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Research paper

Microcellular Oblate Propellant with Skin-core Structure Deterred by Poly(neopentenediol adipate)

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Abstract: In order to solve the issues of high muzzle flash, smoke, residue, migration rate and carcinogenicity of double-base oblate propellants deterred by dibutyl phthalate (DBP), skin-core structure microporous oblate propellants to replace DBP deterring technology were fabricated in the present work by supercritical carbon dioxide (SC-CO₂) foaming technology. Poly(neopentenediol adipate) (NA) was employed as the deterrent to modify the combustion properties because of its lower migration rate in storage. Scanning electron microscopy (SEM) was used to observe the morphology of the microporous oblate propellants generated by different processing conditions, and the combustion properties were investigated by closed bomb tests. The SEM images indicated that the skin region displayed smaller cell diameters and lower cell density compared with cells in the core region. The closed bomb tests demonstrated that it was feasible to adjust the progressive combustion performance by controlling the skin-core structure and the NA deterred layer. The burning time values of the original, the microcellular, and the NA deterred samples were 3.45, 2.14,

and 4.20 ms, respectively. Microcellular oblate propellants, with a skin-core structure foamed by SC-CO₂ and deterred by NA, provides a novel and promising method to realize progressive combustion performance.

Keywords: SC-CO₂, microcellular oblate propellant, skin-core structure, poly(neopentanediol adipate) deterring, combustion performance

1 Introduction

A double-base oblate propellant is a spherical propellant after flattening treatment. The web size is in the range from 0.3 mm to 0.7 mm, and nitrocellulose (NC) and nitroglycerin (NG) are the energetic components for double-base oblate propellants. A double-base oblate propellant is the main energy source for providing the power for the motion of the bullet in light weapons, because of the high loading density and high burning rate. In order to meet the requisite high muzzle velocity and low chamber pressure in the firing process, deterring and coating technology are the common and effective methods to realize the progressive combustion performance of oblate propellants [1]. Dibutyl phthalate (DBP) is used as the traditional deterrent for double-base oblate propellants, and oblate propellants deterred by DBP exhibit high loading densities and progressive combustion performance [2]. However, DBP desensitized double-base oblate propellants produce a lot of muzzle flash and smoke in the firing process, which goes against the shooting for soldiers. The π benzene ring structure of DBP results in a lower oxygen balance of the propellants, leading to a mass of residue in the burning process, and a gas port plugged up by such residues will reduce the service life of the weapon. As DBP is a chemical compound with a low molecular mass, the stepped distribution of the DBP concentration is not preserved in the long-term storage process of double-base oblate propellants, and the fact that the internal DBP migrates to the surface or escapes from the sample makes DBP deterring unworkable for oblate propellants. What is worse, the carcinogenic property of DBP makes it unfriendly to humans and the environment, so DBP has become gradually forbidden in many countries [3].

Some researchers have explored higher molecular weight materials, such as polyurethane elastomer, poly(neopentanediol adipate) (NA), as a replacement in DBP deterring technology for the progressive combustion performance of oblate propellants [4, 5]. The higher molecular weight of this deterrent confers a lower migration rate in storage, which is beneficial

in enhancing the service life of gun propellants. However, NA is difficult to uniformly distribute on the surface of oblate propellants, and the low diffusion rate of NA results in a long time for the deterring process.

On the other hand, some researchers have investigated new methods for controlling the laws of energy release in respect to the propellant structure. According to the geometric burning mode, a high specific surface area promotes the combustion properties of gun propellants. Binbin *et al.* [6] investigated the effects of the particle size and morphology of nitroguanidine (NQ) on the combustion properties of triple-base propellants. He found that a triple-base propellant with a smaller NQ particle size exhibited significantly higher burning rate, as the smaller NQ particle size provided a larger specific surface. Meanwhile, foamed propellants allow potential ways for adjusting the combustion properties through their micropore structure. In chemical foaming technology, Böhnlein-Mauß *et al.* [7, 8] produced foamed thermoset polyurethane-bonded hexogen (RDX) propellants by the reaction injection moulding process, which exhibited good vulnerability and high burning rate. Physical foaming technology gives another way to fabricate foamed propellants. Ping *et al.* [9] employed the leaching method to prepare nitrocellulose-based microporous spherical powder, and the results showed that the surface of the nitrocellulose-based microporous spherical powder was smooth. Ying *et al.* [10, 11] proposed supercritical carbon dioxide (SC-CO₂) foaming technology for the preparation of microcellular gun propellants, and the presence of the cell structure enhanced the specific surface area, promoting the combustion properties of the gun propellants. What is more, SC-CO₂, acting as the physical foaming agent, escaped completely from the propellant at the end of the foaming process. However, it was not simple to control the cell nucleation and growth as the propellants were prepared in cylinders of large size (diameter = 5 mm, length = 10 mm), and the previous work focused mainly on improving the burning rate through the porous core.

In the present work, the microporous oblate propellants were fabricated by SC-CO₂ foaming technology, and the progressive combustion performance was obtained from the skin-core structure. NA, as a replacement for DBP, was used as the deterrent for modifying the progressive combustion performance. The cell morphology of the skin-core structure microporous oblate propellants was characterized by scanning electron microscopy (SEM), and the combustion performance was measured by closed bomb tests.

2 Experimental

2.1 Materials

CO₂ gas (purity ≥ 99.9%) and liquid nitrogen were purchased from Nanjing Wenda Special Gas Co., Ltd., ethyl acetate (analytical reagent) was supplied from Sinopharm Chemical Reagent Co., Ltd., NA and the double-base oblate propellants were provided by Luzhou North Chemical Industries Co., Ltd. The web size of the oblate propellants was 0.62 mm.

2.2 Preparation of microcellular oblate propellant

The skin-core structure microporous oblate propellants were fabricated with SC-CO₂ by the typical intermittent warming-up process, as shown in Figure 1. Firstly, the double-base oblate propellant was placed in a high pressure reactor, and CO₂ gas from the cylinder was injected into the reactor by a pump, to reach the set saturation pressure (P_s , 15 MPa). Secondly, the reactor was immersed in the water bath A at the set saturation temperature (T_s , 40 °C) for a certain period of time (saturation time, t_s , 7 h), while the CO₂ saturation condition in the propellant matrix was reached, as determined from our previous research [12]. Thirdly, the propellant was moved from the reactor into a fixed temperature water bath (foaming temperature, T_f) for several seconds (foaming time, t_f , 40 s); the time interval from the high pressure reactor to the water bath B was called the desorption time (t_d). The sample was then quenched in a water bath C (15 °C) for the cooling process. Finally, the microporous oblate propellant was dried at 60 °C for 1 week to eliminate water. Table 1 lists the desorption times and foaming temperatures for different samples.

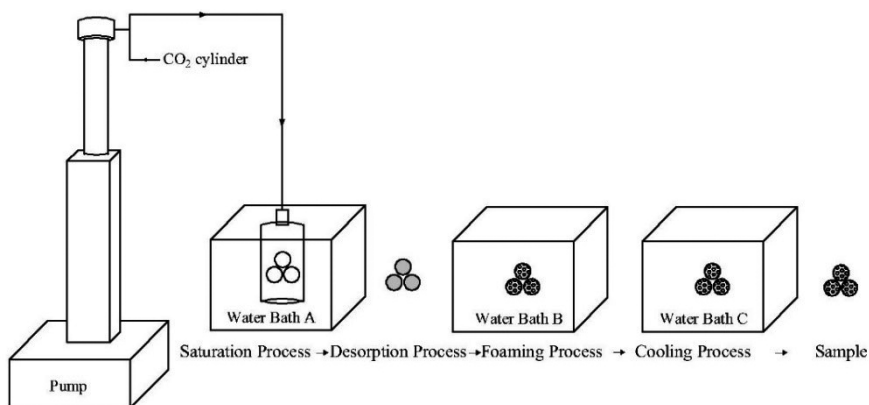


Figure 1. Flow chart of the foaming process

Table 1. Process conditions for the microporous oblate propellants

Sample	1 [#]	2 [#]	3 [#] (6 [#])*	4 [#]	5 [#]
t_d [min]	2	4	8	8	8
T_f [°C]	95	95	95	90	99

* sample 6[#] was the deterred product of sample 3[#]

2.3 Deterring process

NA was applied as the deterrent to modify the combustion properties of the microporous oblate propellants (sample 3[#]) by the wet deterring process; the ethyl acetate and NA contents were 1 and 3 wt.%, respectively. In this work, the deterring temperature and time were 80 °C and 1 h, respectively. The final sample modified by NA was dried at 70 °C for 1 week to eliminate water and ethyl acetate, and it was named as sample 6[#].

2.4 Morphology characterization

The morphology of the microporous oblate propellants was characterized using a QUANTA FEG 250 scanning electron microscope (SEM, FEI LTD). The foamed samples were treated with liquid nitrogen for a certain time, and were then immediately fractured. The fractured surfaces of the samples were sputtered with gold, and the morphology was recorded by SEM. The skin-core structure of the microcellular oblate propellants was observed from the SEM images with the assistance of Image-Pro Plus [13].

2.5 Closed bomb tests

The combustion properties of the double-base oblate propellants and the microporous oblate propellants was investigated by closed bomb tests. The volume of the closed bomb was 50 cm³, and the amount of sample in the bomb was 6 g. All of the samples were fired by 2[#] nitrocellulose under the same ignition pressure (9.8 MPa), and the combustion curves for different processing conditions were calculated from the measured data.

3 Morphology of Microporous Oblate Propellants

3.1 Skin-core structure formation mechanism

In the formation mechanism of the cells, the classical nucleation theory was applied to explain cell nucleation as follows:

$$N_0 = C_0 f_0 \exp\left(\frac{-\Delta G_{\text{hom}}^*}{kT}\right) \quad (1)$$

where N_0 is the cell nucleation rate, C_0 is the fluid concentration, T is temperature, ΔG_{hom}^* is the free energy, f_0 is the frequency factor, and k is Boltzmann's constant. From Equation 1, the SC-CO₂ concentration and the temperature are the main factors affecting the cell nucleation rate [14]. As cell nucleation occurs rapidly, it is difficult to adjust the foaming temperature in the foaming process. Thus, in this work, control of cell nucleation was achieved by changing the concentration distribution of SC-CO₂.

After being saturated for sufficient saturation time (7 h), the SC-CO₂ sorption process is equal to the desorption process, which leads to the dynamic solubility equilibrium. When the propellant is removed from the reactor, the concentration distribution of SC-CO₂ is uniform, as in Figure 2(a), and the SC-CO₂ concentration in the center (C_c) is equal to that in the surface of the sample (C_s). During the desorption process, SC-CO₂ escapes from the oblate propellant, and the escape rate at the surface is faster than in the center. Therefore, C_s is lower than C_c at the end of the desorption process, as shown in Figure 2(b), and the SC-CO₂ concentration decreases gradually towards the surface. Therefore, the desorption time is the key factor determining the concentration distribution of SC-CO₂.

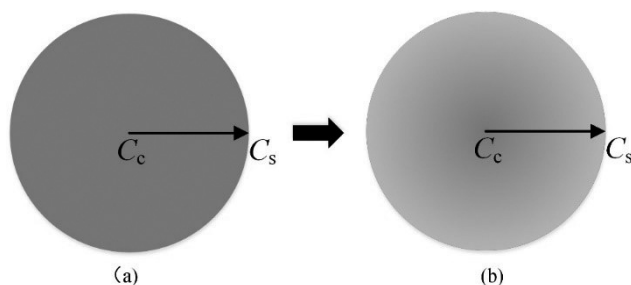


Figure 2. Concentration distribution of SC-CO₂ in the desorption process

In the foaming process, cell nucleation in the core region competes with that in the skin region. As C_c is much higher than C_s , the driving force of the cell nucleation is stronger in the core region, so the quantity of cells is quite small in the skin region after the cooling process. Therefore, there is a critical concentration of SC-CO₂ determining the formation of the skin-core structure, and the driving force is not enough for cell nucleation and growth when

the SC-CO₂ concentration is lower than this critical value. The critical value is named as C^* , and the critical radius is named as r^* as shown in Figure 3. The radius of the core region is r^* , and the thickness of the skin region is $(r - r^*)$. Based on C^* , microporous oblate propellants can be designed with different thickness of the skin region to meet the various needs of combustion performance. In the deterring technology, DBP disperses in the surface of the oblate propellant to adjust the combustion performance, and skin-core structure microporous oblate propellants realize the progressive combustion performance by improving the energy releasing rates of cells in the core region. Thus, this method is novel and promising, to meet the requirements of high muzzle velocity and low chamber pressure in light weapons.

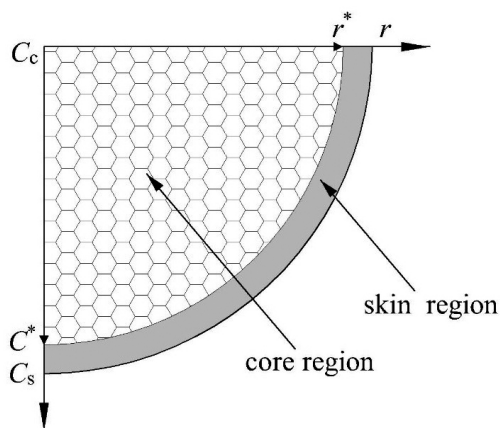


Figure 3. Relationship between the concentration distribution and the radius

According to the formation mechanism above, a microporous oblate propellant is fabricated; Figure 4 shows an SEM image of the skin-core structure. Compared with the cells in the core region, this indicates that the skin region displays smaller cell diameters and a lower cell density. The values of cell diameter and density can be applied to explain the specific surface of microcellular oblate propellants in the two-dimensional structure. In the burning process of a microcellular oblate propellant with skin-core structure, a larger specific surface leads to a higher burning rate in the core region. Therefore, the thickness of the skin and core regions may be adjusted by adjusting the foaming parameters in order to control the combustion performance of the microcellular oblate propellant.

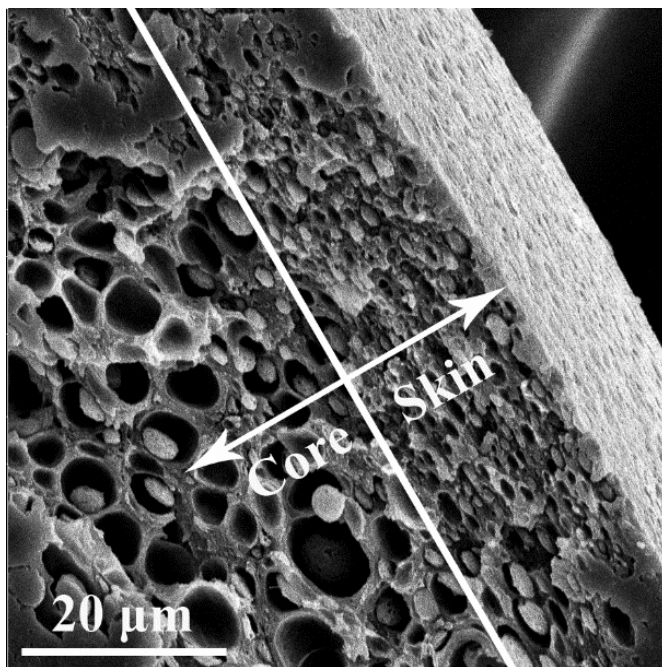
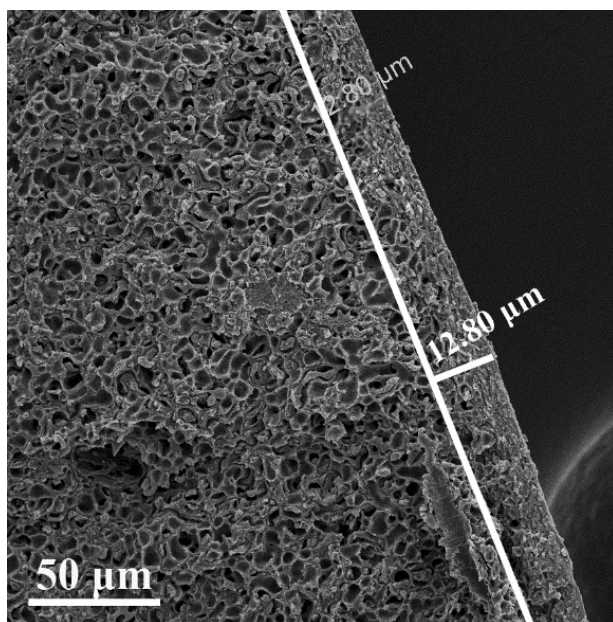


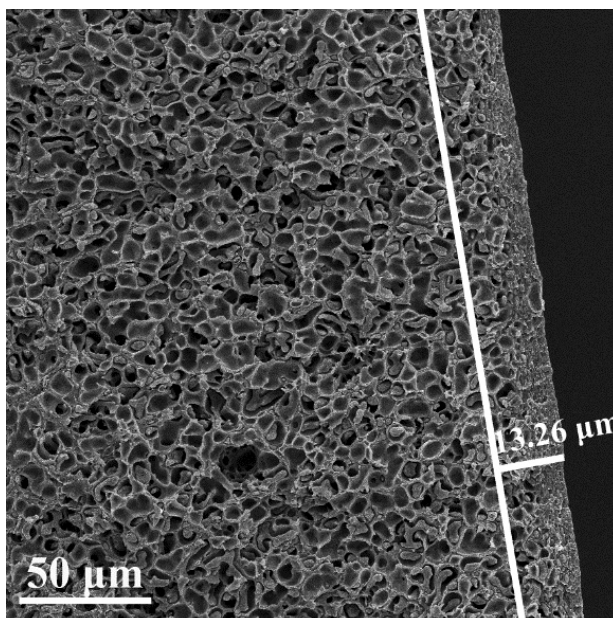
Figure 4. SEM image of the skin-core structure

3.2 Effects of desorption time on cell morphology

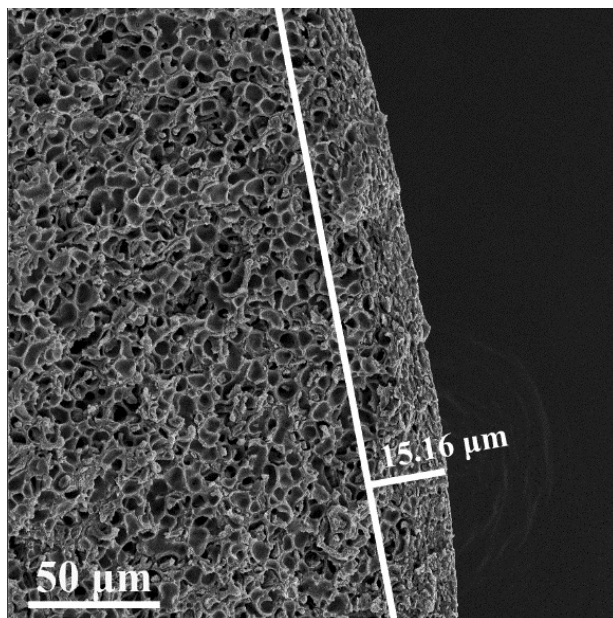
The desorption time determines the concentration distribution of SC-CO₂ in an oblate propellant. Figure 5 shows the SEM images of the cell morphology for various desorption times (5(a): $t_d = 2$ min, 5(b): $t_d = 4$ min, and 5(c): $t_d = 8$ min) when the foaming temperature was 95 °C. This shows that the thickness of the skin region was 12.80 ($t_d = 2$ min), 13.26 ($t_d = 4$ min), and 15.16 μm ($t_d = 8$ min), respectively, which proves that the thickness of the skin region increases with increasing desorption time. According to the skin-core structure formation mechanism, C_s and C_c decrease with increasing desorption time, resulting in a lower cell density and diameter. When C_s is below a certain value, the SC-CO₂ concentration is too low for the growth of cell nucleation, so the thickness of the un-foamed region is higher when the desorption time is longer. Thus, the slow-burning layer can be controlled by the desorption time.



(a)



(b)

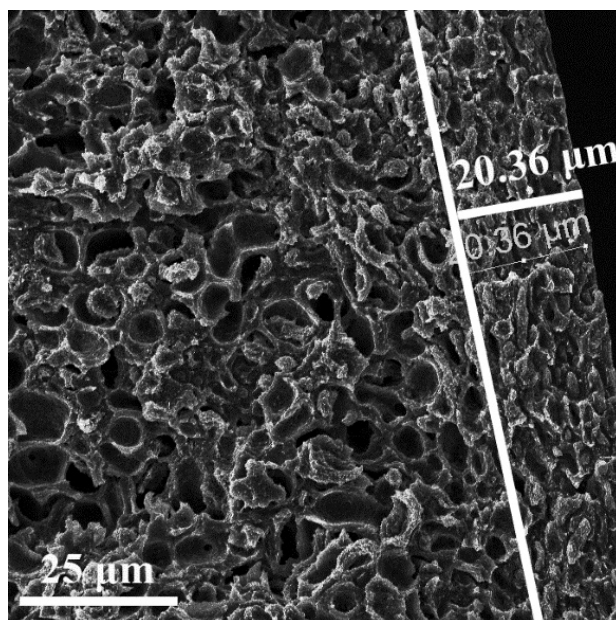


(c)

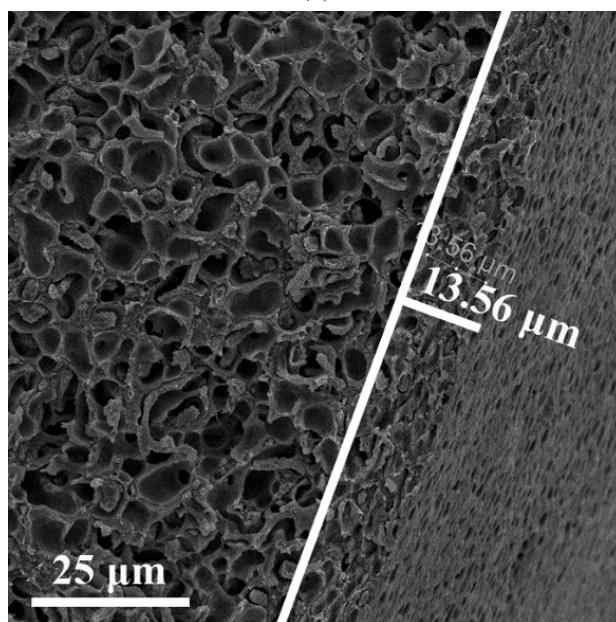
Figure 5. SEM images of the skin-core structure for different desorption times: (a) $t_d = 2$ min, (b) $t_d = 4$ min, and (c) $t_d = 8$ min

3.3 Effects of foaming temperature on cell morphology

Figure 6 shows the SEM images of microcellular oblate propellants from different foaming temperatures (6(a): $T_f = 90$ °C, 6(b): $T_f = 99$ °C), for a desorption time of 8 min. The skin layer thickness values of Figures 6(a), 5(c) and 6(b) were 20.36, 15.16, and 13.56 μm , respectively, for foaming temperatures of 90, 95, and 99 °C, respectively. This reveals that the thickness of the un-foamed layer is smaller when the foaming temperature is higher. Due to the classical nucleation theory, when the oblate propellants are subjected to the same saturation process, the temperature difference between the saturation and the foaming temperature is the main factor for the driving force of cell nucleation, and a higher foaming temperature results in a higher nucleation rate. Therefore, a higher foaming temperature contributes to increasing the cell diameter and density of microcellular oblate propellants, leading to a reduced thickness of the slow-burning layer. Since the cell structure is sensitive to the foaming temperature, but cell nucleation occurs at the level of milliseconds, it is difficult to adjust the cell structure by controlling the foaming temperature. However, the diffusion process of SC- CO_2 is relatively slow, and this is therefore an effective method for changing the desorption time.



(a)



(b)

Figure 6. SEM images of the skin-core structure from different foaming temperatures: (a) $T_f = 90\text{ }^{\circ}\text{C}$, (b) $T_f = 99\text{ }^{\circ}\text{C}$

3.4 Effects of the deterring process on cell morphology

Although the skin-core structure causes the different burning rates, the skin region behaving as the slow-burning layer and the core region behaving as the fast-burning layer, there are still some cells in the skin region, leading to a high burning rate in the initial burning. NA was applied to modify the slow-burning layer as a polymeric deterrent. In this work, the cells existing at the surface of the propellant improved the diffusion rate of NA, which allowed NA to become uniformly distributed in the surface in reduced time. The combination of the skin-core structure foamed by SC-CO₂ and the NA deterred surface can overcome the low diffusion rate of NA and realize the progressive combustion performance of an oblate propellant without DBP.

The skin-core structure of a microcellular oblate propellant after the deterring process is shown in Figure 7, when the desorption time was 8 min and the foaming temperature was 95 °C. The thickness of the skin region deterred by NA was 30.08 μm, while the thickness of the skin region of the microcellular oblate propellant was 15.16 μm, so the deterring process can adjust the combustion performance of microcellular oblate propellants. Meanwhile, most of the cells in the skin region were closed after being deterred by NA. This is attributed to the fact that the presence of ethyl acetate in the deterring process dissolves cells in the skin region, and this causes the compact structure of the slow-burning layer. The results showed that this method can effectively improve the combustion performance of microcellular oblate propellants *via* two aspects. On one hand, NA is distributed in the surface of microcellular oblate propellants, and the cell structure promotes the diffusion of NA. On the other hand, the addition of ethyl acetate leads to a compact structure of the skin region. These two factors make a difference to the progressive combustion performance of oblate propellants.

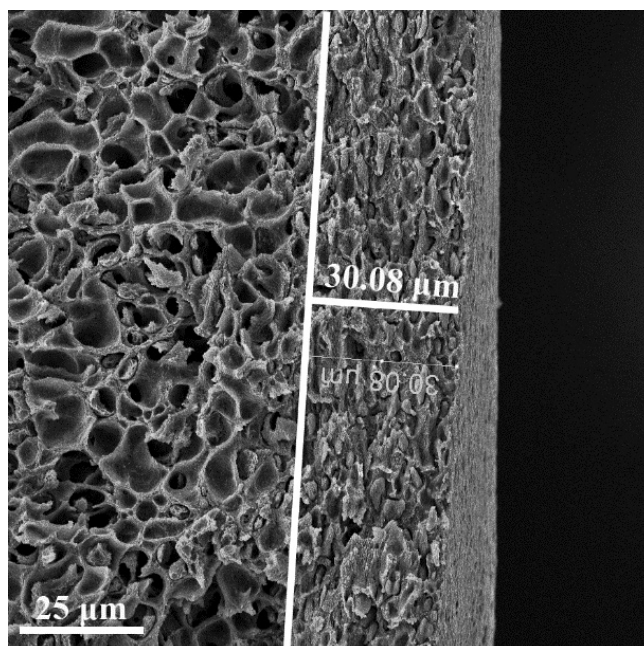


Figure 7. SEM image of the skin-core structure after the NA deterring process

4 Combustion Performance of Microcellular Oblate Propellants

The combustion performance of the original and the microcellular oblate propellants was investigated by closed bomb tests, and the vivacity against burnt fraction (L - B) curves were obtained from the measured data, as shown in Figure 8. L - B curves are the common way to evaluate the progressive combustion performance of gun propellants. Figure 8 implies that the foamed samples have the higher initial dynamic vivacity, and that the microcellular oblate propellant reached the highest dynamic vivacity ($L_{\max} = 9.86 \text{ MPa}^{-1}\cdot\text{s}^{-1}$) when B was 0.31, while the original sample reached $L_{\max} = 5.17 \text{ MPa}^{-1}\cdot\text{s}^{-1}$ when B was 0.15. In the intermediate period of the burning process, the microcellular oblate propellant exhibited a higher generating rate of burning gas, which would promote the muzzle velocity of the gun propellant. The microcellular oblate propellant deterred by NA shows lower initial dynamic vivacity and L_{\max} than those of the microcellular oblate propellant, indicating that the deterring process is effective in the combustion performance of a microcellular oblate propellant. Thus, the results demonstrate that

it is possible to adjust the progressive combustion performance of an oblate propellant by controlling the skin-core structure and the deterring layer with the foaming and deterring processes.

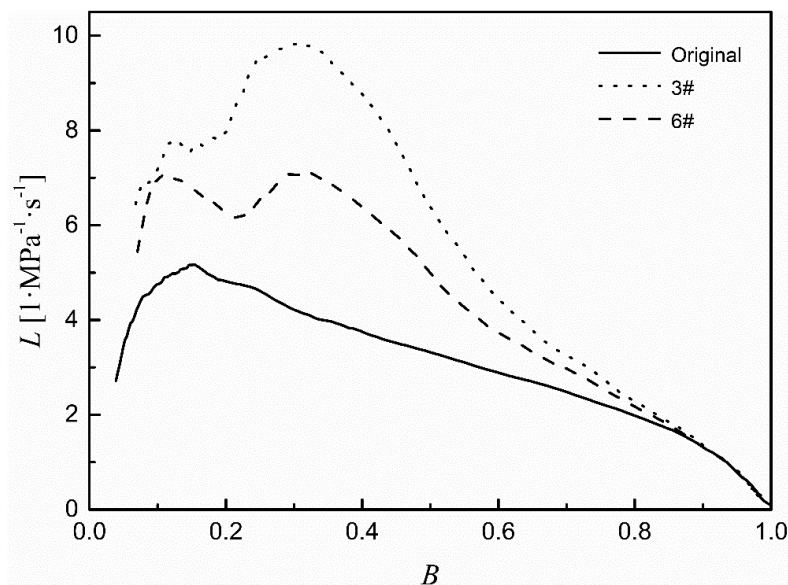


Figure 8. L - B curves of the original and the microcellular oblate propellants

The P - t curves of the samples are shown in Figure 9. The maximum pressure values of the microcellular sample (159 MPa) was close to that of the original sample (159 MPa), while the value of the NA deterring sample was 150 MPa. However, they exhibited different burning times (t_m); the t_m values of the original, the microcellular, and the NA deterring sample were 3.45, 2.14, and 4.20 ms, respectively. Therefore, the SC-CO₂ foaming technology has effects on decreasing the burning time of the gun propellants, resulting from numerous cells in the sample. Meanwhile, the sample deterring by NA exhibited a slow release rate of burning gas in the initial period of burning ($t < 2$ ms), which means that the NA deterring technology plays the main role in decreasing the release rate of burning gas. The sample displayed a fast release rate of burning gas when $t > 2$ ms. Thus, the combination of NA deterring and SC-CO₂ foaming technology can realize a lower chamber pressure, a higher muzzle velocity and a low harmful shooting process without DBP.

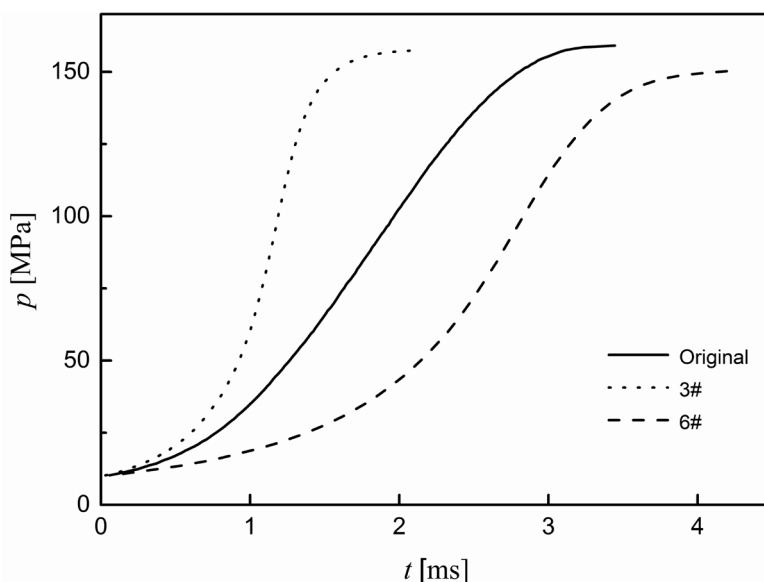


Figure 9. P - t curves of the original and the microcellular oblate propellants

5 Conclusions

In this work, skin-core structure microporous oblate propellants were fabricated by the SC-CO₂ foaming technology and the NA deterring technology. SEM was used to study the morphology of the microporous oblate propellants formed under different conditions, and the combustion properties were investigated by closed bomb tests. The SEM images indicated that the skin region displays smaller cell diameters and a lower cell density compared with those in the core region. The thickness of the skin region increased with increasing desorption time, but the thickness of the skin region was lower when the foaming temperature was higher. When NA was applied to modify the slow-burning layer as a polymer deterrent, the thickness of the skin region deterred by NA was 30.08 μm , while the thickness of the skin region of microcellular oblate propellant was 15.16 μm . The results obtained from the closed bomb tests demonstrated that it is feasible to adjust the progressive combustion performance of an oblate propellant by controlling the skin-core structure and the deterred layer through the foaming and deterring processes. The t_m values of the original, the microcellular, and the NA deterred sample were 3.45, 2.14, and 4.20 ms, respectively. The microcellular oblate propellant with a skin-

core structure formed by SC-CO₂ foaming and NA deterring technology provides a novel and promising method for realizing a progressive combustion performance, by adjusting the energy release rates in the skin and core regions.

Acknowledgements

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