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Process Optimization of Supercritical CO_2 Foamed SF-3 Double-Base Propellant

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Abstract: The supercritical CO_2 foaming process is a preferable way to treat deserted SF-3 propellants and solves problems of environmental pollution and waste of resources related to conventional treatment methods, and this process is an environmentally friendly method. In this paper, the effect of process conditions, including the immersion time of deserted SF-3 propellants in the supercritical CO_2 fluid, on the appearance of SF-3 propellants and detonation performance of the perfusion explosive made from SF-3 propellants are mainly studied. The results show that the diameter of foamed SF-3 propellants increases with the immersion time when the immersion time is less than 60 min. When the immersion time is 60 min, the performance of the perfusion explosive made from foamed SF-3 propellants is the best. The highest detonation velocity is 6683 $m\,s^{-1}$, and the corresponding shock wave energy is 1.02 $kJ\,g^{-1}$. When the immersion time is more than 60 min, the detonation velocity and the shock wave energy of the perfusion explosive made from foamed SF-3 propellants decreases with the increase of the immersion time.

Keywords: SF-3 double-base propellants · supercritical CO_2 · foaming process · perfusion explosive

1 Introduction

The SF-3 double-base propellant is a propellant widely used in world artillery ammunition. It is a double-base propellant containing nitrocellulose (NC), nitroglycerin (NG), dinitrotoluene (DNT) and dibutyl phthalate (DBP). In the past, many countries produced and stored a large amount of SF-3 propellants for future use. As time passes, the stored SF-3 propellants have expired and need to be handled. The treatment of deserted SF-3 propellants has attracted attentions of scholars from world. Conventional treatment methods mainly include incineration and deep well landfill. In many other methods, for example, deserted SF-3 propellants are used in manufacture of chemical raw materials [1], microbial degradation and supercritical water oxidative hydrolysis [2] and so on. These treatment methods all waste resources and pollute the environment [3]. Deserted SF-3 propellants have also been used as main raw materials for civilian explosives [4]. When an SF-3 propellant burns, it has disadvantaged that energy cannot be completely released, and a large amount of black smoke is generated [5–7]. Therefore, it is extremely important to find a treatment method enabling effective utilization of the deserted SF-3 propellants.

P. Wang [8] used a perfusate-containing liquid to fill voids of an SF-3 propellant to obtain an excellent perfusion explosive. J Biegańska [9] presents concerning a cost-efficient and environmentally friendly method of utilization of the nitrocellulose powders extracted from expired ammunition. D. Zhang [10] carried out supercritical CO_2 foaming on a deserted SF-3 propellant, and then infused it with an acrylamide monomer to prepare a perfusion explosive. X.A. Wei [11] preliminarily discussed the preparation process of preparing perfusion explosives from foamed SF-3 propellants and properties of the explosives, which proved that the foaming process can improve the utilization rate of deserted SF-3 propellants. A foamed propellant [12] has a larger burning area and a higher detonation wave velocity than ordinary propellants, and thus foaming of the deserted SF-3 is an effective way to use it. D. Zhang [10] conducted a detailed study on the supercritical CO_2 foaming process of deserted SF-3 propellants, and found that the immersion time and water bath temperature are important factors affecting the performance of SF-3 propellants. The performance of the sample immersed for 120 min was the best. When the immersion time was more than 120 min, the performance of the perfusion explosive made from foamed SF-3 was degraded. However, we did not know the performance of the sample immersed for less than 120 min. In order to better industrialize this process, it is necessary to find the optimal immersion time. In this paper, the appearance and properties of deserted SF-3 immersed for less than 120 min are studied to determine the optimal immersion time and industrialize the process.

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Table 1. Process parameters of the foaming process.

Process parameters	Description	Value
Immersion time	Residence time in the CO_2 pressure vessel	10, 30, 60 and 120 min
Immersion temperature	Temperature in the CO_2 pressure vessel	40 °C
Immersion pressure	CO_2 pressure in the pressure vessel	10 MPa
Foaming temperature	Temperature of the foaming bath	70 °C

2 Experimental

2.1 Preparation of Foamed SF-3 Propellants

In this experiment, an intermittent foaming process was used to foam the SF-3 propellants. The specific process is shown in Figure 1. First, the temperature of the supercritical CO_2 High-pressure vessel was set, and the SF-3 propellant to be foamed was placed in a High-pressure vessel. After the reaction temperature reached the set temperature, the CO_2 pump and the CO_2 cylinder were turned on, to introduce CO_2 into the High-pressure vessel. After the pressure in the High-pressure vessel reached the specified value, the CO_2 pump and the CO_2 cylinder were closed. When CO_2 in the high-pressure vessel turned into a supercritical state, the onset time of immersion was recorded. At this point, the SF-3 propellant began to foam and CO_2 slowly dissolved into the SF-3 propellants. After saturation for a certain period of time, the high-pressure vessel exhaust valve was opened, and the SF-3 sample was quickly taken out of the high-pressure vessel. The sample was placed in a water bath at 70 °C, at which time the supercritical carbon dioxide was in a low-pressure and high-temperature environment. CO_2 would rapidly expand and escape from the SF-3 propellant, leaving a large number of voids inside the SF-3 propellant. Then the foamed sample was placed in an oven at 50 °C to remove water remained.

The parameter conditions during the foaming process, including the pressure and temperature in the high-pressure vessel, the time of supercritical CO_2 dissolution, and the temperature of the final hot water in foaming, have great effects on the performance of the SF-3 propellant. In this paper, the effect of foaming time on the performance of the SF-3 propellant was studied, and the relationship between the immersion time and product performance was explored. Other conditions of the foaming process are shown in Table 1.

2.2 Preparation of Perfusion Explosive

The experimental procedure is shown in Figure 2. The foamed SF-3 propellant was cut into granular explosives with a length of 15 mm, and then these explosives were placed in a cylindrical mold having a diameter of 5 cm and a height of 10 cm. A small amount of a cross-linking agent was dissolved in hot water at 50 °C, and then sodium nitrate, ammonium nitrate and urea were added in proportion to the cross-linking agent solution and stirred well. Subsequently, a retarder and an initiator were added in small amounts and stirred uniformly, and then the mixture was poured into the mold, until voids of the SF-3 propellants were filled up with the solution. After the solution in the mold was solidified, the preparation of the perfusion explosive was completed.

2.3 Structural Characteristics of Foamed SF-3 Propellant

The diameter of the foamed SF-3 was measured with a Vernier Caliper, and the sample before and after the foaming was compared. The cross section of the sample was observed with a scanning electron microscope (JEOLJSM-6380LV, Japan Corporation) to compare the effect of the immersion time on the cross section of the sample.

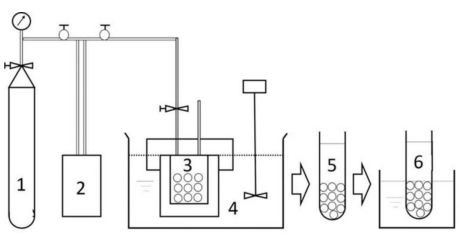

Figure 1. Schematic diagram of supercritical CO_2 foaming of SF-3 propellant [11]. 1.CO_2 cylinder 2.CO_2 pump 3.High-pressure vessel 4. Water bath 5.Saturated sample 6.Water bath.

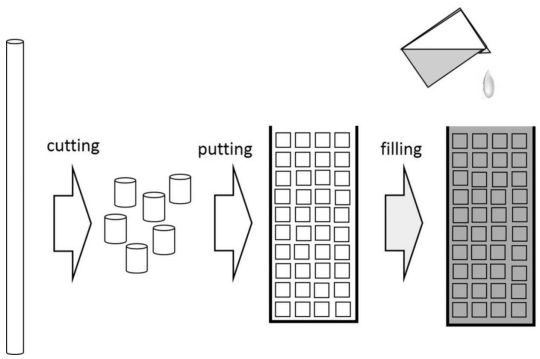

Figure 2. Preparation process of perfusion explosive [11].

2.4 Detonation Velocity Test

Detonation velocity refers to the velocity at which detonation waves propagate stably in explosives and is an important parameter of detonation waves. For industrial explosives, detonation velocity is an important parameter to reflect their performance. The detonation velocity can also be used to derive many other detonation parameters of the explosive, and thus the detonation velocity is an important manifestation of the performance of the explosive. The detonation velocity depends mainly on the nature of the explosive and on the particle size, packing density and water content of the explosive. In this experiment, the detonation velocity was tested by the ion probe method, and the multi-channel digital chronograph was used for timing.

2.5 Witness Board Explosion Experiment

In order to test the detonation performance of the perfusion explosive made from foamed SF-3 more intuitively, a detonation reaction of foamed SF-3 was used to carry out the steel plate impact experiment. The experimental device is shown in Figure 3. A test board (steel A3, 200 mm*200 mm*12 mm) was placed horizontally at a height of 10 cm above the cement floor. Then, an 8# industrial detonator was used as a detonating tool and a passivated RDX (40 g) was used as a booster explosive to start the experiment. After the experiment, the diameter of the blast void was measured and the performance of the samples was compared.

2.6 Confocal Raman Imaging Analysis

In order to study the distribution of propellants in foamed samples more clearly, concentrations of propellants were measured by confocal Raman imaging. In Raman imaging, electromagnetic waves of a certain wavelength act on molecules of the substance to be tested, giving a molecular absorption spectrum with a wavelength within the ultraviolet-visible region. The transition of the electronic energy level is accompanied by the transition of the vibrational energy level and the rotational energy level. The relationship between the intensity of the Raman band and the object tested follows Beer's law, and thus the sample concentration can be measured by Raman imaging. A confocal Raman microscope of WITec alpha 300R, with a 50× Raman objective, an excitation wave number of 532 nm, and a laser power of 2.5 mw, was used in the experiment. The measurement was performed by dividing the sample into outer, middle and inner regions along its radial direction, scanning the surface of each region corresponding to an area of 30*30 um by the surface scanning method and calculating the propellant concentrations. Figure 4 shows the Raman confocal scanning regions of the sample immersed for 10 min.

3 Results and Discussion

3.1 Structural Characteristics of the Foamed SF-3 Propellant

In the sample immersed in supercritical CO_2 for 10 min, a small number of voids were found in the region of inner 1/3 radius and outer 1/3 radius of the sample cross section, while the region in the middle of the sample remained unchanged without voids. In the sample immersed in supercritical CO_2 for 30 min, only 1/10 of the region in the middle of the cross section remained unchanged, and the rest had voids. In the sample immersed for 60 min, residual voids and a few cracks were uniformly distributed on the cross section after carbon dioxide escaped. However in the sample immersed for 120 min, large cracks appeared in the middle of the cross section.

It was found that the diameter of the SF-3 propellant samples changed after the foaming, and increased with the immersion time. Among them, many bulges appeared on the surface of Samples b, c, and d. The increase of the diameter of SF-3 propellant samples after foaming can be explained by the follow foaming principle: in the foamed process, supercritical CO_2 fluid dissolves in SF-3 propellants,

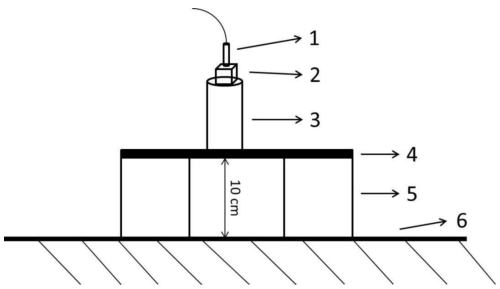

Figure 3. Diagram of witness board experiment. 1.Detonatior8# 2. Passivated RDX 3.Perfusion explosive 4.Test board 5.Cement brick 6. Cement floor

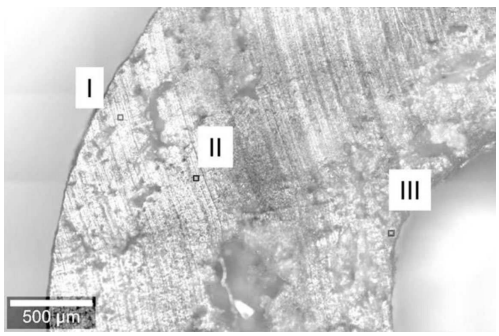

Figure 4. Surface scanning regions in Raman tests.

and as the temperature rises and the pressure drops, CO_2 rapidly expands and escapes, leaving a large number of voids and bulges in the propellants, resulting in an increase in the diameter of the propellants. The diameter of foamed SF-3 propellant is shown in Table 2. As the immersion time in supercritical CO_2 increases, the diameter of the SF-3 propellants also increases. Although supercritical CO_2 has a high diffusion coefficient and strong dissolving power, it takes a certain amount of time for supercritical CO_2 to completely dissolve in the SF-3 propellants. Therefore, as the immersion time of SF-3 propellants in supercritical CO_2 increases, the CO_2 content in the SF-3 propellants also increases. SF-3 propellants containing more supercritical CO_2 fluid during the immersion process naturally release more CO_2, resulting in an increase in the sample diameter.

Electron micrograph of foamed SF-3 propellant is shown in Figure 5. It can be seen from the electron micrograph of SF-3 propellants that, the unfoamed SF-3 propellant has a smooth surface and a uniform texture, and the foamed SF-3 propellant has not only small bulges on the surface, but also many voids in the section. After Sample b was immersed in supercritical CO_2 for 10 min, voids were found in the SF-3 propellant section, making the sample uneven in the texture. The small voids were distributed on the section of the sample, and there were more voids near the inner and outer edges and fewer voids in the middle region, because supercritical CO_2 was dissolved from the surface into the interior of the SF-3 propellant. The number of voids in Sample c was significantly greater than Sample b, because the sample immersed for a longer time had more supercritical carbon dioxide dissolved therein and thus had more voids.

After Sample d was immersed in supercritical CO_2 for 60 min, uniform pores were distributed throughout the cross section, because supercritical CO_2 was gradually and uniformly dissolved in the SF-3 propellant as the immersion time went by, and thus a number of voids were left on and inside the foamed propellant, making the density of the foamed SF-3 propellant relatively uniform. There are even large cracks on the surface of Sample e which was immersed for 120 min, because more supercritical CO_2 was dissloved in the sample and a large amount of CO_2 gas escaped from the pores after a short period of temperature rise and pressure fall.

Table 2. Comparison of foaming time and diameter of SF-3 propellants.

Sample	Immersion time (min)	Immersion temperature (°C)	Propellant diameter (mm)
a	–	–	5.48
b	10	70	5.76
c	30	70	5.80
d	60	70	5.80
e	120	70	5.76

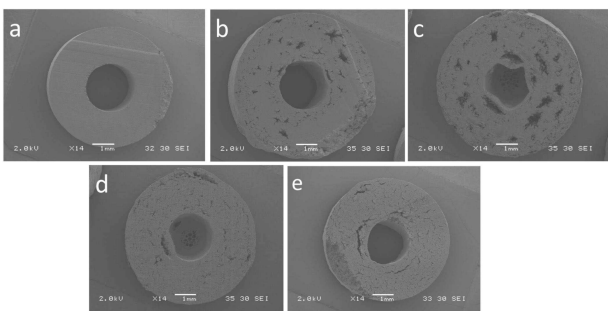

Figure 5. 14X electron micrograph of surface of foamed SF-3.

3.2 Detonation Performance of Perfusion Explosive

Table 3 shows results of detonation velocity measurement of the perfusion explosive made from SF-3 propellants. The perfusion explosive made from the unfoamed Sample a did not detonate, and thus its detonation velocity was 0 $m\,s^{-1}$. The perfusion explosive made from foamed SF-3 propellants could detonate and had a higher detonation velocity and larger shock wave energy. It can be seen from the above experimental results that the detonation velocity increases with the increase of the immersion time of the sample in supercritical CO_2. In this experiment, the highest detonation velocity was 6683 $m\,s^{-1}$ for the perfusion explosive made from foamed SF-3 propellants. This is because the voids left by a large amount of CO_2 in the foaming process increases the internal surface area of the sample, which provides more hot spots for the initiation of the perfusion explosive, thus making the perfusion explosive detonate.

From the experimental results in Table 3, it can be seen that the perfusion explosive made from the propellant immersed for 120 min has a lower detonation velocity than the sample immersed for 60 min. The reason for the low shock wave energy of the perfusion explosive is that the long-term foaming causes more voids inside the SF-3 so that more perfusion solution enters the voids during the perfusion process. In the case of the same mass of foamed SF-3, the sample immersed for a long time has more perfusion solution, and the energy of the perfusion solution is

Table 3. Test results of detonation velocity of perfusion explosives made from SF-3 propellants.

Sample	Immersion time (min)	Detonation velocity ($m\,s^{-1}$)	Shock wave energy ($kJ\,g^{-1}$)
a	–	0	0.23
b	10	5560	0.72
c	30	6350	0.93
d	60	6683	1.02
e	120	6455	0.95

lower than the propellant, so the shock wave energy of the sample immersed for a long time is reduced. The optimum immersion time of the sample in supercritical CO_2 is 60 min. The sample immersed for 60 min in supercritical CO_2 has a higher detonation velocity and larger shock wave energy.

3.3 Witness Board Explosion Experiment

It can be seen from the results of the explosion test of the witness plate in Table 4 that the perfusion explosive made from unfoamed SF-3 propellants had lower explosive power and only caused indentations on the witness plate. The explosive of the perfusion explosive made from foamed SF-3 propellants was more powerful so that the steel plate was broken down and a large diameter blast voids were generated. The diameter of the blast voids generated by the perfusion explosive made from the sample immersed for less than 60 min gradually increased with the immersion time, because the blast void size was increased due to an increased number of detonation hot spots after foaming of the propellant. When the immersion time exceeded 60 min, the size of blasting voids generated by the perfusion explosive decreased with the increase of the immersion time of the SF-3 propellant in the supercritical CO_2, and the explosive power was reduced. Therefore, the optimal immersion time is 60 min, which provides the optimal performance to the perfusion explosive.

Table 4. Test results of witness board explosion.

Sample	Immersion time (min)	Sample density ($g\,cm^{-3}$)	Effect on the impact steel plate	Blast void diameter (mm)
a	–	1.57	Indentation	–
b	10	1.54	Broken down	45
c	30	1.55	Broken down	57
d	60	1.54	Broken down	62
e	120	1.52	Broken down	58

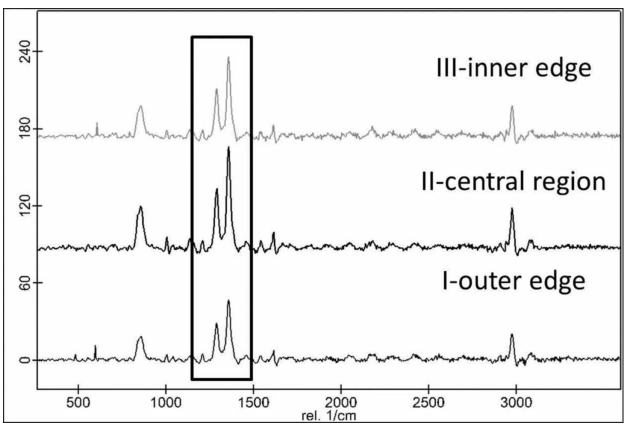

Figure 6. Raman spectra of sample in different regions.

3.4 Confocal Raman Imaging Analysis

Figure 6 shows experimental results of the Raman scan test. The results show that the absorption peaks at 832 cm^{-1}, 1359 cm^{-1} and 2950 cm^{-1} appear in all three test regions. They are Ar–NO_2 peaks, carbon-hydrogen peaks and carbon-hydrogen stretching vibration absorption peaks [13], respectively. It can be seen that the peaks exhibited by the samples in different regions are different so that the sample concentrations in the three regions are different: central region > outer edge > inner edge.

In order to better explain the distribution of propellants in the sample, imaging analysis was performed to indicate the propellant content. The experimental results are shown in Figure 7. The central region has the highest propellant content so that it is the brightest, the outer edge has the second highest propellant content, and the inner edge has the lowest propellant content. The Raman imaging statistical analysis shows propellant contents in different regions. As shown in Figure 8, the propellant concentration is concentrated between 800–900 in the central region, between 600–700 at the outer edge, and between 450–550 at the inner edge. Therefore, the propellant is distributed at different concentrations in the: central region > outer edge > inner edge, of the sample. This result explains why 1/3 of the region of the SF-3 sample immersed for 10 min is unchanged. Because more CO_2 is dissolved inside and outside

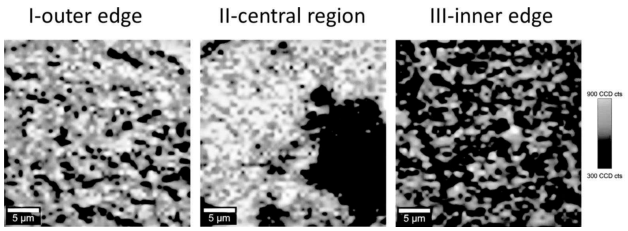

Figure 7. Concentration changes in scanned regions by Raman imaging analysis.

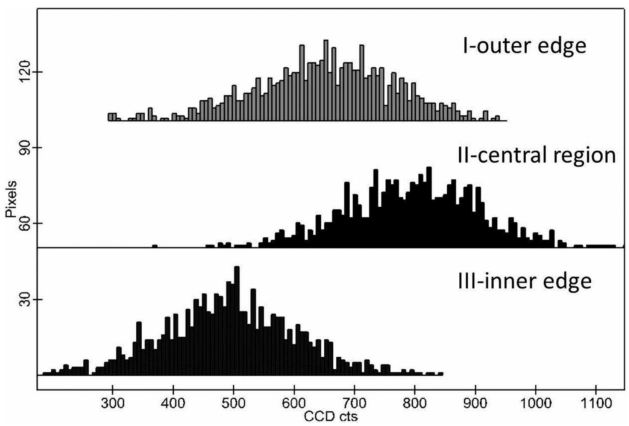

Figure 8. Raman imaging statistical analysis.

the sample, more voids are generated. This verifies the difference in propellant concentration in different regions.

4 Conclusion

The foaming process for deserted SF-3 can realize the reuse of SF-3 propellants. The perfusion explosive made from the foamed SF-3 propellant had detonation properties which were better than the unfoamed. The detonation velocity of the perfusion explosive made from the foamed SF-3 propellant increased first and then decreased as the immersion time in supercritical CO_2 increased. Among the samples immersed for less than 120 min, the perfusion explosive made from the sample immersed for 60 min had the best detonation performance. When the immersion time of the foamed propellant was 60 min, the explosive velocity of the perfusion explosive made from the foamed propellant was the highest, i.e., 6683 $m\,s^{-1}$. When the immersion time in supercritical CO_2 was too long, the long-term foaming causes more voids inside the SF-3 so that more perfusion solution enters the voids during the perfusion process. In the case of the same mass of foamed SF-3, the sample immersed for a long time has more perfusion solution, and the energy of the perfusion solution is lower than the propellant, so the shock wave energy of the sample immersed for a long time is reduced. Therefore, the optimal time for supercritical CO_2 soaking SF-3 propellant is 60 min.

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