A Novel Method for Oblate Spherical Powder with Adjustable Combustion Property

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Abstract. In order to obtain the oblate spherical powder with adjustable combustion property, a novel method was put forward combining the microporous technology and the polymer deterring technology. In this work, the oblate spherical powder was foamed with the cell structure by supercritical carbon dioxide (SC-CO₂), and then poly(neopentanediol adipate) (NA) was employed as the deterrent to modify the energy releasing rates in the surface. The combustion property of oblate spherical powder under different processing conditions was investigated by the closed bomb tests. The results indicated that the microporous oblate spherical powder displayed the desired progressive combustion, and the combustion property of microporous oblate spherical powder could be adjusted by controlling the desorption time, foaming temperature, NA content, desensitization time and desensitization temperature. The spherical powder with skin-core structure foamed by SC-CO₂ and deterred by NA provides a novel and promising method to realize the progressive combustion performance without dibutyl phthalate (DBP).

1. Introduction
In order to meet the development of modern weapons and equipment, the properties of gun propellants are investigated to improve the internal ballistic performance of body-tube weapons [1]. The oblate spherical powder is often applied as the gun propellants in light weapon systems [2]. However, the shape of oblate spherical powder determines the degressive combustion property, which is not conducive to the combustion platform phenomenon. The deterred technology is the main technique to realize the high initial speed and low gun pressure. In 1943, J O Hirschfelder [3] proposed the principle of deterred treatment of propellant. Dibutyl phthalate (DBP) is the most commonly deterent used in the deterred process of double-base oblate spherical powders. However, due to the low molecular mass, the migration of DBP makes the gradient concentration distribution not steady in the long-term storage process. What’s worse, the carcinogenic nature of DBP makes it unfriendly to human beings and environment, because of benzene ring structure [4]. Accordingly, some researchers have selected poly(neopentanediol adipate) (NA) to replace the DBP [5].

Although the surface deterred treatment technology brings obvious progressive combustion property to the oblate spherical powder, it also leads to some inevitable disadvantages. The propellant itself can react completely after combustion, but the deterrent may be incompletely burned, which generates the muzzle smoke and leaves the combustion residue [6]. Meanwhile, the high molecular
mass of NA leads to the high desensitization time and desensitization temperature. Consequently, some studies have begun to focus on changing the physical structure of the propellants to obtain the progressive combustion property. The adoption of microporous technology maybe the promising way to solve the problems above. Ying [7-9] put forward that the supercritical carbon dioxide (SC-CO$_2$) could be used to fabricate oblate spherical powders with gradient microporous structure, which performed the good progressive combustion. What’s more, SC-CO$_2$, acting as the physical foaming agent and solvent, could escape from the propellant completely at the end of foaming process [10]. The introduction of the microporous technology makes the inside of the oblate spherical powder filled with pores, which can effectively increase the specific surface area of propellants [11]. Furthermore, due to the existence of internal pores, the oblate spherical powder follows the law of convection combustion, and the burning rate is dramatically promoted in an extremely short time, leading to the enhancement of the progressive combustion property [12]. As the chamber pressure reaches a large value instantaneously, it not only damages the body-tube weapon itself, but also isn’t beneficial to the full use of the propellant energy [13].

For the purpose of avoiding smoke and residue produced by the DBP deterred technology and solving the problems of large chamber pressure resulting from the microporous technology, a novel method which combines the microporous technology and the NA deterring technology is put forward to realize the adjustable combustion property of oblate spherical power in this paper. The desorption time, foaming temperature, NA deterrent content, desensitization time and desensitization temperature are investigated as the main factors to the progressive combustion property under different conditions by the closed bomb tests.

2. Experimental Section

2.1. Materials

Double-base oblate spherical power and Poly(neopentanediol adipate) (NA) were provided by Luzhou North Chemical Industries Co., LTD. Ethyl acetate (AR) was purchased from Sinopharm Chemical Reagent Co., LTD. Industrial CO$_2$ (purity≥99.9%) was supplied by Nanjing Wenda Special Gas Co., LTD.

2.2. Foaming process

The typical intermittent warming-up process was applied to fabricate the microporous oblate spherical powers foamed with SC-CO$_2$ as figure 1 shown. Firstly, the double-base oblate spherical powers were placed into the high-pressure reactor, and the air in the high-pressure reactor was simultaneously driven out by CO$_2$. Secondly, CO$_2$ liquid was injected into the high-pressure reactor by the pump to 15 MPa (saturation pressure, $P_s$). Thirdly, the high-pressure reactor was immersed into the water bath at 40°C (saturation temperature, $T_s$) for 7 h (saturation time, $t_s$). Then, the samples were removed from the reactor into a water bath at a fixed temperature (foaming temperature, $T_f$) for 20 s (foaming time, $t_f$), and the time difference from the high-pressure reactor to the water bath was called as the desorption time ($t_d$). The samples were quenched into cold water later to prevent the immoderate growth of cells. Finally, the microporous double-base oblate spherical powers were dried at 60°C in a water-jacketed oven for a week to wipe out the water. The desorption time and foaming temperature of samples are listed in table 1.
Figure 1. Flow chart of foaming process.

**Table 1.** Process conditions of microporous oblate spherical powers.

| Sample | 1# | 2# | 3# | 4# | 5# |
|--------|----|----|----|----|----|
| $t_d$/min | 2  | 4  | 8  | 4  | 4  |
| $T_d$/°C  | 84 | 84 | 84 | 76 | 90 |

2.3. Surface modification process

NA was utilized as the deterrent to modify the surface of microporous double-base oblate spherical powers (2#) for adjusting the combustion property. NA was dissolved into ethyl acetate, and then the NA solution was mixed with water. The high-speed emulsification machine was applied to agitate the mixture for NA emulsion. The microporous double-base oblate spherical powers were desensitized by the NA emulsion at a set temperature (desensitization temperature, $T_d$) for a certain time (desensitization time, $t_d$). In the end, the final samples modified by NA were dried at 70° C in a water-jacketed oven for a week to wipe out the water and ethyl acetate. Table 2 is the process conditions of surface modification.

**Table 2.** Process conditions of surface modification.

| Sample | 6# | 7# | 8# | 9# | 10# | 11# | 12# |
|--------|----|----|----|----|-----|-----|-----|
| NA content/wt% | 1.5 | 3.5 | 4.5 | 3.5 | 3.5 | 3.5 | 3.5 |
| $t_d$/min | 60  | 60  | 60  | 30  | 120 | 60  | 60  |
| $T_d$/°C  | 85  | 85  | 85  | 85  | 85  | 75  | 80  |

2.4. Closed bomb tests

The combustion property of oblate spherical powers was investigated by the closed bomb tests. The volume of the closed bomb was 50 mL, and the loading density was 0.12 g·cm$^{-3}$. The ignition pressure was 9.8 MPa, and the combustion curves under different processing conditions were calculated from the measurement data, including pressure-time curve and dynamic vivacity-relative pressure curve.

3. Results and Discussion

3.1. Effect of desorption time

Figure 2 shows the $P$-$t$ curve of oblate spherical powder prepared under the condition of different desorption time (1#, 2# and 3#), and the related values are shown in table 3. It can be seen from figure 2 and table 3 that the maximum pressure values of oblate spherical powder are extremely close (about
155 MPa), which are less than that of the original propellant. The burning time ($t_{m}$) of foamed samples in the maximum pressure ($P_m$) is under 2.8 ms, while the value of original sample is 3.45 ms. And the desorption time has a few effects on the burning time in the maximum pressure. However, the pressure of sample 1# rises most rapidly in the initial stage, and it displays the higher value than those of sample 2# and 3#. This is due to that the dissolved amount of residual CO$_2$ decreases with the extension of desorption time. In the case of the same foaming temperature, the less the dissolved CO$_2$ is, the less nucleation point of cells will be, resulting in the lower nucleation rate and fewer cells density. Therefore, the longer desorption time reduces the transfer efficiency of burning gas and slows down the combustion rate of samples.

![Figure 2. P-t curves of oblate spherical powder with different desorption time.](image)

**Table 3. Burning time parameters with different desorption time.**

| sample label | $t_{m}$/ms | $P_m$/MPa |
|--------------|------------|------------|
| Original     | 3.45       | 159.10     |
| 1#           | 2.47       | 153.35     |
| 2#           | 2.76       | 156.75     |
| 3#           | 2.79       | 155.34     |

Figure 3 is the L-B curve of samples with different desorption time. Compared with the original sample, the dynamic vivacity of microporous oblate spherical powders displays the higher value during the burning process. When relative pressure is less than 0.19, the dynamic vivacity of samples shows the rising tendency, and the dynamic vivacity of the foamed samples has the faster growth rate in this region. When $B$ is located in the range from 0.19 to 1, the dynamic vivacity of original propellant decreases gradually, resulting in the degressive combustion of oblate spherical powder. Sample 2# performs the better combustion platform than sample 1# and 3#, which means that the combustion performance of microporous oblate spherical powder can be adjusted by changing the desorption time. The influence of desorption time on the combustion performance of microporous oblate spherical powder is dominated by the concentration distribution of CO$_2$ in the propellant. Since the escape speed of CO$_2$ in the surface layer is far higher than that in the inner layer, the CO$_2$ concentration drops to the lowest foaming concentration in the surface layer, resulting in a small quantity of cells in the unfoamed cortex. Therefore, sample 2# was selected as the basic propellant in the following experiment as the better combustion platform.
3.2. Effect of foaming temperature

Figure 4 displays the $P$-$t$ curve of the microporous oblate spherical powders prepared at different foaming temperatures ($2\#$, $4\#$ and $5\#$), and the burning time parameters are shown in Table 3. According to the analysis from Figure 4 and Table 4, although sample $2\#$, $4\#$ and $5\#$ have been treated with foaming process, the maximum pressures of oblate spherical powders are in the range from 156.7 MPa to 159.1 MPa, which is similar to that of the original propellant. The burning time to maximum pressure of sample $5\#$ (2.14 ms) is much less than that of the original propellant (3.45 ms), and the decrement is 38%. Moreover, the burning time to maximum pressure decreases gradually with the increase of foaming temperature. As the viscoelasticity of oblate spherical powders will be enhanced with the high foaming temperature, the resistance to cell growth will be reduced, leading to higher cell density and larger cell diameter. Thus, the burning gas transfers fast because of the cell structure in microporous oblate spherical powders.

![Figure 4. $P$-$t$ curves of oblate spherical powder at different foaming temperatures.](image)

**Table 4. Burning time parameters at different foaming temperatures.**

| Sample label | Burning time to maximum pressure $t_{\text{max}}$/ms | Maximum pressure $P_{\text{max}}$/MPa |
|--------------|-----------------------------------------------|-------------------------------------|
| Original     | 3.45                                          | 159.10                              |
| $2\#$        | 2.76                                          | 156.75                              |
| $4\#$        | 2.72                                          | 155.04                              |
| $5\#$        | 2.14                                          | 157.78                              |
Figure 5 is the $L$-$B$ curves of microporous oblate spherical powders prepared at different foaming temperatures. It seems that the sample performs the better progressive combustion when the foaming temperature is $84^\circ$C. On one hand, when the foaming temperature is $76^\circ$C, the temperature difference between saturation and foaming process can’t drive the cell nucleation and growth, and the cell density is low inside the power. On the other hand, when the foaming temperature is $90^\circ$C, the foaming process is so violent that there are too much cells inside the power, and the generating rate of burning gas increases constantly before $B > 0.5$, which leads to the excessive value of $L$. Therefore, $84^\circ$C is set as the suitable foaming temperature.

**Figure 5.** $L$-$B$ curves of microporous oblate spherical powder at different foaming temperatures.

3.3. **Effect of NA content**

Although the microporous oblate spherical powders perform the progressive combustion property, the generating rate of burning gas is fast in the initial burning period, so NA is applied to improve the combustion property of microporous oblate spherical powders. Figure 6, figure 7 and table 5 are the $p$-$t$ curves, $L$-$B$ curves, and with burning time parameters different NA content, respectively. As the addition of NA reduces the energy releasing rate of propellants, the propellants modified by NA have the lower maximum pressure and longer burning time than the original propellant and sample 2#.

When NA infiltrates into the interior of microporous oblate spherical powder, the concentration gradient of NA is generated along the radial direction, and there is the higher NA concentration in the surface of powders. This surface desensitization layer plays an important role in the improvement of progressive combustion. The increase of NA content increases the thickness of surface desensitization layer, which inhibits the sharp promotion of the burning rate.

**Figure 6.** $P$-$t$ curves of oblate spherical powder with different NA content.
Table 5. Burning time parameters with different NA content.

| Sample label | Burning time to maximum pressure $t_m$/ms | Maximum pressure $P_m$/MPa |
|--------------|------------------------------------------|----------------------------|
| Original     | 3.45                                     | 159.10                     |
| 2#           | 2.76                                     | 156.75                     |
| 6#           | 4.19                                     | 150.25                     |
| 7#           | 3.59                                     | 149.21                     |
| 8#           | 5.41                                     | 144.36                     |

As shown in figure 7, the foamed samples (2#, 6#, 7#, 8#) performs the obvious progressive combustion property, and their dynamic vivacity begins to drop off until $B > 0.5$. The maximum dynamic vivacity of these deterred samples is about 8.7 MPa^{-1}s^{-1}, and the minimum value is about 5.6 MPa^{-1}s^{-1}, which are much lower than that of sample 2#. According to the hot spot theory, once the microporous oblate spherical powder begins to burn, a proportion of burning gas penetrates into the inner pore structure, and then the hot spots are formed, resulting in the simultaneous combustion on both internal and external surface consequently. The phenomenon described above is called as the convective combustion, making the oblate spherical powder change from degressive surface combustion into progressive surface combustion, which is the fundamental reason for the improvement of progressive combustion. Obviously, the addition of deterrent slows down the reaction degree of propellant and reduces the rate of gas generation.

![Figure 7. L-B curves of oblate spherical powder with different NA content.](image)

3.4. Effect of desensitization time

Figure 8, table 6 and figure 9 are $P$-$t$ curve, burning time parameters and $L$-$B$ curve of microporous oblate spherical powder with different desensitization time, respectively. It can be seen from figure 8 that sample 7# and 9# have the similar value of maximum pressure and burning time, while the datum of sample 10# are significantly different from the other two samples. The sample 10# shows the longer burning time and less maximum pressure, which undoubtedly brings about the better internal ballistic performance.
Figure 8. $P$-$t$ curves of microporous oblate spherical powder with different desensitization time.

Table 6. Burning time parameters with different desensitization time.

| Sample label | Burning time to maximum pressure $t_{m}$/ms | Maximum pressure $P_{m}$/MPa |
|--------------|--------------------------------------------|-------------------------------|
| Original     | 3.45                                       | 159.10                        |
| 2#           | 2.76                                       | 156.75                        |
| 7#           | 3.59                                       | 149.21                        |
| 9#           | 3.58                                       | 150.78                        |
| 10#          | 4.07                                       | 148.87                        |

Figure 9. $L$-$B$ curves of microporous oblate spherical powder with different desensitization time.

It can be concluded that all the foamed samples present good progressive combustion in figure 9. However, there are still a few small differences between the four curves. The overall values of dynamic vivacity of sample 2# and 9# are remarkably higher than those of sample 7# and 10#. It indicates that the combustion reaction of sample 2# and 9# before reaching to the maximum pressure is more intense than that of sample 7# and 10#, which is not conducive to the improvement of progressive combustion. Although the dynamic vivacity of sample 7#, 9# and 10# almost reaches their maximum values when $B$ is 0.5, but the dynamic vivacity of sample 9# increases faster than the other two samples when $B<0.5$, and it decreases faster when $B>0.5$ too. There is a clear fact that the sample
7# and 10# achieve a better progressive burning. This is due to that as the desensitization time becomes longer, the NA solution has more opportunities to diffuse towards the inner of the microporous oblate spherical powder, which leads to the penetration of NA deeper and more pores be filled up in the outer layer.

3.5. Effect of desensitization temperature

As figure 10 and table 7 shown, the burning time to maximum pressure of the microporous oblate spherical powder is shortened to a certain degree and the maximum pressure is hardly changed under the condition of different desensitization temperature, compared with the sample Original. The value of burning time for sample 7# is larger than those of the other two samples. NA suspension disperses more evenly with higher desensitization temperature under the mechanical agitation, which contributes to thickening outer modification layer and slowing burning rate.

![Figure 10. P-t curves of oblate spherical powder at different desensitization temperatures.](image)

**Table 7.** Burning time parameters at different desensitization temperatures.

| Sample label | Burning time to maximum pressure t<sub>mu</sub>/ms | Maximum pressure P<sub>mu</sub>/MPa |
|--------------|---------------------------------|-----------------|
| Original     | 3.45                            | 159.10          |
| 2#           | 2.76                            | 156.75          |
| 7#           | 3.59                            | 149.21          |
| 11#          | 2.75                            | 156.95          |
| 12#          | 3.27                            | 154.62          |

Figure 11 shows the L-B curve of microporous oblate spherical powder at different desensitization temperatures. Compared with sample Original, there is a significant decrease in the overall dynamic vivacity of these samples after surface modification, and their initial dynamic vivacity are very close, about 4 MPa<sup>-1</sup>s<sup>-1</sup>. The maximum value of sample 11# is 8 MPa<sup>-1</sup>s<sup>-1</sup> when B is 0.5, which is higher than those of sample 7# and 12#. To a certain extent, the sample 11# also achieves improvement to the combustion performance. However, there is no doubt that sample 7# and 12# have the better progressive combustion property. This is due to the fact that the NA suspension is not dispersed evenly and has sediment at the lower modification temperature. In this case, NA can not penetrate into the interior of propellant smoothly with the solvent, which results in the reduction of thickness of surface modification layer. Therefore, the modification temperature should be reasonably risen to obtain the microporous oblate spherical powder with excellent progressive combustion property.
Figure 11. L-B curves of microporous oblate spherical powder at different desensitization temperatures.

4. Conclusion
The combination of the microporous technology and the polymer deterring technology was put forward to obtain the oblate spherical power with adjustable combustion property. Compared with the microporous oblate spherical powder, the original propellant had longer burning time to maximum pressure and larger maximum pressure. Apart from that, the initial dynamic vivacity and the overall dynamic vivacity of microporous oblate spherical powder were both higher than the original propellant, which was beneficial for the convection combustion caused by microporous structure. The microporous oblate spherical powder displayed the desired progressive combustion, and the combustion property of microporous oblate spherical powder could be adjusted by controlling the desorption time, foaming temperature. Meanwhile, NA was employed as the deterrent to modify the energy releasing rates in the surface by changing NA content, desensitization time and desensitization temperature. The experimental results showed that the NA deterred samples had longer burning time, lower maximum pressure and smaller dynamic vivacity. Generally speaking, the thickness of surface modification layer played the most important role in the adjustment of combustion property. All of these factors were ultimately controlled by changing the thickness of surface modification layer, resulting in the effects of progressive combustion. And the spherical powder with skin-core structure foamed by SC-CO2 and deterred by NA provides a novel and promising method to realize the progressive combustion performance without dibutyl phthalate.

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