have great impact on the tensile strength, elongation at break, and bonding strength of the material [11, 12]. Inorganic fillers used in waterproof coatings include fly ash, lime, quartz sand, light calcium carbonate, heavy calcium carbonate, talcum powder, and wollastonite. It is a reuse of wastes and the cost is reduced by adding these inorganic fillers. Moreover, adding an appropriate amount of the inorganic fillers can make the solidified coating denser. However, the added amount of the inorganic fillers should be properly controlled, otherwise the performance of the material can suffer [13].

The aim of this study was to develop a waterproof coating used in coal mine roadways by selection of inorganic adhesive and inorganic filler to polymer base of the coating. Three types of adhesives were investigated, namely, white cement, Portland cement, and alumina cement. As inorganic fillers quartz powder, talcum powder, calcium carbonate powder, and fly ash were studied. The properties of various prepared waterproof coatings were determined and compared in order to choose the best type of adhesive and filler.

EXPERIMENTAL PART

Materials

Acronal® CN 18 ap emulsion with styrene-acrylate copolymer as the main component (industrial product, BASF) was used. Several types of adhesives and fillers were selected:

– 425# white cement (industrial product, Hebei Tianshi Shuangxiong Special Cement Co. Ltd.);

– 625# high alumina cement (industrial product, Shanxi Zhongchang Ruineng Refractory Materials Co. Ltd.);

– 425# Portland cement (industrial product, Taiyuan Lionhead Cement Co. Ltd.);

– quartz powder (industrial product);

– talcum powder (industrial product);

– calcium carbonate powder (industrial product);

– fly ash (wet fly ash, Lu'an Group).

Preparation of samples

Acronal® emulsion was mixed with water and placed in the SFJ-400 laboratory dissolver (Shanghai Environmental Engineering Technology Co. Ltd.). The amount of water was selected depending on the kind and amount of solid particles added so as to ensure that no cracks occur in the obtained coatings. The mass ratio of the emulsion to a solid powder (cement and other filler) was 0.5:1. The mixing of emulsion lasted for about 1 min and the particles were evenly dispersed in the emulsion. Then the properly mixed cement and inorganic filler were slowly added to the emulsion, and the mixing continued for 5 min at 600 rpm. After 3 min the mixture was poured into the mold frame (150 x 150 x 3 mm). To make it easier for demolding, Vaseline was applied to the surface of the mold before coating. The surface of the coating was scrapped with a scraper, and the coating was cured under standard conditions for 7 days [14].

Testing methods

GB/T 16777-1997 standard was applied for detection of surface drying time, hard drying time, tensile strength, and elongation at break. The ratio of water absorption after 7 days was determined according to US ASTM-D471 standard. Each experiment was repeated three times and the average value was taken as experimental result.

RESULTS AND DISCUSSIONS

The coating in this research is treated as a protection against water and gas permeation in coal mine roadways. The cement material easily cracks, and the polymer has insufficient mechanical properties. So a kind of low cost polymer modified cement was investigated in order to provide better mechanical properties and waterproofness.

Effect of inorganic adhesive on coating performance

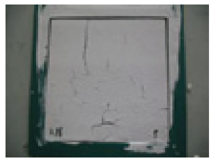
In this part of study the coatings were prepared with addition of white cement, Portland cement, or high alumina cement as the inorganic adhesive and quartz powder as a filler. The mechanical performance and the ratio of water absorption of the coating were determined. The results are shown in Table 1.

It can be seen from Table 1 that the elongation at break of the specimen prepared with white cement satisfied the standard for class II in GB/T 23445-2009 (higher than 80 %), while that of the specimens prepared with Portland cement and high alumina cement satisfied the stan-

T a b l e 1. The mechanical properties of coatings with various types of cements

Property	Type of cement additive		
	white cement	Portland cement	alumina cement
Elongation at break, %	80	60	70
Tensile strength MPa	2.60	2.14	2.08
7 days water absorption ratio, %	4.5	5.1	6.4

T a b l e 2. The properties of coatings with various types of inorganic fillers

Property	Type of cement additive		
	quartz powder	talcum powder	calcium carbonate powder
Coating photos			
Elongation at break, %	72	40	10
Tensile strength, MPa	2.97	2.96	2.6
7 days water absorption ratio, %	3.1	3.0	5.0

dard for class III (higher than 30 %). The tensile strength of all specimens was above 2.0 MPa, thus satisfying the standard for any class in GB/T 23445-2009. Since the coating prepared with white cement had lower ratio of water absorption and the best comprehensive performance, white cement is preferred to other types of cement. Moreover, to white cement can be added various pigments to give different colors. However, white cement is more expensive than Portland cement, so Portland cement is also a good choice if there is not requirement on color.

Effect of inorganic filler type on coating performance

Quartz powder, talcum powder, and calcium carbonate powder are commonly used as fillers in waterproof coatings in underground coal mines and these were used in our study. The mass ratio of emulsion to water and to solid powder (cement and other filler) was 0.5:0.12:1. As far as the solid powder is concerned, the mass percentage of Portland cement was 40 wt % and the percentage of one of the three inorganic fillers (quartz powder, talcum powder, or calcium carbonate powder) was 60 wt %. The surface morphology, tensile strength, elongation at break, and water absorption ratio after 7 days were investigated.

As shown in Table 2, the surface of the coating prepared with quartz powder was even without cracks. The coating prepared with talcum powder had small cracks, and that prepared with calcium carbonate powder had large cracks. The polymer emulsion and cement envelope the inorganic filler particles during preparation. Quartz powder has higher bulk density and the total surface area of quartz powder is the smallest for the same mass of inorganic filler. Therefore, the quartz powder particles were best enveloped by polymer emulsion and cement when the same mass percentage of filler was used. In contrast, the internal structure of the coating is loose and less dense due to poor enveloping of talcum powder and calcium carbonate powder particles. This explains the cracking of the coatings prepared with talcum powder and calcium carbonate powder.

It can be seen from Table 2 that the tensile strength of all specimens satisfied the standard for class I to III according to GB/T 23445-2009 (standard for class I ≥ 1.2 MPa, standard for class II and III ≥ 1.8 MPa). The elongation at break for the specimens prepared with quartz powder and talcum powder satisfied the standard for class III (≥ 30 %). However, the elongation at break for the specimen prepared with calcium carbonate powder did not satisfy the standard. The ratios of water absorption for

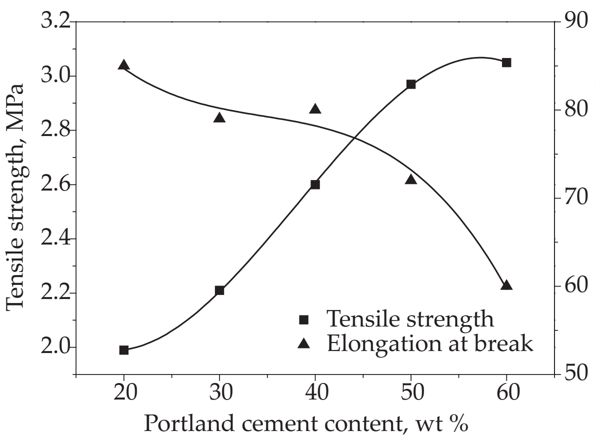


Fig. 1. Influence of Portland cement dosage on the tensile strength of prepared coatings

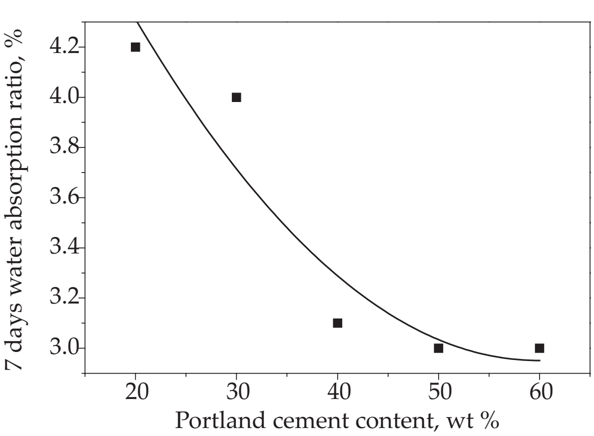
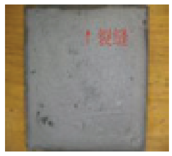


Fig. 2. Influence of Portland cement dosage on the 7 days water absorption ratio for prepared coatings

T a b l e 3. Influence of fly ash dosage on the apparent property of prepared coatings

Amount of coating component					Surface drying time, min	Hard drying time, h	Coating photos
fly ash g	quartz powder, g	white cement g	emulsion g	water dosage cm^3			
0	60	40	50	12	25	7.5	
10	50	40	50	15	30	8	
20	40	40	50	21	30	8	
30	30	40	50	24	30	8	
40	20	40	50	35	50	8	
50	10	40	50	45	60	9	

coatings prepared with talcum powder and quartz powder were lower, being only about 3 %. Therefore, the coating prepared with quartz powder had the best performance. This is because quartz particles have the smallest specific surface area and they can be effectively enveloped by polymer network and cement hydrate. Thus the coating has less defects, higher tensile strength and elongation at break and lower ratio of water absorption.

Effect of cement content on coating performance

The coating specimens were prepared using emulsion to solid powder mass ratio of 0.5:1. Among the solid powder, the percentage of Portland cement increased in the range of 20–60 wt % and the content of quartz powder decreased, to give the total of 100 wt %. The effect of cement content on tensile strength, elongation at break, and the ratio of water absorption after 7 days was discussed. The results are shown in Figs. 1 and 2.

It can be seen from Fig. 1 that as the cement content increased, the tensile strength of the coating increased and the elongation at break decreased. Cement hydrate would be produced in the polymer coating, and as the cement content increased, more hydrates were formed, being calcium silicate hydrate (CSH) and calcium hydroxide [15]. The geometrical complex substances resulted in higher density and tensile strength of the material. However, the addition of cement would also reduce the free stretching of large polymer chain, leading to lower flexibility of the organic matter network and the reduction in elongation at break of the coating.

As it was shown in Fig. 2, the ratio of water absorption decreased as the cement content in the coating increased. Higher cement content allows the cement hydrate to better fill the pores in the organic polymer network. Through solidification, the cement hydrate would further grow, thus filling the pores of the coating and making the coating denser. As a result, 7 days water absorption ratio of the coating decreased with increase of Portland cement content.

The above results indicated that the proper dosage of cement was about 40–50 wt %, corresponding to the bet-

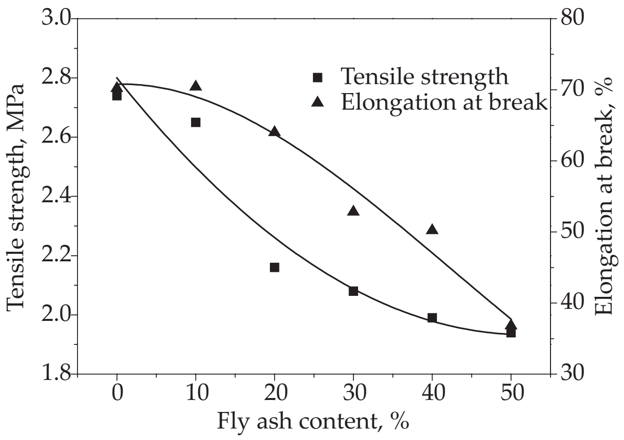


Fig. 3. Influence of fly ash dosage on the tensile strength of prepared coatings

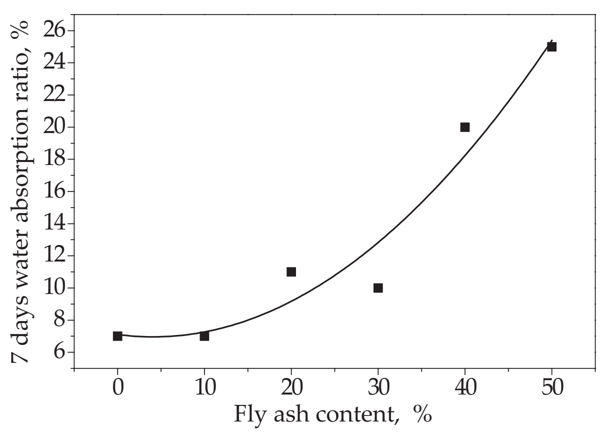


Fig. 4. Influence of fly ash dosage on the 7 days water absorption ratio of prepared coatings

ter comprehensive mechanical performance and the lower ratio of water absorption.

Effect of fly ash content on coating performance

Fly ash has the properties similar to volcanic ash, and the addition of an appropriate amount of fly ash can effectively reduce the cost and improve the material performance [16]. The composition of fly ash is: SiO_2 30.0 wt %, Al_2O_3 22.0 wt %, CaO 4.0 wt %, and traces of Fe_2O_3. The loss on ignition of fly ash was 15 wt % and the proportion remaining after sieving through 200-mesh sieve was 45.1 wt %. The grain size and the loss on ignition were relatively higher, and according to fly ash used for cement and concrete (GB/T 1596-2005), the fly ash belonged to class III. The content of free CaO in the fly ash was 4.0 wt % and the sum of SiO_2, Al_2O_3, and Fe_2O_3 was 52 wt % (more than 50 wt %), so the fly ash was high-calcium class C ash.

Effect of fly ash content on water addition and drying time

Various contents of the fly ash were taken and the coating specimens were prepared using emulsion to solid powder mass ratio of 0.5:1. In the solid powder part there was 40 wt % of cement and 60 wt % of fly ash with quartz powder together. Thus the effect of fly ash content on coating performance was analyzed.

It can be seen from Table 3 that as the fly ash content increased, more water was needed in the coating and the surface drying time and hard drying time were longer. However, the drying time of the coatings all met the requirements of Q/140402LA 003-2015 Chinese standard, noting that the surface drying time of coating is below 4 h and hard drying time is below 48 h. When the fly ash content was 0–30 wt %, the surface of the coating was relatively smooth without cracks. When the fly ash content reached over 30 wt %, more cracks appeared. The fly ash used had larger grain size and loss on ignition and hence higher content of residual carbon and glass. Therefore, the fly ash content should not be too high to avoid the adverse effect on the surface morphology.

Effect of fly ash content on tensile strength

It can be seen from Fig. 3 that as the content of fly ash increased, both the tensile strength and the elongation at break of the coating decreased. The elongation at break for sample with 10 wt % of fly ash was higher than that without fly ash. This is because the fly ash particles are evenly dispersed in the emulsion, thus improving the thixotropy of the emulsion and the uniformity of the polymer network. In addition, the pozzolanic effect of fly ash caused a decrease in porosity and increase in density of the materials [17]. As the fly ash content increased, more water was added, thus extending the curing time. The network formed by the cement and the polymer had lower tensile strength and elongation at break at early stage.

Effect of fly ash content on water absorption ratio

It can be seen from Fig. 4 that the 7 days water absorption ratio was slightly lower for sample with 10 wt % of fly ash compared with the coating without fly ash. The fly ash added in a small amount would undergo secondary reaction with cement and the fly ash particles would fill the pores of the network. And the presence of interweaving polymer film made the fly ash and cement join compactly, increasing the compactness of the coating and reducing water absorption [18]. However, the fly ash used in the experiment had larger grain size, resulting in higher content of residual carbon and irregular glass. With more fly ash added, more large pores would be formed in the coating, reducing the compactness of the coating. Thus the 7 days water absorption ratio increased dramatically with the increase of fly ash content.

Since the fly ash used had large grain size, high loss on ignition, and low activity, it was classified as class III of ash. The addition of a large amount of fly ash would cause the deterioration of the comprehensive performance of the coating and the optimal fly ash content is 10 wt %.

CONCLUSIONS

White cement is preferred in the preparation of waterproof coating in underground coal mines, and the coating prepared has lower ratio of water absorption and better comprehensive mechanical performance. Quartz powder is the preferred inorganic filler, leading in the coating to less cracking and excellent tensile strength, elongation at break, and water absorption ratio. The optimal cement content was determined as 40–50 wt %. The fly ash manufactured by Lu'an Group had low activity, large grain size, and high loss on ignition and thus belonged to class III of ash. The addition of too much fly ash would cause the deterioration of comprehensive performance of the coating and the fly ash content should be less than 10 wt %.

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