

Fabrication and Characterization of a Novel Underground Mining Emulsion Explosive Containing Thickening Microcapsules

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Abstract: In order to solve the sloughing problem of explosives in upward blast holes, a novel underground mining emulsion explosive with thickening microcapsules was developed. The microcapsules in the emulsion explosive would be damaged by high-speed shearing at the moment of entering the blast hole, releasing their internal thickening agents to the emulsion explosive in the blast holes. These thickening agents were evenly distributed with a linear network structure in the emulsion explosive to make it thickened in the hole. The microcapsules were spherical and could encapsulate the thickening agent effectively, and the viscosity of the emulsion matrix with 2 mass % of them

was close to that of the reference emulsion matrix at ca. 127.9 Pa·s. Experimental results of TG-DSC and detonation performance showed that the novel underground mining emulsion explosive had a good thermal stability and its detonation velocity was 5133 ms⁻¹ and still up to 4618 ms⁻¹ after storing at the temperature of -20 °C for 12 h. The novel underground mining emulsion explosive with thickening microcapsules not only achieved the goal of thickening in the blast holes, but also had excellent detonation performance and low-temperature resistance capability.

Keywords: Upward hole · Emulsion explosive · Underground mine · Microcapsule · Thickening agent

1 Introduction

An emulsion explosive is one kind of industrial explosives developed in the 1960s, which has been widely used in engineering blasting for its excellent water resistance, safety and environmental protection [1,2]. Long-term open pit mining makes the strip mine resources scarce, so development of underground mining has become an inevitable trend in the future [3]. The block caving method is commonly used in underground mining, and the depth of upward blast holes has reached more than 40 m to improve the mining efficiency. The underground mining emulsion explosives not only should satisfy the fluidity for the pumping process but also ensure the adhesion after injecting into the blast hole [4]. However, the fluidity and adhesion of emulsion explosives are mutually restrictive under normal conditions. When the emulsion explosive is required to have good fluidity, the friction between emulsion explosives and the conveying pipe wall should be small, but its adhesion would be low in the blast hole. While if the emulsion explosive is designed with strong adhesion, it would seriously affect the pumping effect in spite of attaching well to the wall of blast hole. In addition, the viscosity of the emulsion explosive would increase and crystallisation would occur when the temperature drops to -20 °C, so low-temperature is also one of the problems faced by emulsion explosives in underground mining.

In order to reduce the viscosity of emulsion explosives, Zhang et al. [5,6] tested the viscosity of emulsion explosives prepared with different emulsifiers and shear rates, and concluded that the viscosity of an emulsion explosive developed with Span-80 and low shear rate was relatively low. Wang et al. [7] studied the influence of emulsifier structure and function on the viscosity of emulsion matrix, and the results showed that an emulsion matrix containing imine/amide functional emulsifier had a high viscosity at room temperature but a better fluidity at a higher temperature. Ashok et al. [8] suggested that the viscosity of emulsion explosives decreased with the decreasing content of water

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(dispersed phase) and increased with the rising viscosity of oil (continuous phase) in a certain range, and then it varied inversely with the average particle size of the emulsion matrix. In order to improve the pumping capacity of emulsion explosives, researchers adopted a new technology called "core-annular flow" [9], that is, during the transportation of emulsion explosive in the pipe, water with foaming agent was transported between the pipe wall and emulsion explosive, so that the water layer separated the emulsion explosive from the pipe wall to reduce the friction. However, the addition of superfluous water would significantly reduce the explosion power [10]. In the process of blasting construction in the winter, the viscosity and detonation performance of emulsion explosives with high water content were significantly affected by low-temperature. Ganguly et al. [11] studied the freezing behaviors of emulsion explosives at a low temperature, and the results showed that the freezing behavior of emulsion explosives was mainly affected by electrolyte concentration, surfactant concentration and physico-chemical characteristics of the surfactant. Smith et al. [12] added polymers of liquid state or solid state with good particle dispersion in the oil phase, so that the emulsion explosive had a better stability and detonation performance at -17°C .

Microencapsulation technology refers to encapsulating the functional materials in micro-containers, which could regulate and control the release rate, the time of volatilization and dissolution, and isolation of functional materials from the environment. It has a great potential in the fields of biological, medical, agriculture and chemical industry, etc [13,14]. Sodium polyacrylate is a thickening agent to improve the viscosity of water-based systems by forming a three-dimensional network structure as a result of interacting with water, and it could significantly increase the viscosity of the system with a small quantity [15]. Alginates are widely used as the shell material to form microcapsules, and sodium alginate could react with Ca^{2+} to form microcapsules with high mechanical strength and elasticity under mild conditions [16]. Therefore, in this study, sodium polyacrylate was encapsulated in a microcapsule of calcium alginate shell and added into the emulsion explosive. The addition of microcapsules did not affect the viscosity of the emulsion explosive in the pumping process, but these microcapsules would be damaged by high-speed shearing at the moment of leaving the pipe nozzle, which could achieve the goal of thickening the emulsion explosive in the blast hole. In addition, the stability and low-temperature resistance of the novel underground mining emulsion explosive could be enhanced by improving the formula of on-site mixed emulsion explosive, which ensured the normal

use of emulsion explosives in the long-distance pipeline transportation and low-temperature environment.

2 Experimental

2.1 Materials

Ammonium nitrate (NH_4NO_3 , 99%) and sodium nitrate (NaNO_3 , AR) were purchased from Anhui Huaihua Group Co., Ltd, China. Polyisobutylene succinimide (T155, AR) was purchased from Chengdu Huaxia Chemical Reagent Co., Ltd, China. Diesel oil ($\text{C}_{12}\text{H}_{26}$) and engine oil were purchased from Sinopec group. Carbamide ($\text{CH}_4\text{N}_2\text{O}$, AR), Span-80 ($\text{C}_{24}\text{H}_{44}\text{O}_6$, CP), sodium alginate (SA, AR), calcium chloride (CaCl_2 , AR) and sodium polyacrylate (PAAS, AR) were purchased from Shanghai Macklin Biochemical Co., Ltd, China. The bulk density and average particle size of glass microballoons (GMs) were 0.25 g cm^{-3} and $55\text{ }\mu\text{m}$, respectively, purchased from Minnesota Mining and Manufacturing Company of USA. Deionized water was produced in the laboratory.

2.2 Preparation of the Novel Underground Mining Emulsion Explosive

The emulsification process of the emulsion matrix was conducted in a shearing mixer of 100 g per batch (AM300-H, Shanghai Angni instrument Co., Ltd, China). Firstly, 68 g NH_4NO_3 , 8 g NaNO_3 , 2 g $\text{CH}_4\text{N}_2\text{O}$ and 15 g H_2O were mixed and heated to 105°C to form the dispersed phase, and 3.11 g $\text{C}_{12}\text{H}_{26}$, 1.55 g engine oil, 1.17 g $\text{C}_{24}\text{H}_{44}\text{O}_6$ and 1.17 g T155 were mixed evenly and heated to 90°C to form the oil phase. Then, the oil phase was sheared in the mixer at a speed of 1200 r min^{-1} , and the dispersed phase was added into the oil phase slowly at the same time. Finally, the underground mining emulsion matrix (emulsion matrix I) was prepared by stirring the mixture for 2 min. The mass ratios of raw materials of emulsion matrix I are listed in Table 1.

2.3 Preparation of the Thickening Microcapsule

The preparation process of the thickening microcapsule was divided into three steps (Figure 1). Firstly, 0.4 g SA and 0.2 g PAAS were dissolved into 20 g H_2O and stirred evenly to form a viscous thickening agent, and bubbles in the thickening agent were removed under ultrasonic action for 1 h. Then, a certain amount of thickening agent was ab-

Table 1. Composition of an novel underground mining emulsion matrix.

Component	NH_4NO_3	NaNO_3	H_2O	$\text{CH}_4\text{N}_2\text{O}$	$\text{C}_{12}\text{H}_{26}$	Engine oil	$\text{C}_{24}\text{H}_{44}\text{O}_6$	T155
Mass Ratio (%)	68	8	15	2	3.11	1.55	1.17	1.17

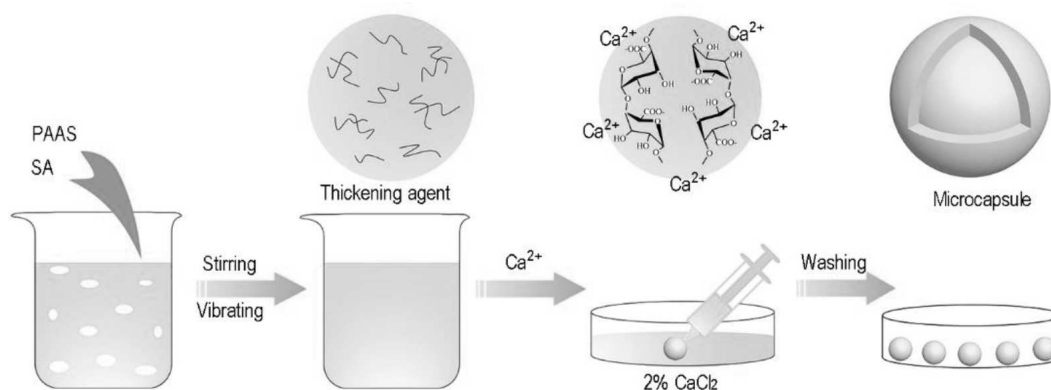


Figure 1. Schematic diagram for the preparation of thickening microcapsules.

sorbed with a syringe, and slowly dropped into a culture dish containing 2% CaCl_2 solution with the help of a thin slice. Next, SA in the thickening agent reacted with Ca^{2+} in the CaCl_2 solution to form the calcium alginate shell, and then these microspheres were quickly removed from the CaCl_2 solution. The superfluous CaCl_2 solution on the surface of microspheres was washed with deionized water and microcapsules encapsulating the thickening agent were obtained at last. In the future, the production of thickening microcapsules can be scaled up by a capsule encapsulation machine, which is widely used in the pharmaceutical industry.

As shown in Figure 2, when charging the upward blast holes in the underground mine, an emulsion explosive with thickening microcapsules was pumped through a rubber hose to the blast hole. During the pumping process, the microcapsules were intact and had no harmful influence on the stability and viscosity of the emulsion explosive, but when reaching the point of the pipe nozzle, they would be damaged by high-speed shearing action and then released

the thickening agent to the emulsion explosive. As a result, the viscosity of emulsion explosive was enhanced when it reached the blast hole, which could solve the sloughing problem of explosives in upward blast holes.

2.4 Characterization

The microstructure changes of emulsion explosive before and after thickening with microcapsules were observed by an optical microscope (OM, 3A43L, SAGA), and its viscosity varying with temperature and time were tested using a digital display and rotary viscometer (RVDV-1). The thermal property and low-temperature stability of the novel underground mining emulsion explosive were tested by a low temperature storage tank at -20°C and a thermogravimetric analyzer (Mettler Toledo TGA/DSC 2+, Switzerland), respectively. The detonation performance of emulsion explosives before and after thickening as well as at low-temperature were tested by lead column compression, detonation velocity and air explosion experiments.

3 Results and Discussion

3.1 Microstructure Characterization

Figure 3a-c are macroscopic pictures of spherical thickening microcapsules and emulsion matrix before and after thickening, respectively, and Figure 3d-f are their corresponding microscopic images. Figure 3d shows that calcium alginate shell formed on the surface of microcapsules with a particle size of about 2 mm. As shown in Figure 3b, the structural strength of the microcapsule shell was strong enough to be preserved completely in the emulsion matrix, and Figure 3e shows that the emulsion matrix with microcapsules was dispersed evenly without crystallization, which indicates that the microcapsules had no bad effect on the stability of the emulsion matrix. Figure 3c shows the macroscopic picture

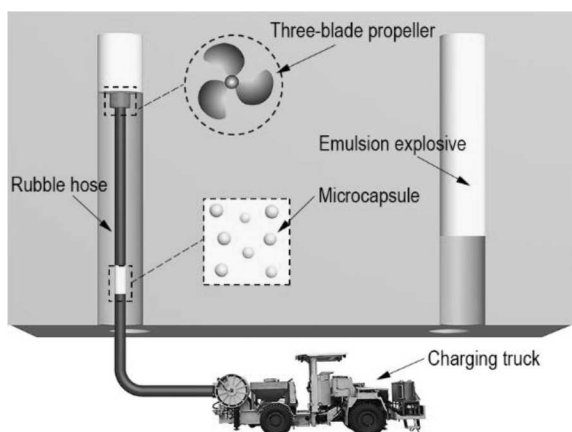


Figure 2. Schematic diagram for novel underground mining emulsion explosive pumping.

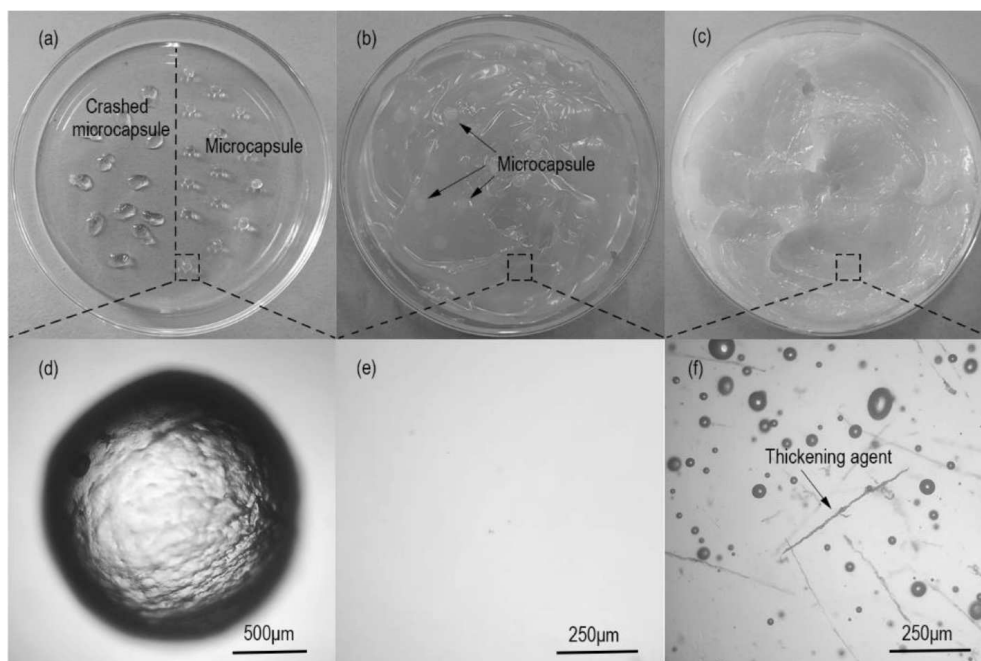


Figure 3. Macroscopic and microscopic images: (a, d) thickening microcapsules; (b, e) emulsion matrix before thickening; (c, f) emulsion matrix after thickening.

of the emulsion matrix with microcapsules after high-speed shearing, and Figure 3f illustrates that the thickening agents were distributed in the emulsion matrix in a linear network structure. Droplets of oil-in-water structure of emulsion matrix were connected with the filamentous thickening agent, which formed a three-dimensional network structure to fix the location of these droplets, so the viscosity of the thickened emulsion explosive increased.

3.2 Effects of Thickening Microcapsule on the Viscosity of Emulsion Matrix

As shown in Figure 4a, the viscosity of emulsion matrix with microcapsules before shearing all decreased with increasing temperature, and the viscosity of the emulsion matrix was 49.6 Pa s at the room temperature and 96.9 Pa s at the temperature of -20°C . Figure 4b shows that the viscosity of emulsion matrix increased with the rising content of thickening microcapsules after shearing at the same temper-

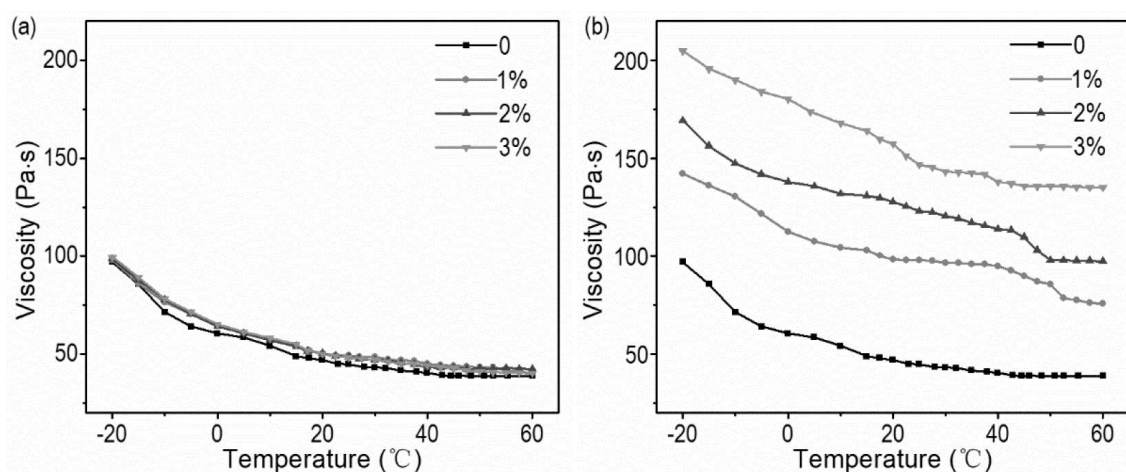


Figure 4. Viscosity-temperature curves of an emulsion matrix with different mass ratios of microcapsules: (a) emulsion matrix before thickening; (b) emulsion matrix after thickening.

ature, and the viscosity of emulsion matrix with microcapsules after shearing also decreased with increasing temperature.

Figure 5 shows the viscosity change of emulsion matrices with different mass ratios of thickening agents before and after shearing with time, and the viscosity of each sample was measured once per hour at room temperature. Figure 5a shows that the viscosity of emulsion matrices with different ratios of microcapsules before shearing were nearly the same at equal time intervals and did not change significantly with time, which indicated that the microcapsules had a good encapsulation effect during pumping. As shown in Figure 5b, the viscosity of emulsion explosive with various amounts of microcapsules after shearing all changed inconspicuously with time, which illustrated that the thickening effect of microcapsules would be very stable in the blast holes, in addition, the viscosity of emulsion matrix after shearing increased with the rising amount of thickening microcapsules.

A traditional emulsion matrix (emulsion matrix II) contains about 2 mass% of paraffin wax, which is nearly in a solid state at room temperature. Although the viscosity of traditional emulsion explosives did not meet the pumping requirements, it could achieve a stable adhesion in the upward hole. In order to determine the optimum content of microcapsules of the novel underground mining emulsion explosive, emulsion matrix II was prepared as a reference (see Table 2) and its viscosity was 132 Pa·s. As shown in Figure 5, when added with 2 mass% of thickening microcapsules, the viscosity of novel underground mining emul-

sion explosive after thickening was 127.9 Pa·s, which was close to the viscosity of emulsion matrix II. In addition, its viscosity before thickening was only 50.2 Pa·s and suitable for the pumping. Therefore, the content of microcapsules added into the novel underground mining emulsion explosive was determined to be 2 mass%.

In conclusion, the microcapsules had a good encapsulation effect in the pumping process, which would not affect the viscosity of the novel underground mining emulsion explosive and meet the requirements of pumping. When the emulsion explosive reached the blast hole, the thickening agent in the microcapsules could achieve the goal of sticking the emulsion explosive in blast holes. The viscosity of the novel underground mining emulsion explosive before and after shearing both increased with the decreasing temperature, which affected the pumping process but were beneficial to the adhesion of explosive in the upward hole. Comparison of experimental results showed that the viscosity of the novel underground mining emulsion explosive would meet the requirement of upward blast holes if the amount of the thickening microcapsules in it was 2 mass%.

3.3 Thermal Properties

The thermal stability of the emulsion explosive samples were studied by a thermogravimetric analyzer (Mettler Toledo TGA/DSC 2+, Switzerland) with a heating rate of 5 °C min⁻¹. Figure 6a shows that the explosive samples exhibited two stages of weight loss: the first stage was the

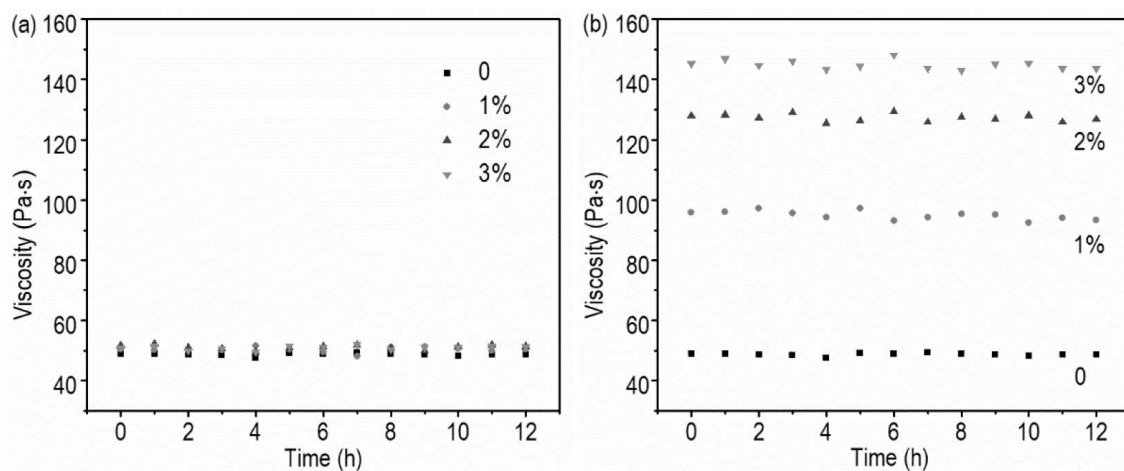


Figure 5. Viscosity-time curves of an emulsion matrix with different mass ratios of microcapsules: (a) emulsion matrix before thickening; (b) emulsion matrix after thickening.

Table 2. Composition of emulsion matrix II.

Component	NH ₄ NO ₃	NaNO ₃	H ₂ O	C ₁₂ H ₂₆	C ₁₈ H ₃₈	C ₂₄ H ₄₄ O ₆	T155
Mass Ratio (%)	75	8	10	2	2	1.5	1.5

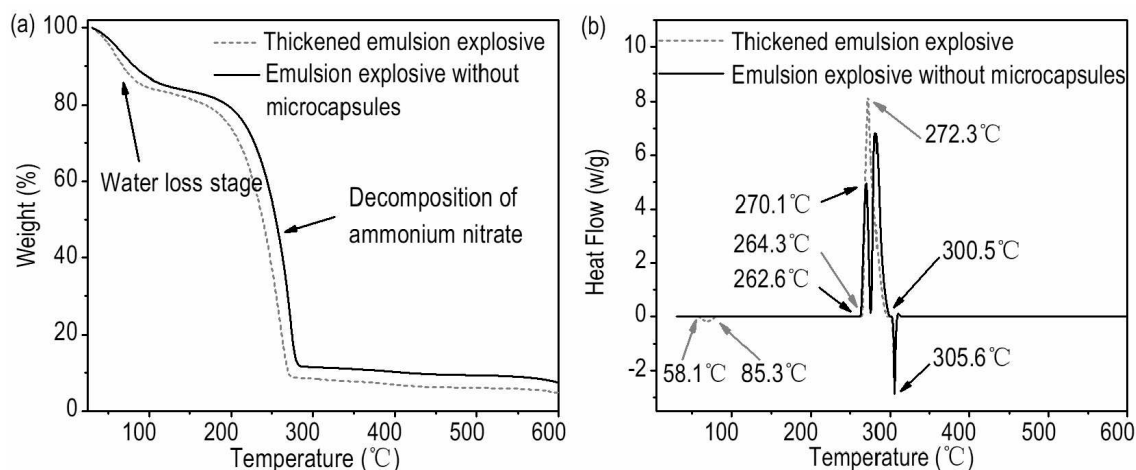


Figure 6. Thermal stability of emulsion explosive samples: (a) TG curves; (b) DSC curves.

evaporation of water in emulsion explosive below 120°C with an approximately 14.5 mass% of weight loss. In addition, the weight loss of the thickened emulsion explosive was larger than that of emulsion explosive without microcapsules due to the evaporation of water in the thickening agent. The second stage of weight loss was from 120 to 280°C corresponding to the weight loss of ammonium nitrate, and then no obvious weight loss of the samples was observed. Figure 6b illustrates that the initial thermal decomposition temperature and exothermic peak temperature of emulsion explosive without microcapsules were 262.6 and 270.1°C, respectively, while 264.3 and 272.3°C for thickened emulsion explosive, respectively. The initial thermal decomposition temperature and exothermic peak temperature of the emulsion explosive after thickening only increased 1.7 and 2.2°C, respectively, and the endothermic peak temperatures were both concentrated at about 305.6°C. Therefore, the thermal stability of emulsion explosive before and after thickening was basically the same.

3.4 Explosion Performance Experiments

3.4.1 Sample Preparation

The energy of emulsion explosive could reach the maximum when the mass ratio of GMs and emulsion matrix was

4:96 [17], and a GMs sensitized emulsion explosive was used as the reference explosive in the experiments. The formulations of emulsion explosive samples are presented in Table 3. The compositions of the novel underground mining emulsion matrix (emulsion matrix I) and the traditional emulsion matrix II are presented in Tables 1 and 2, respectively. It needs to be noticed that Sample A₃ used in the following experiments was thickened (after shearing) to simulate its utilization in blast holes.

3.4.2 Lead Column Compression Experiments

The lead column compression value is an important parameter to evaluate the detonation performance of an emulsion explosive, which can be measured by the lead column compression method, and the diameter and length of the initial lead columns were 40 and 60 mm, respectively. Because of the high water content and low detonator sensitivity of the novel underground mining emulsion explosive, 45 g of tested emulsion explosive should be added with 5 g of passivated RDX as the primary explosive, as shown in Figure 7. Passivated RDX was composed of bulk RDX and paraffin with a mass ratio of 100:5, and its charge density was 1.65 g cm⁻³. The primary explosive and the emulsion were cylindrical and encapsulated by a polyethylene plastic bag. It is worth noting that the compression value of the

Table 3. Different formulations of emulsion explosives.

Sample	Emulsion matrix I, (mass%)	Emulsion matrix II, (mass%)	GMs, (mass%)	Microcapsule (mass%)	storing time at -20°C, (h)
Sample A ₁	0	96	4	0	0
Sample A ₂	96	0	4	0	0
Sample A ₃	94	0	4	2	0
Sample A ₄	96	0	4	0	12

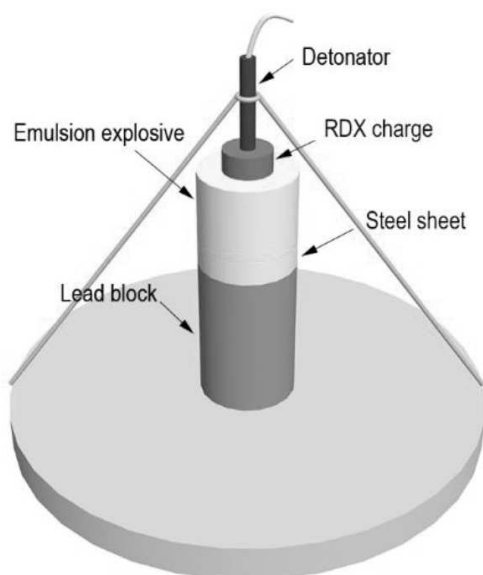


Figure 7. Schematic diagram of lead column compression test.

lead column in this study was a relative value (not a standard value) to assess the brisance of emulsion explosives, and a larger compression value meant a higher explosion power. Each explosive sample was tested at least three times and the average compression value of the lead column was obtained.

3.4.3 Detonation Velocity Measurement

Detonation velocity is an very important detonation parameter that is defined as the propagation velocity of detonation wave in an explosive. The detonation velocity of of emulsion explosives were measured with electric probes (as shown in Figure 8). The emulsion explosive was filled into a poly vinyl chloride (PVC) tube with the diameter and length

Table 4. Detonation parameters of four types of emulsion explosives.

Sample	Density, (g cm^{-3})	lead column compression values, (mm)	Detonation velocity, (m s^{-1})
Sample A ₁	1.18	18.5 ± 0.4	5176 ± 32
Sample A ₂	1.12	18.1 ± 0.6	5133 ± 37
Sample A ₃	1.10	17.6 ± 0.9	5030 ± 63
Sample A ₄	1.12	17.0 ± 0.5	4618 ± 52

of 40 and 400 mm, respectively. An emulsion explosive (Sample A₁) with a higher power was used as the primary explosive and its mass was 50 g. In order to reduce the influence of primary explosive on the novel underground mining emulsion explosive, the distance between the primary explosive and the first electric probe was over 16 cm. Furthermore, the distance between the adjacent probes was 50 mm and there were four electrical probes in total.

3.4.4 Experimental Results and Analysis

Figure 9 shows the compression results of lead columns compressed by different kinds of emulsion explosive samples, and from left to right, they were uncompressed lead column, lead column compressed by Sample A₁, A₂, A₃ and A₄. As shown in Table 4, the lead column compression values of Sample A₁, A₂ and A₃ were 18.5, 18.1 and 17.6 mm, respectively, and their detonation velocity were 5177, 5133 and 5030 m s^{-1} , respectively.

This shows that a higher content of water would reduce the explosion power of the emulsion explosive. While compared to Sample A₂, the lead column compression value and detonation velocity of Sample A₃ were only reduced by 0.5 mm and 103 m s^{-1} , respectively, which indicated that the addition of the thickening agent had little impact on the explosion power of emulsion explosive. In addition,

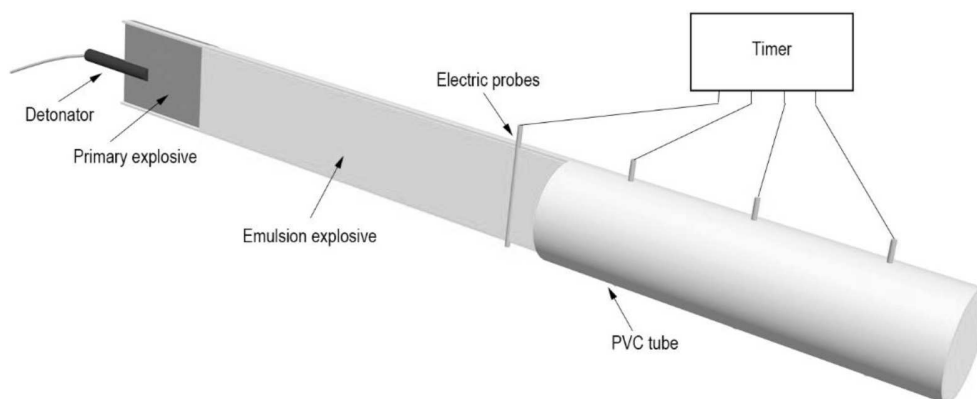


Figure 8. The schematic diagram of detonation velocity test apparatus.

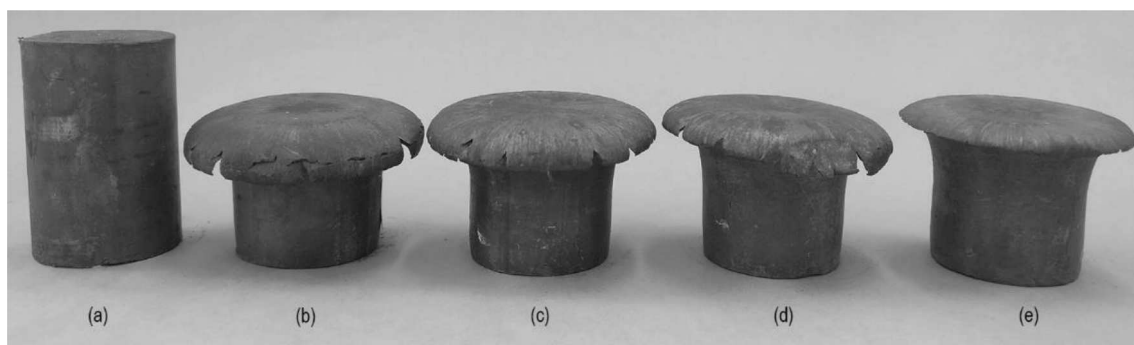


Figure 9. Lead column compression experimental results of four types of emulsion explosives.

compared to Sample A₂, the lead column compression value and detonation velocity of Sample A₄ (stored at the temperature of -20°C for 12 h) only decreased respectively by 1.1 mm and 515 ms^{-1} , which indicated that the novel underground mining emulsion explosive had an excellent low-temperature resistance performance.

3.5 Air Blast Experiments

The air explosion peak pressure and positive pressure duration are required parameters to assess the potential destructive effect of shock waves. In the experiments, 5 g of passivated RDX were used as the primary explosive and 45 g of emulsion explosive were used as the tested explosive, and they were wrapped by a polyethylene plastic film to be a spherical explosive charge. It is worth noting that the explosion parameters in this study were relative values (not standard values) to assess the power of emulsion explosive with the use of passivated RDX. As shown in Figure 10, the air blast experiments were carried out in an explosion vessel (partially open) with the diameter of 3 m and volume of 25 m^3 , and the center of the explosive

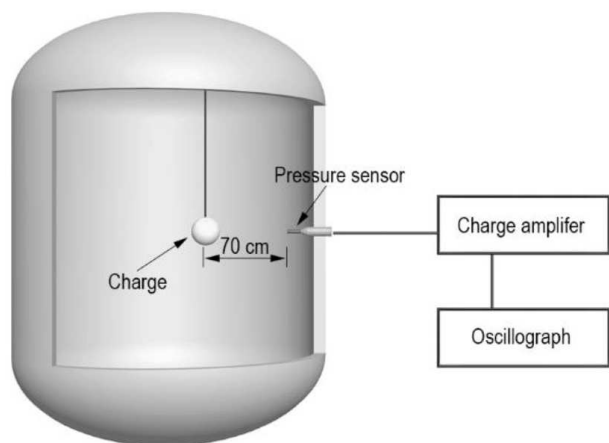


Figure 10. Air explosion testing device of emulsion explosives.

charge was 70 cm away from the pressure sensor (CY-YD-202, Jiangsu lianneng Electronic Technology Co., Ltd, China). The experimental data was enlarged 300 times by a charge amplifier and recorded by a digital storage oscilloscope.

In order to obtain the peak pressure, the optimum curve was drawn by the least square method and extrapolated to the zero time [18]. Figure 11 shows the typical shock wave pressure-time curves of the three different explosive samples, and Table 5 shows that the values of shock wave peak pressure from the largest to the smallest were Sample A₃, A₄ and A₂. The shock wave peak pressure of Sample A₃ was larger than that of Sample A₂, indicating that the addition

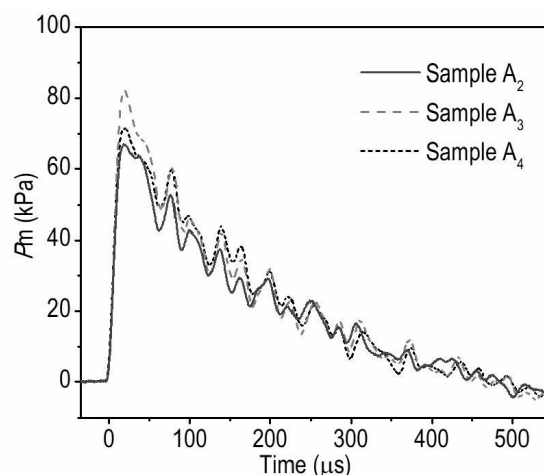


Figure 11. Pressure-time curves of three types of emulsion explosives in air explosion.

Table 5. Air blast parameters of three types of emulsion explosives.

Sample	L, (cm)	t_{+r} (μs)	$P_{m'}$ (kPa)
Sample A ₂	70	468.2	67.2
Sample A ₃	70	462.8	82.1
Sample A ₄	70	484.7	71.6

of thickening agent could improve the peak pressure of emulsion explosive to some extent. This phenomenon also happened in Sample A₄ when compared with Sample A₂, which indicated that low-temperature would also improve the peak pressure of emulsion explosive under certain conditions. The possible reason for this phenomenon was that the different physical state of water in the emulsion matrix (the total of water content in each sample was nearly the same), the addition of thickening agent or freezing treatment would change the phase of water in the emulsion matrix from liquid to solid, which would enhance the constraint on the emulsion explosive samples, thus the peak pressure of shock waves increased. The positive duration of pressure curve is an important index directly reflecting how long the damaging forces are applied [18]. The positive duration of Samples A₂ and A₃ were approximately equal, which indicated that the addition of a thickening agent had a small impact on the damaging forces duration of emulsion explosive. However, Sample A₄ (stored at the temperature of -20°C for 12 h) had the longest positive duration (484.7 μs), which illustrated that a low-temperature environment increased the damaging forces duration of emulsion explosives.

4 Conclusions

A novel underground mining emulsion explosive was prepared by adding thickening microcapsules into an emulsion matrix. The addition of microcapsules did not affect the viscosity of the emulsion explosive in the pumping process, but these microcapsules would be damaged by high-speed shearing at the moment of leaving the pipe nozzle, which could achieve the goal of thickening the emulsion explosive in the blast hole. The viscosity of the novel underground mining emulsion explosive added with 2 mass% thickening microcapsules was 50.2 Pa s in the pumping process, which suggested that the novel underground mining emulsion explosive had a good fluidity and stability to meet the requirement of long-distance transportation in pipelines. Compared to Sample A₂, the lead column compression value and detonation velocity of the novel underground mining emulsion explosive (Sample A₃) after shearing were only reduced by 0.5 mm and 103 m s^{-1} respectively, while its viscosity increased by 1.58 times, which indicated that a small amount of thickening microcapsules could significantly improve the viscosity of emulsion explosives with little negative effect on the detonation performance. The thickening function of microcapsules took effect after they were injected into the blast holes (after shearing), which solved the contradiction between fluidity in pumping process and adhesion in blast holes of traditional emulsion explosive.

The viscosity of emulsion matrix with microcapsules before and after shearing both decreased with increasing temperature. The microcapsules had a good encapsulation effect during pumping and the thickening effect of the

microcapsules after shearing would be very stable in the blast holes, and the viscosity of emulsion matrix after shearing increased with the rising amount of thickening microcapsules. Moreover, TG-DSC experimental results showed that the thermal stability of the novel underground mining emulsion explosive was basically the same before and after the thickening. The air blast experiments illustrated that the addition of thickening agent and low-temperature environment could improve the shock wave peak pressure of emulsion explosives to a certain extent due to the water phase change. Meanwhile, compared with the normal temperature, the detonation velocity and lead column compression value of the novel underground mining emulsion explosive stored at the temperature of -20°C for 12 h were only reduced by 10 and 6.1 %, respectively, which indicated that the novel underground mining emulsion explosive had a good low-temperature resistance performance.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Nos. 11972046 and 51801202), Open Project Foundation of CAS Key Laboratory of Mechanical Behavior and Design of Materials (NO. Imbd201701), China Postdoctoral Science Foundation (2017M610381 and 2019M651085), and Anhui University of Science and Technology Postgraduate Innovation Fund (2019CX2056), and the authors would like to thank these foundations for the financial support.

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Manuscript received: October 15, 2019

Revised manuscript received: January 17, 2020

Version of record online: February 26, 2020