

Mining Polyethylene Glycol-Based Thermosensitive Hydrogel Materials: Preparation and Flame Retardant Properties

Hao Shao, Zihang Wang, Shuguang Jiang,* Yue Zhang, Xian Xi, and Zhengyan Wu



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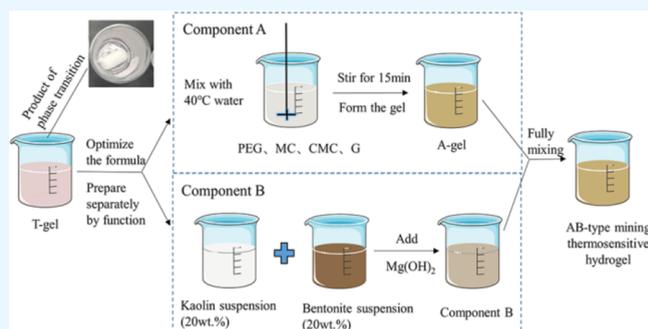
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ABSTRACT: A new type of efficient and anti-extinguishing materials to inhibit coal spontaneous combustion is required because of the current situation of the short activity cycle of existing anti-extinguishing technology. Now, polyethylene glycol (PEG) was used as a water-absorbing monomer to polymerize various substances to prepare an AB-type mining thermosensitive hydrogel that was obviously thermoresponsive. The thermosensitive hydrogel, which is low-cost and stable, can be stored for a long time, and it is prepared by compounding A and B components. The orthogonal experiments determined the optimal ratio of component A, while the controlling variable experiments determined the optimal ratio of component B. The thermal stability and flame-retardant properties of the AB-type thermosensitive hydrogel were analyzed during the process of natural oxidation of coal, and the temperature responsiveness of thermosensitive hydrogels was investigated at different temperatures. The results showed that the optimal ratio of polyethylene glycol:methyl cellulose:sodium carboxymethyl cellulose:guar gum of component A was 6:6:1.2:1.5; and the ratio of bentonite:kaolin:Mg(OH)₂ of component B was 2:1:1. When the ratio of component A to component B was 1:2, the AB-type thermosensitive hydrogel shows the best flame retardant properties. When this ratio of gel was applied to coal samples, the weight loss was just 6%, and the reduction of CO was as high as 72.6%. The gel, which was convenient for transportation in mining pipelines, had strong fluidity at low temperatures and rapid temperature response. As the temperature rose, a phase transition occurred gradually, and after the phase transition, a high-viscosity solid substance was formed, whose viscosity was approximately 11 times that of the room temperature. It plugged the pores effectively, and in the high-temperature region, the occurred phase transition gathered to extinguish the fire. It is a new type of high-efficiency anti-extinguishing material with excellent properties.



1. INTRODUCTION

Coal will continue to play a crucial economic role in China as the energy pillar industry for a long time. However, coal spontaneous combustion fires as the main cause of mine fires pose a major danger to the safety production of enterprises and result in massive deaths and property losses.¹ Many scholars focused on how to efficiently prevent the fires of coal spontaneous combustion.^{2–4} However, the current anti-extinguishing techniques applied in mines are mainly slurry injection, spraying inhibitor, foam injection, colloid injection, etc.⁵ These technologies primarily reduce the contact with oxygen by enveloping the coal body and forming a protective film on its surface, and the huge volume of water contained inside it absorbs the heat of the coal body while evaporating to inhibit the coal spontaneous combustion.⁶ Whereas, in fact, the temperature-rising process of coal spontaneous combustion in the goaf is uneven, and the coal temperature will gradually increase in areas with sufficient oxygen supply and small heat dissipation.⁷ The produced high-temperature point has a higher temperature, which increases the oxygen demand and

heat generation.⁸ The temperature will gradually increase at a fast speed and eventually develop into the rapid heating and combustion stages.^{9–11} Therefore, preventing and controlling the spontaneous combustion of coal in the high-temperature area is the key to preventing and putting out a fire in a goaf. However, the current anti-extinguishing measures strive to cover the entire goaf area of the mine,¹² which results in a large amount of waste of anti-extinguishing materials. Once these materials are injected into the goaf, the moisture in the materials frequently starts to evaporate at the low-temperature stage of the coal due to air leakage of the goaf. The anti-extinguishing efficacy significantly diminished and even

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disappeared ineffectively after the protracted process of low-temperature oxidation and heating.^{13–15} Thus, it is crucial to search for new and effective mining anti-fire extinguishing materials. Such materials should be able to continuously maintain good fluidity and fire-extinguishing activity in the low-temperature region of coal, gradually undergo a phase change, and weaken fluidity in the high-temperature region of coal, which causes them to gather in the high-temperature region, achieving the effective prevention and control of spontaneous combustion fires in the goaf and getting a multiplier effect.

Thermosensitive hydrogels can change their state in response to temperature changes and are employed in tissue engineering,¹⁶ medical drug delivery,¹⁷ and other fields due to their good biocompatibility. According to the state changes, at different temperatures, the gel can be divided into two types: low critical solution temperature (LCST) and high critical solution temperature (UCST).¹⁸ Take LCST-type gel as an example, it has excellent fluidity and is in a solution state when the temperature was low; more than LCST, the volume-phase transition occurs to form a gel, which covers the coal body and cools the fire,¹⁹ but UCST changes in the opposite direction. Because thermosensitive hydrogels have the characteristics of the rapid response of temperature sensitivity and good fire-prevention effect, scholars pay more effort to explore the possibilities in the field of coal mine fires. Cheng et al. prepared a new type of smart gel for mining, which could effectively utilize corn stalks, contained expandable graphite that responded rapidly to temperature, and had good thermal stability and fire extinguishing properties.²⁰ Guo et al. physically cross-linked an MC-PEG-SDS ternary thermosensitive hydrogel, characterized its properties, and found that it could effectively suppress coal oxidation.²¹ Tsai et al. prepared five coal spontaneous combustion inhibitors such as P(NIPAA-co-SA) thermosensitive hydrogel and compared their comprehensive properties by FTIR, TG, and other characterization methods.²² Although these gels have good thermal stability, they must be prepared on site and cannot be stored for long periods.

In order to obtain a cost-effective, performance-stable, field-applicable anti-extinguishing suppressing material that can maintain the activity of inhibiting coal oxidation and spontaneous combustion for a long time, this paper used poly(ethylene glycol) (PEG), a hydrophilic ethylene oxide polymer, as a water-absorbing monomer to prepare gels.²³ PEG can interact with the active hydroxyl functional groups on the surface of coal to etherify and improve the oxidation resistance of coal to inhibit the spontaneous combustion of coal.^{24,25} Meanwhile, the homopolymer of PEG can adjust the degree of micellar aggregation in the solution of the amphiphilic block copolymer and thus affect the temperature of gelation.^{26,27} Based on the properties of PEG, an AB-type thermosensitive hydrogel that shows different properties at different temperatures is prepared by thermal polymerization by cross-linking PEG monomers and various polymer compounds. To study the flame retardant properties and thermoresponsive properties of the thermosensitive hydrogel, the experiments of thermogravimetric analysis and temperature-programmed tests were used to characterize the gel properties.

2. EXPERIMENTAL SECTION

2.1. Preparation Process of AB-Type Thermosensitive Hydrogel.

2.1.1. Materials. The materials used in the experiments were poly(ethylene glycol) (PEG), methyl cellulose (MC), sodium carboxymethyl cellulose (CMC), guar gum (G), bentonite, kaolin, and Mg(OH)₂, respectively. Table 1 shows the function of various ingredients in the gelation process.

Table 1. Experimental Materials

name	gel-forming function	specification
poly(ethylene glycol) (PEG)	water-absorbent monomer	AR
methyl cellulose (MC)	cross-linking agent	AR
sodium carboxymethyl cellulose (CMC)	thickener	AR
Mg(OH) ₂	flame retardant	AR
kaolin	filling agent	Tech
bentonite	filling agent	Tech
guar gum (G)	binder	Tech

2.1.2. Preparation of Thermosensitive Hydrogel. The majority of existing thermosensitive hydrogel materials are prepared by polymerization with *N*-isopropyl acrylamide (NIPAAm) as the monomer; nevertheless, the mechanical properties of thermosensitive gels obtained from this polymerization are poor, and thus a large number of modified monomer materials appear and are used to improve the properties of this type of gel.^{28,29} According to the relevant literature, NIPAAm monomers were excluded and thermosensitive hydrogels were obtained by adding appropriate ratios of PEG, MC, CMC, Mg(OH)₂, bentonite, and kaolin to meet the requirements. Among them, Mg(OH)₂ exhibited high thermal stability and smoke suppression as a flame retardant, while a suitable mix of bentonite and kaolin could boost the mass fraction of inorganic components and fire extinguishing performance in the gel system. Taking the viscosity of the gel at different times as the index of evaluation, the polymerization temperature, stirring time, and the ratio of flame retardant and filling agent were determined by controlling variable experiments. The proportion of flame retardants and filling agents, in the end, was kaolin suspension (20 wt %):bentonite suspension (20 wt %):Mg(OH)₂ in 2:1:1. Then, it was added to a mixed aqueous solution of PEG, MC, and CMC, and stirred in a 40 °C mixture solution for 15 min to form the gel. The prepared T-gel had a high LCST; the solution underwent a phase transition when the water bath was heated to approximately 80 °C; and a solid-like substance is precipitated. The phase transition results are shown in Figure 1.

To reduce the cost of T-gel, the temperature of the phase transition was adjusted and the storage time of the gel was extended; the formula was optimized based on retaining the properties of the phase transition of T-gel. From the functional point of view, the two components, A and B, which were stable in the system, were separated for preparation. Component A, which inherited the thermosensitive properties of T-gel and strengthened the stability of the system by adding G, included PEG, MC, and CMC. Moreover, component B mainly played the role of filling and flame retardant and was composed of inorganic components such as Mg(OH)₂, bentonite, and kaolin. The optimal material ratio of component A was



Figure 1. Product of the T-gel after a high-temperature phase transition.

determined by the orthogonal experiment of L9 (3⁴). The levels of factors affecting the gel viscosity and stability of component A are shown in Table 2. The optimal material ratio

Table 2. Influencing Factors and Levels of Gel Performance of Component A

level	PEG concentration/ wt %	MC concentration/ wt %	CMC concentration/ wt %	G concentration/ wt %
1	6	2	0.6	0.5
2	7	4	1.2	1
3	8	6	1.8	1.5

of component B followed the results determined by the control variable experiments in the previous article (bentonite suspension:kaolin suspension:Mg(OH)₂ of 2:1:1). Finally, PEG:MC:CMC:G was added in the optimal ratio of 3:3:0.6:0.75 and stirred with 40 °C water to form a gel to obtain the A component gel (A-gel). To obtain a thermosensitive hydrogel with better practicability and better performance, this study further investigated the performance of the experimental group with different component ratios in the AB thermosensitive hydrogel.

2.2. TG-DSC Experiment. The proportion of each component in the gel sample was used as a subscript to simplify the names of the coal samples. Taking the AB-type thermosensitive hydrogel with A:B of 1:1 as an example, the experimental group was named as A₁B₁. Therefore, in order to compare the performance of A₁B₂ and A₁B₃, the A-gel coal samples were used as the control group, and the mass and weight changes of coal samples after adding the gels were studied by using a TG-DSC experiment by an STA339F5 synchronous thermal analyzer. Four sets of coal samples with the same mass were prepared, i.e., one set of raw coal samples and three sets of gel coal samples with equal mass of raw coal and gel mixed uniformly (the coal sample combinations were

raw coal sample + A, raw coal sample + A₁B₂, and raw coal sample + A₁B₃). After standing for 20 min, 10 mg of each SD coal sample was taken at a flow rate of 60 mL/min under an air atmosphere, and the temperature increased from 30 to 300 °C with a heating rate of 1 K/min.

2.3. Characterization Test of Temperature Responsiveness. The characterization test was conducted in terms of both rheological characteristics and phase transition states to investigate the characteristic performance of thermosensitive hydrogels at different temperatures. To meet the requirements of the experiments, three sets of samples with equal quality were prepared: (i) A-gel (sample no. 1), (ii) A₁B₂ gel (sample no. 2), and (iii) A₁B₃ gel (sample no. 3), and the rheological properties of the samples were tested using an MCR302 rotational rheometer to test the changes of apparent viscosity and shear stress with shear rate (0–14 s⁻¹) at 30, 60, and 80 °C. The state test of phase transition was then done using the iron plate heating method to monitor and analyze the phase shift of gel at various temperatures.

2.4. Temperature-Programmed Test. To investigate the effect of the thermosensitive hydrogel on the spontaneous combustion process of low-temperature oxidation of coal samples, three groups of coal samples with equal masses of 16–80 mesh were prepared for the temperature-programmed test. The raw coal was used as the blank control group, and the other two experimental groups were coal samples treated with calcium chloride and thermosensitive hydrogel. During the simulated spontaneous combustion of coal, the gas collected by the high-precision gas sensor was used as the index to analyze the inhibition effect of different inhibitors. The test conditions were as follows: temperature in the range of 20–180 °C, heating rate of 1 °C/min, air flow of 10 mL/min, and cycle of data collection of 10 s.

Table 3. Results of the Viscosity Test for the A-Gel Orthogonal Experimental Groups

time/h	P ₁ M ₁ C ₁ G ₁	P ₁ M ₂ C ₃ G ₂	P ₁ M ₃ C ₂ G ₃	P ₂ M ₁ C ₂ G ₃	P ₂ M ₂ C ₃ G ₁	P ₂ M ₃ C ₁ G ₂	P ₃ M ₁ C ₃ G ₂	P ₃ M ₂ C ₁ G ₃	P ₃ M ₃ C ₂ G ₁
1/6	20.5	308.1	955.1	256.8	195.1	359.5	71.9	205.4	616.2
1/5	30.8	297.8	934.6	246.5	205.4	359.5	71.9	208.4	650.9
24	50.8	864.3	3610.0	355.9	406.7	1017.0	152.0	559.3	1220.0
48	102.7	482.7	2064.0	400.5	359.5	718.9	102.7	369.7	985.7
72	layered	559.3	1525.0	203.4	254.2	559.3	Layered	203.4	915.2
96		layered	513.5	layered	215.7	472.4		82.2	174.6
120			layered		layered	layered		layered	layered

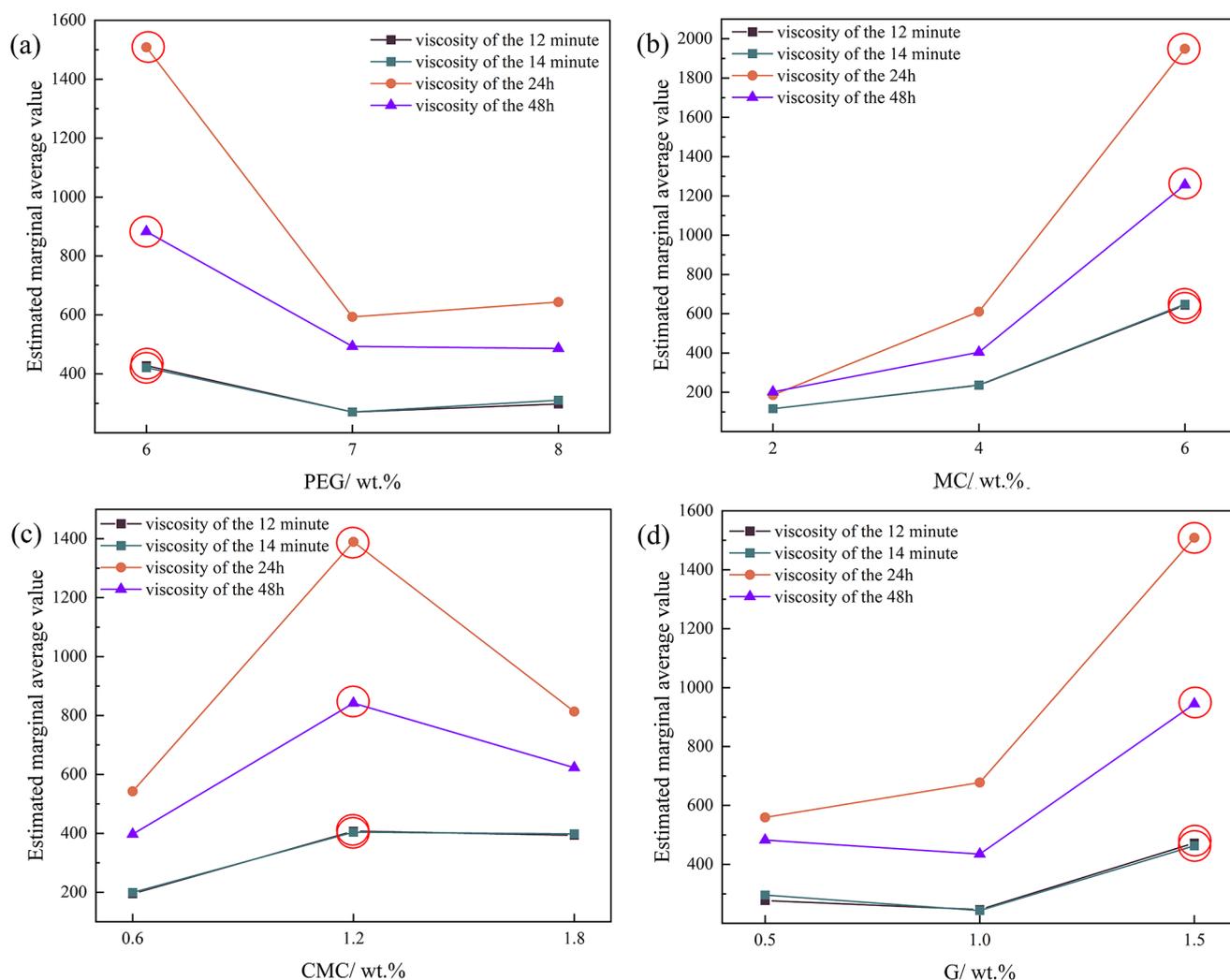


Figure 2. Graphs of the estimated marginal average value for A-gel: (a) PEG, (b) MC, (c) CMC, (d) G.

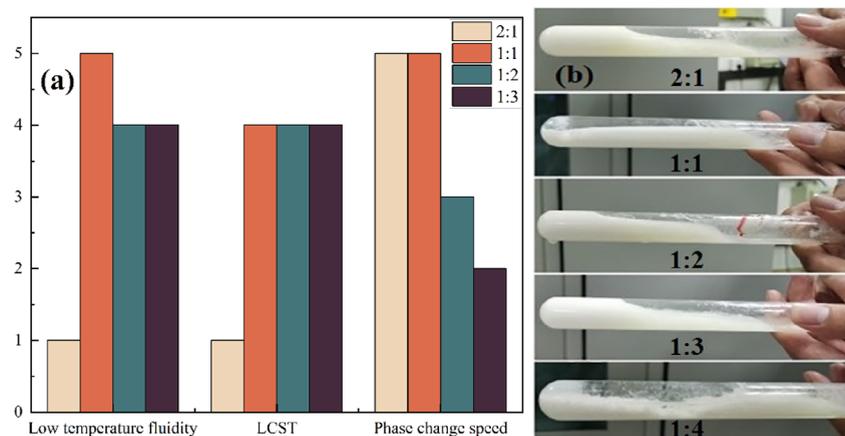


Figure 3. Mixing proportion tests of the AB-type thermosensitive hydrogel: (a) performance of experimental groups with different ratios; (b) gel state of experimental groups.

3. RESULTS AND DISCUSSION

3.1. Selection of Optimal Component Ratios for Gels.

3.1.1. Optimal Ratio of Compound Component of A-Gel. Based on the orthogonal experiment, the state that the different proportional experimental groups remained for a period was briefly measured, and the viscosity changes are

recorded in Table 3 (in this section, the materials were referred to simply as: PEG (P); MC (M); CMC(C); the subscripts represented the corresponding levels of the materials). The results showed that the addition of G enhanced the viscosity of the gel of component A, and five groups in the experimental groups of the gels maintained long-term stability. Among them,

the $P_1M_3C_2G_3$ and $P_2M_3C_1G_2$ gel systems performed the best, namely, the two experimental groups with the ratio of P:M:C:G in 6:6:1.2:1.5 and 7:6:0.6:1. To determine the theoretical optimal ratio, the viscosity data of each experimental group, before the gel system was delaminated, were used for univariate ANOVA in SPSS. Figure 2 displays the relevant graphs of the estimated marginal average value. The concentration of all four components had a significant effect on the gel properties, and the mean square value of the main effect test revealed that MC and G had the greatest influence, indicating that the experiments were supposed to pay more attention to the selection of two doses. In Figure 2, the optimal concentration of each component is determined according to the peak value, i.e., the optimal ratio of P: M: C: G was 3:3:0.6:0.75.

The results of the macroscopic stability analysis and the mean peak value were used to determine that the ideal ratio of A-gel within the scheme was P:M:C:G in 6:6:1.2:1.5.

3.1.2. Proportional Tests of AB-Type Thermosensitive Hydrogel. Five groups of AB-type gels with the same mass of 20 g were placed in the test tube, and the mass of A to B in each group was 13.3 to 6.7 g (2:1), 10 to 10 g (1:1), 6.7 to 13.3 g (1:2), 5 to 15 g (1:3), and 4 to 16 g (1:4), respectively. The experimental group was heated in a water bath, and the flow state of the gel in different test tubes was observed as the temperature increased. The properties of the gel obtained with the distribution of different ratios of AB experimental groups were roughly investigated based on the fluidity, LCST, and speed of phase transition at the low temperature of the gel. Different levels were represented by different numbers, and as the number grew smaller, so did the degree (1: low; 2: lower; 3: average; 4: higher; 5: high). The observation results are shown in Figure 3. When A to B was 1 to 4, the gel generated flocculent precipitate at high temperatures, the system was loose, and the fire extinguishing effect was greatly weakened. As the ratio was 2 to 1, the fluidity of the gel was too low to meet the experimental purpose. The remaining other three groups showed little difference in performance, so the ratios of gels in 1:2 and 1:3 were selected for in-depth study to reduce the cost, and they were named A_1B_2 and A_1B_3 .

3.2. Results of TG-DTG. Figure 4 shows the experimental outcomes of TG-DTG. During the whole heating process, the

TG curve shows a downward trend, and the DTG reaches a peak at 180 °C. The quality of the raw coal samples declined by 15% as the temperature increased from 50 to 300 °C. The changes of the three groups of gel coal samples relatively lagged, and the mass reductions were all within 13%. Among them, the A_1B_2 gel coal samples performed the best, with good thermal stability and a weight loss rate of only 6%. It indicates that the addition of gel could effectively inhibit the spontaneous combustion of coal, and the water contained in it took away part of the heat in the form of evaporation and slowed down the oxidation process of coal. The gel with A:B = 1:2 (A_1B_2) had the best flame retardant effect among the three groups of gel coal samples. As a result, in the next temperature-programmed test that follows, the ratio of thermosensitive hydrogels chosen was A:B = 1:2.

3.3. Results of DSC. The thermosensitive hydrogel undergoes a phase transition in response to changes at ambient temperature. At the critical temperature, the hydrogen bond is damaged and the hydrophobic interaction is enhanced. This process will generate a peak of heat absorption in the DSC curve.³⁰ The enthalpy change occurred at the gel point where the gel underwent a sol–gel transition, and the value of the LCST could be judged accordingly. Figure 5 shows the DSC curves of each coal sample from 25 to 95 °C. The curve of raw coal samples formed the peak of heat absorption at 47.6 °C, while the formation of the absorption peak of A-gel was about 54 °C, and the two groups of AB-type thermosensitive hydrogels named A_1B_2 and A_1B_3 formed the peak of heat absorption at about 52 and 50 °C, respectively. It was found that the addition of the B component had a tendency to decline the phase transition temperature of the gel, and the curve of the AB-type thermosensitive hydrogels had an obviously slow and wide tendency of glass transition.

3.4. Thermoresponsive Analysis of Gels. Figure 6 shows the change curves of the apparent viscosity of the three-sample groups. The curves of the nine groups all decrease with an increase in the shear rate, showing the shear-thinning characteristic. The reason for this phenomenon was that the nodes of molecular entanglement in the chains of the network in the gel were heavily disrupted at high shear rates, resulting in weaker interactions between the molecules of the solvent and reduced flow resistance, which led to a decrease in the apparent viscosity of the samples. According to these characteristics, some rheological properties of the three groups of samples were preliminarily determined, and all three groups of samples were supposed to be pseudoplastic fluids in non-Newtonian fluids, thus providing a reference value for the field application of the gel. Combined with Figure 6b, the viscosity of the sample groups of AB-type gel at the same temperature is much lower than that of the A-gel (sample no. 1 is A-gel, nos. 2 and 3 samples are AB-type thermosensitive hydrogels), demonstrating that the addition of component B, which contained a lot of water, could significantly improve the fluidity of the gel system.

As shown in Figure 7, the viscosity of the gel sample no. 2 in the same set of samples at 80 °C is approximately 4.6 times that of the viscosity at 30 °C, and the viscosity increases sharply due to the temperature change. This phenomenon could be reflected at any shear rate and was especially obvious at the shear rate of 0, with an 11-fold change. Hence, it could be inferred that the gel went through a phase transition and separated into a solid-like substance with a high viscosity during the warming process. In Figure 7, compared with two

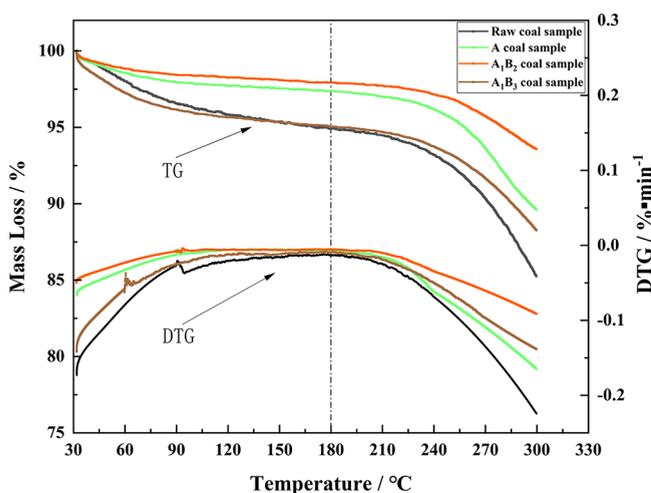


Figure 4. Changing curve of quality of coal samples during thermal analysis.

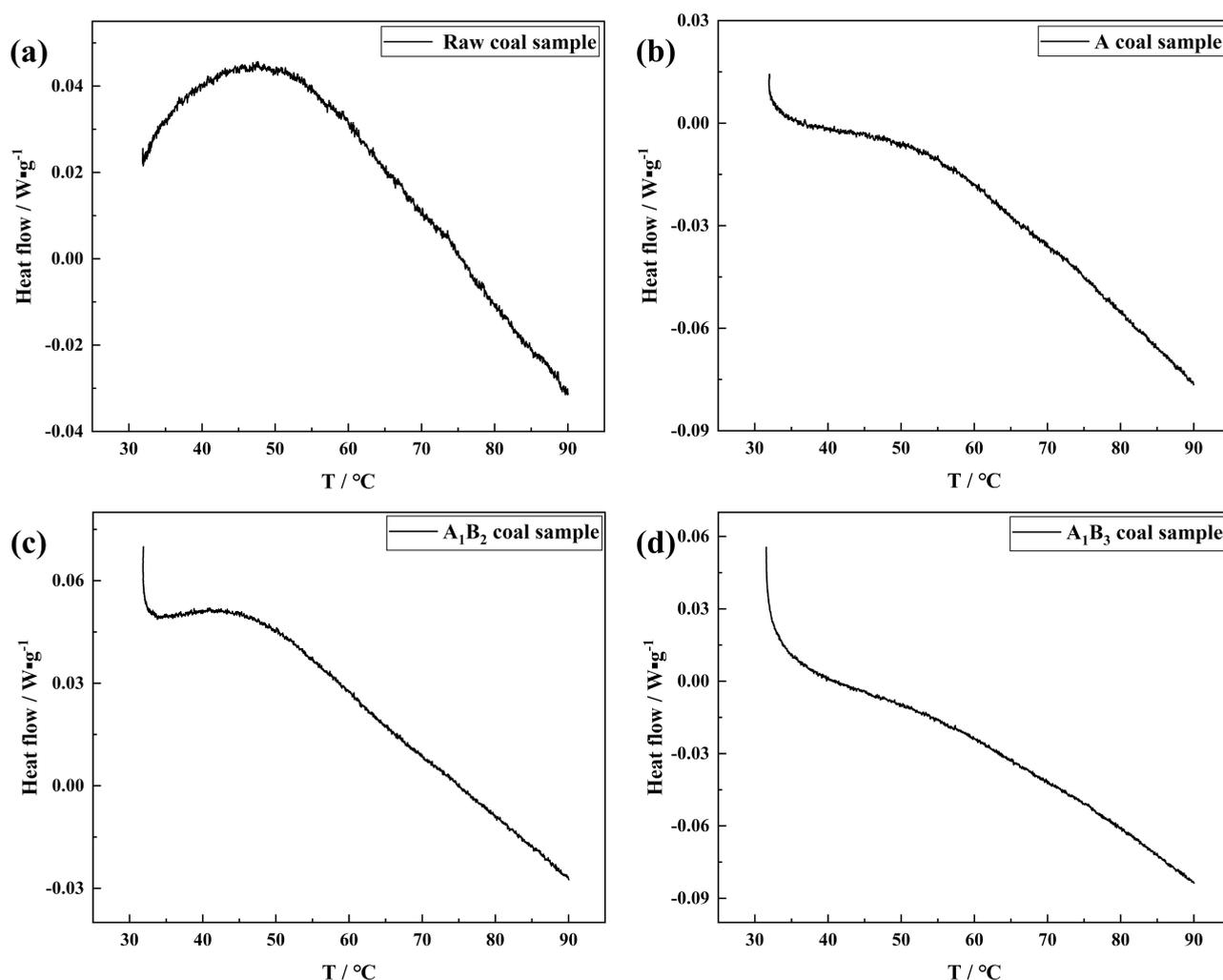


Figure 5. Thermal analysis curve of DSC for each coal sample: (a) raw coal sample, (b) A coal sample, (c) A_1B_2 coal sample, and (d) A_1B_3 coal sample.

samples at 60 and 30 °C, the viscosity of the A gel decreased, but the viscosity of the AB gel increased. The reason was as follows: due to the limitation of the instrument, only a certain temperature point of the sample could be selected for testing, the span between the two characteristic points was too large, and the effect of the phase change process of the gel in this temperature interval was counteracted by the effect of shear-thinning characteristics. The apparent viscosity of all samples in the three groups was supposed to decrease theoretically as the free volume in the solution increased and the entanglement of molecular chains was weakened by an increase in temperature. However, the LCST of A gels was higher than that of AB gels, and the process of phase transition occurred later than the latter. The temperature responsiveness of AB gels was more sensitive, and the phase separation started to occur approximately within the second half of the temperature interval from 30 to 60 °C. The solid-like particles formed by the phase transition of the thermosensitive hydrogel exhibited extraordinarily high viscosity, and thus the increase rate of resulting viscosity was greater than the decrease rate of viscosity caused by temperature increase. As a result, at 60 °C, the sample viscosity of AB thermosensitive hydrogel rose instead. This was also reflected by the macroscopic state. The dense film formed by the AB thermosensitive hydrogel at 60

°C had denser bubbles, a thicker film, and the presence of granular material compared with the A-gel. It indicated that the phase transition of the AB thermosensitive hydrogel had started before 60 °C, and the degree of phase transition was deeper than that of the A-gel.

To further clarify the state changes of the gel in the heating process, the gel was analyzed by integrating the macroscopic phenomena observed in the iron plate, and the pictures of the state of the gel during the heating process are shown in Figure 8. According to the rheological properties exhibited by the samples, the Ostwald–de Waele rheological model was used to fit the data, and the rheological equation is shown in the following formula.³¹

$$\tau = K\dot{\gamma}^n \quad (1)$$

where τ is shear stress (Pa), K is consistency index ($\text{Pa}\cdot\text{s}^n$), $\dot{\gamma}$ is shear rate (s^{-1}), and n is the flow behavior index.

The fitting results of the samples are shown in Figure 9. The analysis demonstrates that the shear stress of samples in the three groups shows a nonlinear increasing trend at 30 °C. All samples have n less than 1, which is consistent with the characteristics of pseudoplastic fluids.³² As the temperature increased, the rheological parameters of the samples changed significantly, which proved the sensitive temperature respon-

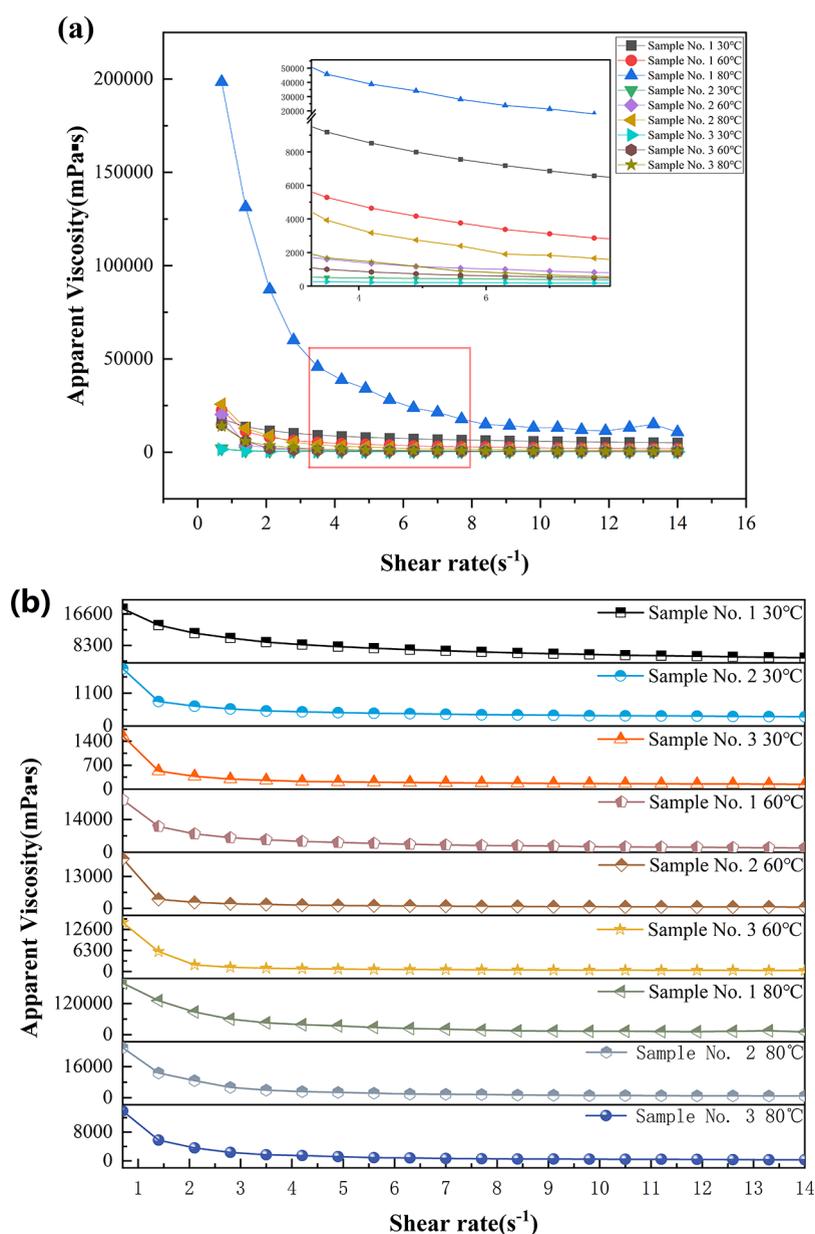


Figure 6. Apparent viscosity curve of the samples: (a) overall diagram (b) stacking diagram.

siveness of the gel. At this time, the gel had certain yield stress. When the shear stress applied to the gel was less than this value, the fluid only deformed but did not flow. This characteristic boosted the adhesion of the gel on the surface of sloped coal seams and alleviated the hindrance of preventing and controlling mine fires caused by complicated topography. Simultaneously, the high fluidity of the gel could facilitate the use of pipelines for transporting it in the field application and its usage in the mine. The state diagram of the sample reveals that the A-gel is overly viscous, with a partial accumulation of folds, while the other two groups of AB-type gels are more uniform.

When the temperature rises to 60 °C, the coincidence degree between the actual trend curve and the fitted trend curve of each group of samples was obviously lower. It was presumed that the free radical polymerization occurred between different polymers in the gel system under the influence of temperature and initiator; the change of the

molecular chain of the gel is shown in Figure 10; and the coexistence of multiple phases formed the phenomenon. The macromolecules of solvent in the solution were induced by the groups of PEG and aggregated in large quantities, and the macromolecules were synthesized under the action of cross-linking agents. Distinct polymer chains, which originally existed in the form of occasional interspersed, were intertwined with each other by covalent cross-linking bonds; varied clusters and microregions with branching structures were generated with cross-linking bonds as nodes; uneven network architectures with different cross-linking densities were formed; and gelation happened. The trend curve of sample no. 3 was the closest to the curve of Bingham fluid, which was generally a multi-phase mixed fluid with high bonding strength between particles and had a high inward concentration, assisting in confirming the inference of gel transition. According to the state pictures of samples in the three groups at 80 °C shown in Figure 8, the volume of the samples was reduced and a white

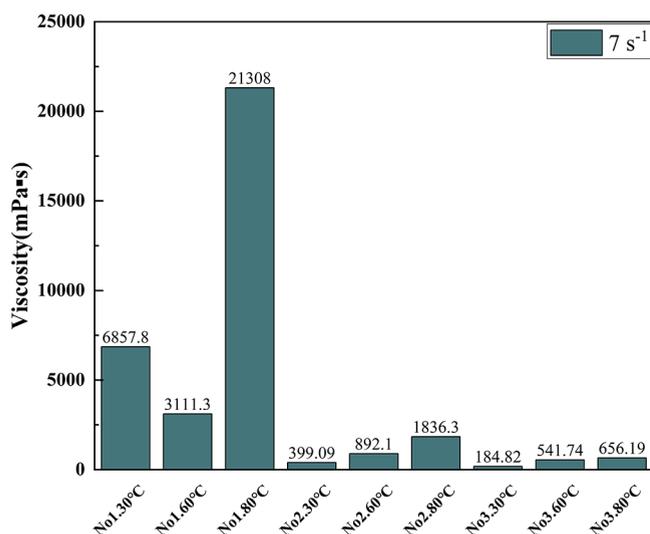


Figure 7. Viscosity values of samples at different temperatures at a shear rate of 7 s^{-1} .

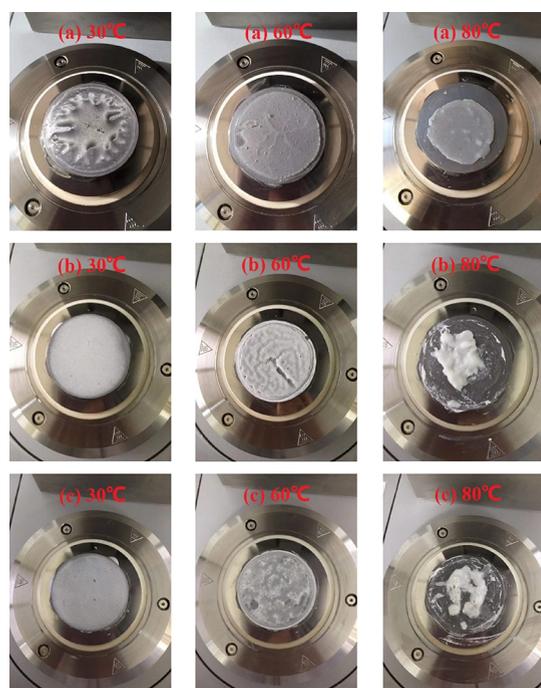


Figure 8. Phase transition states of each group of gel samples at 30, 60, and 80 °C in the rotational rheometer: (a) A-gel, (b) A_1B_2 thermosensitive hydrogel, and (c) A_1B_3 thermosensitive hydrogel.

cloudy gel was precipitated. It showed that the thermosensitive hydrogel had been transformed into a solid-like substance at this time, and the viscosity was greatly enhanced.

From the whole characterization test of temperature responsiveness, although all samples in three groups of gel characterized the properties of thermosensitive phase change, the A-gel was too viscous at low temperatures, and the substances generated after the phase change of A_1B_3 type thermosensitive hydrogel at 60 °C were looser and slightly flocculent. Therefore, after a comprehensive analysis, considering the sensitivity of temperature response, cost of material, and stability of the system, the A_1B_2 gel was more consistent with the expected effect of a stronger fluidity at the low

temperatures, a more sensitive temperature response, and a phase transition that occurred and aggregated at the high-temperature areas to form a plugged solid. At low temperatures, the gel system was a high water-containing compound, and the network structure formed a dense film with strong water retention, allowing the components of the gel to maintain chemical activity for an extended period; at high temperatures, the phase change of thermal polymerization generated substances, which could effectively plug the leaky pores. When the ratio of AB thermosensitive hydrogel is A:B = 1:2, the performance is the best, and the temperature response is the most sensitive.

3.5. Analysis of the Inhibitor Performance. Based on the temperature-programmed test, the CO concentration curves of the three coal samples during the oxidation process are shown in Figure 11. In Figure 11, the analysis shows that the volume fraction of CO of the three sets of curves increases with an increase in temperature. The rate of growth was slow before 120 °C and then rapidly increased. The trend of growth in the raw coal samples was the most obvious, and the amount of CO generated was also the largest. The curves of the two groups of inhibited coal samples were all below the curve of the raw coal samples, indicating that the inhibitor contained in the coal samples inhibited the oxidation process of coal to varying degrees. Among them, the thermosensitive hydrogel had the greatest effect of inhibition, reducing CO by 72.63% compared to the raw coal samples, whereas the inhibition coal samples of calcium chloride only decreased CO by 30.73%. It can be shown that the addition of thermosensitive hydrogel improves the activation energy of coal samples considerably and efficiently, inhibits the process of low-temperature oxidation of coal, and has strong flame retardant properties.

4. CONCLUSIONS

In this study, an AB-type mining thermosensitive hydrogel that inhibited the spontaneous combustion of coal was prepared by thermal polymerization with the polyethylene glycol as a water-absorbing monomer, and the flame retardant properties and temperature responsiveness of the gel were experimentally studied. The main conclusions are as follows:

- (1) A phase-changeable AB-type thermosensitive hydrogel, one new type of anti-extinguishing material, was prepared by compounding a variety of materials, which had good stability and could be divided into two components, A and B, for preparation and storage to prolong storage time. By comparing the viscosity performance when the gel was stable, it was determined that the optimal ratio of the A component was polyethylene glycol:methyl cellulose:sodium carboxymethyl cellulose:guar gum of 6:6:1.2:1.5, and the optimal ratio of the B component was bentonite:kaolin: $Mg(OH)_2$ = 2:1:1. When the two components were composited, the gel with the ratio of A:B of 1:2 had the best comprehensive performance; the low-temperature oxidation process in the TG experiment only reduced the weight by 6% when it acted on the coal sample; the generation of CO during the entire oxidation process of coal spontaneous combustion was greatly reduced; and the reduction was as high as 72.63%, with excellent flame retardant performance.
- (2) The AB-type thermosensitive hydrogel had a sensitive temperature response. Through analyzing the perform-

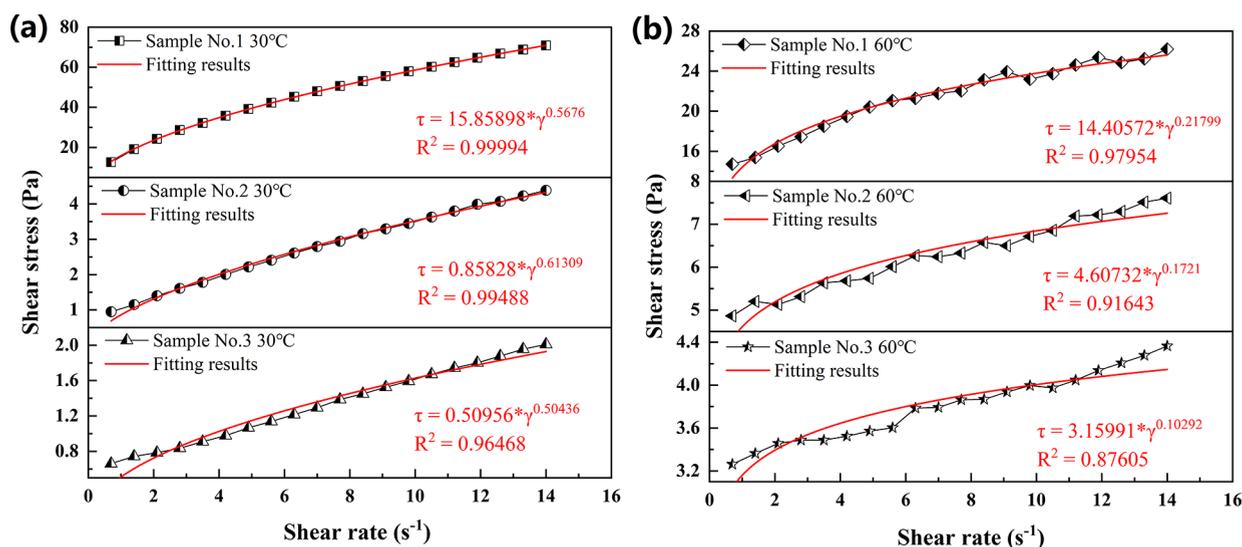


Figure 9. Rheology curves of samples: (a) rheological curve of 30 °C and (b) rheological curve of 60 °C.

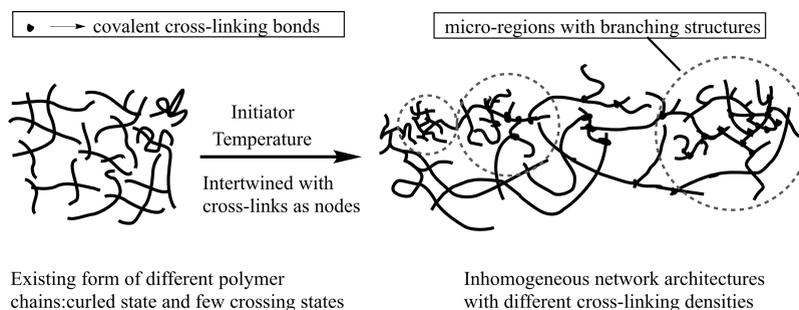


Figure 10. Changes of molecular chains during gelation.

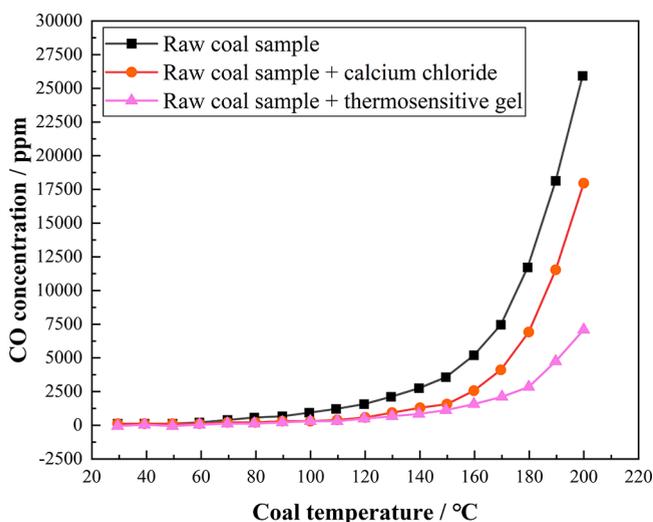


Figure 11. Changing curves of CO concentration during the oxidation process of coal samples.

ance of temperature response, the gel had good fluidity at low temperatures, which was convenient for pipeline transportation and could maintain anti-extinguishing activity for a long time; after the temperature rose to the low critical solution temperature, the volume-phase transition would occur, resulting in extremely viscous solid-like substances. At a shear rate of 0 s⁻¹, the

viscosity value of the same group of gels at 80 °C was as much as 11 times that of the viscosity at 30 °C, with a sharp increase in viscosity, thus realizing the effect of the aggregation of gels in the high-temperature zone, efficient fire prevention, and effective plugging of pores.

AUTHOR INFORMATION

Corresponding Author

Shuguang Jiang – Key Laboratory of Gas and Fire Control for Coal Mines, China University of Mining & Technology, Ministry of Education, Xuzhou, Jiangsu 221116, People's Republic of China; State Key Laboratory of Coal Resources and Safe Mining and School of Safety Engineering, China University of Mining & Technology, Xuzhou, Jiangsu 221116, People's Republic of China; orcid.org/0000-0002-3985-4340; Email: papperpublic@163.com

Authors

Hao Shao – Key Laboratory of Gas and Fire Control for Coal Mines, China University of Mining & Technology, Ministry of Education, Xuzhou, Jiangsu 221116, People's Republic of China; School of Safety Engineering, China University of Mining & Technology, Xuzhou, Jiangsu 221116, People's Republic of China

Zihang Wang – State Key Laboratory of Coal Resources and Safe Mining and School of Safety Engineering, China University of Mining & Technology, Xuzhou, Jiangsu 221116, People's Republic of China

Yue Zhang – State Key Laboratory of Coal Resources and Safe Mining and School of Safety Engineering, China University of Mining & Technology, Xuzhou, Jiangsu 221116, People's Republic of China

Xian Xi – Key Laboratory of Gas and Fire Control for Coal Mines, China University of Mining & Technology, Ministry of Education, Xuzhou, Jiangsu 221116, People's Republic of China; State Key Laboratory of Coal Resources and Safe Mining and School of Safety Engineering, China University of Mining & Technology, Xuzhou, Jiangsu 221116, People's Republic of China

Zhengyan Wu – State Key Laboratory of Coal Resources and Safe Mining and School of Safety Engineering, China University of Mining & Technology, Xuzhou, Jiangsu 221116, People's Republic of China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.2c07827>

Author Contributions

H.S. did the writing of the review & editing. Z.W. did the visualization, conceptualization, formal analysis, and writing of the original draft. S.J. did the supervision, funding acquisition. Y.Z. did the investigation and project administration. X.X. did the writing of the review & editing. Z.W. did the methodology.

Notes

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