Research Article

Study on the Gelation of Foamed Gel for Preventing the Spontaneous Combustion of Coal

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According to the existing deficiencies in fire prevention technology, a new technique named foamed gel is developed to prevent coal mine fire efficiently. Foamed gel, formed by adding the type F3 foam agent, polymer H, and AL into water, introducing nitrogen and stirring physically and mechanically, is a complex multicomponent foam system. The effects of the mass fraction and mixed ratios of polymer H and polymer AL blends on gelation were comprehensively studied. The results show that the optimum performance can be got when the mass fraction of blends was 0.6% and the mixed ratio was 5 : 5. In addition, the interaction between molecules of these polymer blends was also investigated with the help of atomic force microscope. It can be found that the polymers H and AL, through having crosslinking reaction with each other, formed three-dimensional network structures, which can not only increase the nodes of the foamed gel system but also enhance the structures.

1. Introduction

Spontaneous combustion of coal in goaf is one of the main natural disasters in coal mine production [1, 2]. In recent years, in China, technology of fully mechanized sublevel caving mining is extensively used; besides, gas extraction technique has been widely promoted in the gas treatment. The significant improvement of production efficiency and the dramatical reduction of gas emission have caused leakage serious in goaf, making the coal spontaneous combustion occur frequently [3–5]. For the past few years, the number of the working face of China key state-owned coal mines closed has been over one hundred because of spontaneous fire and the freezing coals caused by the work of closing were more than ten million tons. Closing working face often makes tens of millions of equipment of fully mechanized face and fully mechanized sublevel caving face closed in spontaneous fire area, a great deal of coal frozen and reasonable sequence of deploitation dispose and mining preparation broken, which bring a large economic loss and major hidden danger to mine. In order to prevent the spontaneous combustion of coal, the techniques of grouting, nitrogen, inhibitor, gel, foam, and

so on are adopted to prevent coal spontaneous combustion since 1950s [6–8]. Although those techniques have supplied an important guarantee for the mine safety production, due to the extremely complex condition of coal mine, all of them can not completely meet the need of fire prevention and extinguishing. When grouting, slurry can only flow to the low-lying areas and can not cover the coal in higher places in goaf. While injecting nitrogen, it is easy for gas to spread with air but it is difficult to stay in the infuse area and thereby the effect of fire extinguishing and cooling is not ideal. If injecting inhibitor, which is hard to evenly disperse on the coal and has corrosive action, threatening both equipment and the health of workers. When injecting polymer gelatin, the small flow is difficult to be applied to put out the fire in large areas of goaf. If injecting foam, which can not realize curing and whose normally stability is 8~12 h. Therefore, the work of fire prevention and extinguishing in coal mine is still an arduous task for scholars at home and abroad [9].

In order to overcome the deficiencies in conventional fire prevention and extinguishing technology, foamed gel, for the first time, is developed to prevent the spontaneous combustion of coal. Foamed gel, a complex mixed system, is

formed by adding polymers and foaming agent into water and stirring physically and mechanically under the function of nitrogen. After a while, different polymers take crosslinking reaction in foam films and form three-dimensional network structures, which constitute the rigid backbone of foamed gel. The foamed gel not only has the properties of gel but also has the characteristics of foam; at the same time, it can also overcome the shortages of both and thus significantly improve the effect of fire prevention and extinguishing. At present, foamed gel, preliminarily investigated in petroleum exploitation and related industries, is mostly used as plugging agent and profile control so as to increase the mining rate of petroleum. Researchers at home and abroad have made many great contributions in this field. Fogler research team of Michigan College carried out a deep experiment on foamed gel's infiltration, flow direction, mechanical strength, and so on in the 1990s [10–14]. Zhiguo et al. studied the selective water plugging agent of foamed gel [15]. Qibin et al. explored the stability of foamed gel [16]. Although the foamed gel has a lot of advantages and good application result, the study on the effect of fluidity and formation mechanism is far from satisfactory, limiting its application. Furthermore, foaming multiple of foamed gel adopted in petroleum exploitation is small and gelation time is long, while those of foamed gel used in coal mine for fire prevention and extinguishing are high and controllable (generally 10~20 min), more difficult to investigate, and with more complex influencing factors.

This paper takes type F3 foaming agent, polymer H, and AL as the basic material, pays more attention to the effect of mass concentration and mixed ratio of polymer blends on gelation property, and analyzes the mechanism of crosslinking action between two polymers with the help of atomic force microscope, which provide a foundation for this system as a new type of material for preventing spontaneous combustion of coal.

2. Experimental Preparation

2.1. Experimental Material. Polymers H and AL are produced by Henan Kuangyuan Chemical Product Co., Ltd. The polymer H is an anionic polysaccharide produced by fermentation from *Xanthomonas campestris*. The polymer AL is a kind of galactomannan polysaccharide obtained from *Cyamopsis tetragonoloba* seeds. Both of them dissolve readily in water at room temperature. They are polysaccharides, which are particularly used for the food industry. The main role of these is to serve as a thickening agent and texture modifiers for food products. The unique characteristic of them is that not only do they owe significant viscosity values at lower concentrations in aqueous solutions but also they can exhibit excellent crosslinking when they are mixed.

Type F3 foaming agent was made by us; the concentration of active matter was 30~32%.

2.2. Experimental Equipment. Philips type HR2006 agitator, atomic force microscope, and type NDJ-5s digital viscometer

FIGURE 1: Gelation against the mass fraction of polymer blends.

are used. The viscometer is divided into four crosspieces: 4.2, 8.5, 22.2, and 42.4/s, respectively.

2.3. Experimental Methods

- (1) Put polymers H and AL blends into a suitable amount of water, then add certain type F3 foaming agent, and finally form the base fluid of foamed gel.
- (2) Take 100 mL of the base fluid into agitator, foam by means of stirring physically and mechanically (for 5 min), measure the foam volume and liquid dropout volume through its own measuring device, and use viscosimeter to test the viscosity of foamed gel.

3. Results and Analysis

3.1. Effect of Mass Fraction of Polymer Blends on Gelation of Foamed Gel. At room temperature, mass fraction of type F3 foaming agent is fixed at 0.4%, and mixed ratio of polymers H and AL is 1:1, investigating the effects of mass fraction of the polymer blends on the foam volume and liquid dropout volume, which is shown in Figure 1.

As shown in Figure 1, with the increase of the mass fraction of polymer blends, the foam volume first increased and then decreased, but the liquid dropout volume rapidly decreased to zero. This is because the optimal polymer H has the high surface activity, which can increase the intersolubility between components and control cell size and uniformity, increasing the foam volume. However, the viscosity of the solution was low when the mass fraction of polymer was small, and crosslinking points in the polymers were less and three-dimensional network structures can not be formed; thus a small amount of liquid can be seen in the foam bottom after standing for some time. With the increasing of mass fraction of polymer blends, polymers H and AL firstly fully diffuse in foam films and then have crosslinking reaction with each other to form three-dimensional network structures, constituting the rigid backbone of foam and greatly enhancing the stability of foam [17]. Furthermore, the molecular chains of the polymers contain a lot of -OH,

FIGURE 2: The influence of mixed ratio on gelation of foamed gel.

which can interact with the water molecules by hydrogen bonds. Consequently, water is absorbed in three-dimensional network structures, which can maintain the stability of foam. If the mass fraction of polymer blends exceeds 0.6%, the viscosity of the system rapidly increases, the penetration of gas is poor, and foam volume decreases gradually [18]. Therefore, when the mass fraction of polymer blends is 0.6%, the best foaming effect of polymer solution can be got and the gelation properties of foamed gel produced are the best.

3.2. Effect of Mixed Ratio of Polymer Blends on Gelation of Foamed Gel. The mass fraction of type F3 foaming agent is fixed at 0.4%, the total mass fraction of polymer blends is 0.6%, and the polymers H and AL are mixed at different compound proportions so as to form foamed gel, respectively. The effects of mixed ratios on foam volume and foam viscosity are shown in Figure 2.

From Figure 2, it can be seen that, with the increase of compound ratio, both foaming multiple and foam viscosity first rise and then decline. When the compound proportion of polymers H and AL is 5:5, foaming multiple and foam viscosity are the maximum. If the ratio continues to change, foaming multiple and foam viscosity begin to fall, which means that there exists a best compound ratio of the blends, and by this time, their crosslinking reaction with each other is maximum.

The reason for this phenomenon is that when polymers H and AL mixed in the solution, they can fully react with each other and form three-dimensional network structures, making the viscosity of foamed gel increase. Whereas if the mass fraction of polymer H is less, the polymer AL will be excessive, unexpectedly its dense galactose will hinder the interaction with polymer H, causing the viscosity of the system to descend and not to form foamed gel with satisfactory stability and good appearance. With the rise of polymer H, foaming property and stability of the solution increase gradually. However, when mass fraction of polymer H is more than 50%, the polymer AL relatively reduces and the crosslinking points decrease, unhelpful to form gel [19–21]. Foam property becomes worse and stratification

FIGURE 3: Relationship between apparent viscosity and shear rate of foamed gel.

FIGURE 4: Relationship between mass fraction of blends and gelation time of foamed gel.

phenomenon can be seen after standing for a while. Consequently, when the mixed ratio of the blend is 5:5, foam property and gelation effect are the best.

3.3. Characteristics of Gelation of Foamed Gel. According to the research conducted above, the foamed gel is formed when the mass fraction of type F3 foaming agent is fixed at 0.4% and the mass fractions of polymers H and AL are both 0.3%. Viscometer is adopted to measure the apparent viscosity so as to discuss the relationship between gelation property and shear rate, as shown in Figure 3.

According to the research conducted above, the concentration of type F3 foaming agent is fixed at 0.4%, and the mass ratio of polymers H and AL is 1:1. Then change the concentration of mixture so as to form the foamed gel samples at different concentrations and use viscometer to measure the apparent viscosity at different shear rate, as shown in Figure 3.

It can be seen from Figure 3 that the apparent viscosity of foamed gel at various concentrations of the mixture formed

FIGURE 5: AFM images of foamed gel samples in the scanning range of 500 nm. (a) Polymer H; (b) polymers H and AL blends.

by polymers H and AL drops rapidly with the shear rate increasing, and the higher the concentration is, the more obviously apparent the viscosity decrease is. This law fits the fluid character of shear thinning. In static foamed gel, the arrangement of molecular chains in polymers is ruleless. And those molecular chains entangle with each other to form three-dimensional network structures, producing viscous resistance to flow [22]. Therefore, when the shear rate is low, the apparent viscosity of foamed gel is high. With the increase of shear rate, the shear effect subjected to three-dimensional network structures rises, and the molecules curved and entangled was open. Molecules nodes reduce, thus apparent viscosity decreases. When the shear rate reaches a certain value, the apparent viscosity is stable [23, 24]. Hence, under the function of shear rate, polymers H and AL can not have crosslinking reaction with each other in foam films, which can meet the property of large range flow and diffusion of foamed gel in goaf.

3.4. Gelation Time. The formation process of foamed gel is that, after the system foams, polymers H and AL contained in foam films react with each other and form foamed gel. If the time of crosslinking reaction between polymers is too early, the viscosity of solution will be too high and hard to form foam. Even if foamed gel is formed, the large viscosity makes it difficult to flow; the limited overage can not meet the need of fire prevention and extinguishing. Foam belongs to unstable system of thermodynamics; if the time of crosslinking reaction between polymers is too late and even exceeds its stable time, it will break and dehydrate. At this time, even if crosslinking reaction has been taken place, the foamed gel can not be formed. Therefore, the best gelation time is after the solution foaming and before its breaking. Considering that the pipe transport is used in coal mines, the time is controlled between 10~20 min. After the blends

FIGURE 6: The flowchart for preparation of foamed gel.

mixed, the viscosity begins to increase. After some time, the viscosity is essentially constant and forms stable foamed gel. Polymers H and AL are chosen to investigate how the gelation time changes at different mass concentrations of the polymer blends.

The mass fraction of type F3 foaming agent is fixed at 0.4%. The compound proportion of polymers H and AL is 1:1; then prepare the polymer blends with the mass fraction of 0.6%, 0.8%, and 1%, respectively. To study on the effect of various mass fractions on gelation time, the results are shown as follows.

From Figure 4, it can be found that, when the mass fraction of blends was 0.6%, the gelation time was 20 min. When the mass concentration of the blends increased to 1%, the gelation time decreased to 10 min. This is because the rise of mass fraction leads to shortening of the distance and increasing of the collision between molecules. The crosslinking reaction between polymers H and AL becomes stronger, which makes great contributions to forming three-dimensional network structures with strong continuity [25]. Therefore, the gelling rate of foamed gel increased with the rise of the mass fraction of polymer blends. Moreover, the highest gelation viscosity of the system increased with the rising of the mass concentration. Nevertheless, if the mass concentration is too high, the reaction rate among polymers increases and gelling rate of the system speeds up, not easy to

FIGURE 7: The foamed gel prepared in lab. (a) Foaming, (b) fluidity, and (c) film forming ability.

control the gelation time. Furthermore, the rise of the mass fraction of polymer increases the viscosity of the solution, reducing foaming ability.

3.5. Microstructure Analysis. Prepare the mass fraction of 0.3% of polymer H and the mass fraction of 0.3% of both polymers H and AL, respectively; take $10\ \mu\text{L}$ of the two solution samples on mica sheet, and make it spread as possible as you can, heating slightly into membrane. Use AFM to observe the microstructure under the scanning range of 500 nm, as shown in Figure 5.

We can see from Figure 5 that the microstructure map of polymer H without polymer AL is chaotic, granularly distributed in the solution, and thus unable to form three-dimensional network structures, as shown in Figure 5(a). With the adding of polymer AL, filled in the molecules of polymer H, making the scattered polymer H form a uniform continuous phase and thereby form three-dimensional network structures, as shown in Figure 5(b). This is because when polymer H is dispersed into water, it first becomes pieces of random line structures. Then the random molecular chains will coalesce together to the double helix rigid structures similar to the rod by hydrogen bond between the side chain and main chain of polymer H. The rod-like structures, with the help of Na^+ , K^+ , and Ca^{2+} ionized by polymer H itself, make the double helix structures decentralized in the solution connected together to the helical mesh polymer or double helix cluster by chains of $-\text{COO}-\text{Na}-\text{H}_2\text{O}-\text{Na}-\text{COO}-$, $-\text{COO}-\text{K}-\text{H}_2\text{O}-\text{K}-\text{COO}-$, and $-\text{COO}-\text{Ca}-\text{COO}-$ [17, 26]. If polymer AL is not added, polymer and cluster can only be uniformly dispersed into the solution and can not form three-dimensional network structures. After adding polymer AL, $-\text{CH}_2\text{OH}$ in polymer or cluster and the $-\text{CH}_2\text{OH}$ in main chain of polymer AL contact and fully collide, forming three-dimensional network structures in the form of $-\text{CH}_2-\text{O}-\text{CH}_2-$ and making the scattered polymer and cluster form a uniform continuous phase [27–29]. Consequently, polymer AL and polymer H can react with each other in foam films to form foamed gel and keep the stability of foam.

4. Preparation and Effect

In order to investigate the foaming effect of foamed gel, compressed air replacing nitrogen is used, and foaming device of foamed gel has been constructed to conduct a simulation test. Firstly, directly mix and stir polymer H, polymer AL, and water based on the fixed proportion to form the solution of blends. Then, put the blends solution into grouting pipes through consistency pump and take type F3 foaming agent into grouting pipes by fixed displacement pump. After fully mixed in the flow mixer, solution of polymers and foaming agent flow to the foaming generator. Then compressed air is introduced. Finally the air interacts with the blends solution with type F3 foaming agent and forms foamed gel. The process of preparing foamed gel is shown in Figure 6.

According to the experimental parameters above, the mass fraction of 0.4% of type F3 foaming agent and the mass fraction of 0.3% of both polymer H and polymer AL are used to form foamed gel, as shown in Figure 7(a). And the foamed gel prepared has good fluidity, as shown in Figure 7(b). After one day, polymer H and polymer AL have crosslinking interaction with each other in foam films and obtain compacted thin films, as shown in Figure 7(c).

5. Conclusions

- (1) Experimental study on the properties of foamed gel shows it has the characteristics of high foaming multiple, strong stability, good fluidity, adjustable gelation time, and so forth. So using the foamed gel can significantly improve the efficiency of preventing spontaneous combustion of coal.
- (2) The mass fractions of polymers H and AL and the compound proportion of the blends greatly influence the performances of foamed gel. When the mass fraction of polymer H and polymer AL blends is 0.6% and the mixed ratio is 1 : 1, the properties of foamed gel formed for fire prevention and extinguishing are the best, and the foamed gel prepared has the maximum viscosity without affecting its fluidity.

- (3) Through the analysis of AFM, polymers H and AL have crosslinking reaction with each other and form three-dimensional network structures, increasing the nodes of the system and enhancing the structures. Moreover, foaming device of foamed gel is constructed in lab and foamed gel for fire prevention and extinguishing with optimum performance is prepared.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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