Study on performance improvement of oil well cement slurry by poly ether ether ketone

Fuchang You¹, Jin Tian, Man Shu
Jingzhou Jiahua Technology Company, Ltd, Jingzhou, Hubei 434000 China
¹1029415926@qq.com

Abstract. After the oil well cement solidifies, the internal original void causes the inherent strength of the cement stone to be insufficient, and the structural integrity of the cement stone is damaged after the external load, which is not conducive to the subsequent oil and gas exploitation. In order to make up for the inherent deficiency of cement paste strength, the effect of PEEK with high strength and high elastic modulus on the properties of oil well cement was studied. The conventional properties and mechanical properties of PEEK cement paste with different contents were evaluated. The microstructure of PEEK cement paste was observed by scanning electron microscope. The experimental results show that compared with the cement paste without peek, the rheological properties of cement paste with 1% ~ 6% peek are worse, the thickening time is shorter, and the water loss is reduced. After curing for 28 days, the compressive strength of 5% peek cement paste decreased by 15%, the flexural strength and impact strength increased by 21% and 11% respectively, and the elastic modulus decreased by 50%. Peek is uniformly dispersed and filled in the cement paste. When the cement paste is subjected to external load, peek will deform, absorb part of the energy and hinder the crack propagation, which improves the ability of the cement paste to resist external load.

1. Introduction
Cementing is a process in which cement slurry is injected into the well wall and casing string from the wellhead. The purpose of cementing is to seal oil, gas and water in different pressure formations and provide guarantee for subsequent construction [1]. After the completion of cementing operation, in the process of oil and gas exploitation, fracturing, perforation and pressure test are often accompanied [2]. These operations often cause uneven stress distribution of cement sheath, produce annulus micro gap, damage the integrity of cement sheath, and cause interlayer sealing failure of cement sheath [3]. Cement sheath is formed after the oil well cement is squeezed into the annulus and solidified. The quality of oil well cement determines the quality of cement sheath, which requires the cement stone researched in laboratory to have excellent resistance to external load. One of the common methods of strengthening and toughening is to add elastic particles into the slurry. The elastic particles with appropriate particle size can fill the original pores of cement paste and make up for the inherent defects of cement paste. When the cement stone is compressed and squeezed, the particles, as a part of the cement stone skeleton structure, transmit the impact force, deform themselves and absorb energy, so as to improve the mechanical properties of the cement stone. Agapiou K and other studies show that rubber particles can reduce the elastic modulus and improve the impact strength of cement paste. L Zaoyuan [4] studied the effect of hydrophilic rubber powder treated with surfactant on the properties of oil well cement, and determined that the optimal particle size range of rubber powder is 0.15mm ~ 0.18mm, and the optimal dosage is 2%. At the same time, L Zaoyuan [5] also studied the effect of elastic granular material JF on the toughness of cement paste. The 24h compressive strength of 5% JF granular cement paste is 77% higher than that of blank cement paste. P
Shuo [6] studied the effect of emulsified asphalt powder on the mechanical properties of cement paste. When the dosage is 10%, the 28d tensile strength of emulsified asphalt cement paste increases by 20%, the compressive strength decreases by 31%, the flexural strength increases by 49%, and the elastic modulus decreases by 19%. The results of K Nova [7] show that epoxy resin can improve the compressive strength, reduce the elastic modulus and improve the impact strength of cement paste. L Yuliang [8] studied the strengthening and toughening effect of high proportion epoxy resin on cement paste. The results show that the compressive strength of 60% epoxy resin cement paste is 47% higher than that of blank cement paste, the tensile strength is 78% higher, and the elastic modulus is 76.5% lower. These studies show that the proper elastic particles can improve the mechanical properties of cement paste.

Poly Ether Ether Ketone (PEEK) is a kind of special polymer elastic material with high strength, high elastic modulus, chemical resistance and wear resistance, which has been widely used in automobile manufacturing, rail transit, medicine, electronics, aerospace and other industries [9]-[14]. However, there is no report that peek has been used to toughen oil well cement paste. In order to explore the application effect of peek in oil well cement slurry, this paper evaluates the influence of peek on the comprehensive performance of oil well cement slurry, and analyzes the mechanism of PEEK as an external toughening filler to strengthen the mechanical properties of cement paste, so as to provide some reference and guidance for improving the elastic toughness of oil well cement paste.

2. Experiment

2.1. Materials
Water loss agent (Flo-82L) is polyethyleneimine. Its main function is to reduce the amount of water loss of cement slurry. Expansive agent (Bond) is a kind of non-metallic oxide with micro expansion characteristics, which can effectively make up for the volume shrinkage of cement paste. The dispersant (Fsg-S) is sulfonated acetone formaldehyde condensate, the main function is to improve the rheological properties of cement slurry. Reinforcing agent (STR) is a kind of inorganic mineral material with high chemical activity, which can promote the hydration reaction of cement slurry and improve the initial strength of cement paste. The main function of defoaming agent (DFM21) is emulsified silicone oil, which is to eliminate foam in cement slurry. Retarder (H21L) is a mixture of tartaric acid and borate, the main role is to prolong the curing time of cement paste; they all come from Jingzhou Jiahua Technology Co., Ltd.

| Average grain size /μm | Density / (g/cm³) | Melting point /°C | Tensile strength/MPa | Bending strength/MPa | Impact strength/J/m |
|------------------------|-------------------|-------------------|----------------------|----------------------|---------------------|
| 50                     | 1.320             | 334               | > 93                 | 140                  | 60–80               |

**Table 1. Basic properties of PEEK**

![Figure 1. The basic microscopic morphology of PEEK](image-url)
Grade g cement of the Three Gorges project comes from Gezhouba special cement plant. Peek comes from Jilin Engineering Plastics Co., Ltd. The performance parameters of PEEK are shown in Table 1, and the micro morphology is shown in Figure 1.

2.2. Experimental formula design
In this paper, the configuration of cement slurry, the performance test of cement slurry and the performance test of cement paste are carried out in accordance with the corresponding provisions of GB 10238-2005 oil well cement and GB / T 19139-2012 test methods for oil well cement. The curing and testing temperature is 90 ℃. The experimental formula is as follows:
1#: 100% Grade g cement + 45% Water + 2.5% Flo-82L+ 1.5% STR + 1% Bond + 1% Fsg-S + 0.5% DFM21 + 0.5% H21L
2#: 1#+PEEK

3. Results and discussion
3.1. Basic properties of PEEK cement slurry
In cementing operation, the rheology of cement slurry affects the displacement efficiency of cement slurry, the thickening time determines the height position of cement slurry, and the water loss affects the cementing quality of cement sheath, casing and formation. The conventional properties of cement pastes with different peek dosages were evaluated in laboratory. The experimental results are shown in Table 2 and Figure 2.

| Amount/% | φ300 | φ200 | φ100 | φ6 | φ3 | Δρ/ g/cm³ |
|----------|------|------|------|----|----|----------|
| 0        | 195  | 130  | 68   | 4  | 3  | 0.02     |
| 1        | 204  | 138  | 65   | 4  | 3  | 0        |
| 2        | 215  | 144  | 76   | 4  | 3  | 0        |
| 3        | 220  | 152  | 80   | 4  | 3  | 0        |
| 4        | 287  | 175  | 122  | 9  | 5  | 0        |
| 5        | 289  | 233  | 136  | 10 | 7  | 0        |
| 6        | 300+ | 223  | 156  | 18 | 16 | 0        |

Table 2. Rheological properties of PEEK powder cement slurry

![Figure 2. Water loss and thickening time of PEEK cement slurry](image-url)
The experimental results show that: the settlement stability of cement slurry added with PEEK is good, peek can improve the settlement stability of cement slurry, but peek has an effect on the fluidity of cement slurry. When the dosage of PEEK is less than 3%, it has little effect on the fluidity of cement slurry. With the increase of PEEK, the fluidity of cement slurry becomes worse. When the dosage of PEEK reaches 6%, the reading of φ 300 has exceeded 300. Therefore, peek should be applied in cementing slurry. If the dosage of PEEK is increased, the rheological property of cement slurry should be monitored in time to prevent the high reading of rheological property from making it difficult for cement slurry to pump into the well. Peek can shorten the thickening time of cement slurry, and the thickening time of 6% peek cement slurry is shorter than that of cement slurry without peek 51 min, which is because the void of cement stone containing water is filled with PEEK, the reduction of water greatly shortens the thickening time of cement stone. As can be seen from Figure 2, compared with the blank group, peek can effectively reduce the water loss of cement slurry. When the dosage of PEEK is 6%, the water loss is 46 mL, which is 34 mL less than the blank group. The reason may be that peek is dispersed in cement slurry. When the filter cake is formed, peek fills the narrow pores in the filter cake, making the filter cake more compact and reducing the subsequent water loss.

3.2. Mechanical properties of PEEK cement paste

3.2.1. Compressive strength

The compressive strength of cement paste is the force needed to destroy cement paste per unit area, which is an important parameter in the mechanical properties of cement paste. The compressive strength of cement stone with different dosage of PEEK is tested by universal mechanical testing machine in laboratory. The experimental results are shown in Figure 3.

![Figure 3. Compressive strength of cement stone at different cured time](image)

After curing for 1 day, the compressive strength of 6% peek cement paste is 21% lower than that of blank cement paste; after curing for 28 days, the compressive strength of 6% peek cement paste is 34.2MPa. Compared with the cement paste without peek particles, the compressive strength of cement paste with 1%, 2%, 3%, 4%, 5% and 6% peek particles decreased by 5%, 8%, 11%, 12%, 15% and 20% after curing for 28 days. Although this does not conform to the principle of material mechanics, it reflects that the filling of elastic materials in cement paste is a double-edged sword. Because peek particles are a kind of foreign material compared with the whole cement paste, the free peek outside the gap will destroy the integrity of the original skeleton structure of cement paste, which is reflected in the mechanical properties, that is, the compressive strength decreases. When the dosage is low, peek particles do not fill the voids in the cement paste and do not share the external load of the cement paste. The loading of PEEK is equivalent to the impurities in the cement paste, which is harmful to the compressive strength of the cement paste. At the optimum dosage, the primary pores of cement paste
are basically filled, and the external load is transferred to the interface of the pores. Peek particles are equivalent to a part of the skeleton structure of cement paste, and bear the external load together, with little loss of compressive strength. If the dosage exceeds the optimum, the extra part of PEEK will be harmful to the compressive strength of cement paste as a foreign material, resulting in the decrease of compressive strength of cement paste.

3.2.2. Flexural strength
Flexural strength reflects the ability of cement stone to resist external bending strain, which is a characterization of the toughness of cement stone. The greater the impact strength is, the stronger the ability of object to resist external bending is. The flexural strength of PEEK cement paste was evaluated in laboratory. The results are shown in Figure 4.

![Figure 4. Flexural strength of cement stone at different cured time](image)

It can be seen from the experimental results that peek can significantly improve the flexural strength of cement paste. The longer the curing time, the greater the flexural strength of cement stone. However, it is not that the more peek is added, the better. The flexural strength of 5% peek cement paste develops fastest, and the flexural strength reaches 9.73 MPa after 28 days of curing.

3.2.3. Impact strength
Impact toughness refers to the energy consumed by cement specimen after impact fracture, which can quantitatively characterize the toughening effect of cement paste. The impact strength of PEEK cement paste at different curing time is tested by simply supported beam impact tester indoor. The experimental results are shown in Figure 5.

![Figure 5. Impact strength of cement stone at different cured time](image)
It can be seen from Figure 5 that peek particles can improve the impact strength of cement paste. With the increase of curing time, the impact strength of cement increases. After curing for one day, the impact strength of 6% peek cement increased by 10% compared with the blank group. After curing for 28 days, the impact strength of six groups of PEEK particles increased by 2%, 3%, 7%, 8%, 10% and 8% respectively. The addition of PEEK particles can improve the impact toughness of cement paste, and the impact strength of 5% peek particles is the highest.

3.3 Stress strain curve of PEEK cement paste
The stress-strain curves of cement paste without peek and cement paste with 5% peek after curing for 1 day were studied in laboratory. The experimental results are shown in Figure 6.

![Stress-strain curves of cement stone](image)

**Figure 6.** Stress-strain curves of cement stone

According to the stress-strain curve, the elastic modulus of the blank cement paste is 10.3 GPa. Compared with the blank cement paste, the elastic modulus of the cement paste with 5% peek decreases by 50%, reaching 5.1 GPa. It can be seen from Fig. 6 that before reaching the maximum stress, i.e. the cement stone is not damaged, under the same load, the shape of the cement stone added with PEEK changes greatly and the elastic ratio is large. When the maximum stress is reached, i.e. the cement stone is destroyed, the stress reduction rate of the cement stone containing 5% peek is much lower than that of the blank cement stone, and the toughness is relatively large. The reason is that after the cement stone containing 5% peek is destroyed, peek particles have a buffering effect against the pressure exerted by the press by virtue of their excellent elastic toughness, so the stress-strain curve declines slowly compared with the blank group. In conclusion, peek can significantly reduce the elastic modulus of cement paste and improve the elastic toughness of cement paste.

3.4 Toughening mechanism of PEEK cement paste

![Micro morphology of blank cement paste](image)

**Figure 7.** Micro morphology of blank cement paste
The micro morphology of cement stone in blank group was observed by scanning electron microscope. It can be seen from Figure 7 that there are many kinds of micro voids in cement stone in blank group. The main components of grade g cement are tricalcium silicate, tetracalcium ferroaluminate and dicalcium silicate. The material itself presents a multilateral pore structure, and the cemented cement stone is easy to present a porous structure. These voids cause the inherent strength and toughness deficiency of cement paste, which needs the supplement of external materials to achieve the effect of strengthening and toughening.

It can be seen from Figure 8 that peek can fill in the cement paste and hinder the crack propagation. When peek is added into cement paste, part of PEEK is filled in the primary void of cement paste, which forms a whole with the original space grid structure of cement paste under the cementation of cement. When the external load does not exceed the yield strength of the cement paste space grid structure, peek, as the filling particles in the cement paste space grid structure, acts as the transmission medium of the external load, deforms itself, absorbs part of the energy, and slows down the force of the external load on the cement paste, so as to improve the ability of the cement paste to resist the external load. On the other hand, when the external load exceeds the yield strength of the space grid structure, the cracks in the cement paste will expand along a certain direction until the whole cement paste is destroyed. However, when the crack propagates to peek, it is necessary to destroy peek or change the propagation direction to bypass the filling material. Peek is a kind of material with high strength and high elastic modulus. It is difficult to destroy peek and continue to expand along the original direction. Most of the cracks bypass the filling material to change the direction of crack propagation and continue to expand along the new direction. This will greatly delay the destruction process of cement stone, reduce the brittleness of cement stone, and enhance the ability of cement stone to resist external load to a certain extent.

4. Conclusions
(1) Peek has little effect on the thickening time and water loss of cement slurry, and the cement slurry has good settlement stability. However, peek will lead to poor rheological properties of cement slurry. In practical application, if the dosage of PEEK is increased, the rheological property of cement slurry should be monitored in time to prevent the cement slurry from being difficult to pump into the well due to too high rheological reading.
(2) The results show that peek can enhance the ability of cement stone to resist external load, and the best dosage is 5%. After curing for 28 days, the flexural strength and impact strength of PEEK cement stone with 5% peek are increased by 31% and 24% respectively compared with those without peek.
(3) The results show that peek can reduce the elastic modulus of cement paste. The elastic modulus of cement paste containing 5% peek is about 50% lower than that of the blank sample, reaching 5.1 GPa, and the elastic toughness of cement paste is obviously improved.
(4) When the cement paste added with PEEK is subjected to external load, peek itself will deform and absorb energy. Meanwhile, peek will prevent and change the crack expansion of cement paste and improve the ability of cement paste to resist external load.

5. Acknowledgments
This work was supported by the National Natural Science Foundation of China (Grant No. 519040334, 5180404-4). And the National Major Science and Technology Projects of China (Grant number 2016ZX05060 and 2017ZX05032004-004).

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