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Research Article

Thermoplastic Rubber (TPR) Modified by a Silane Coupling Agent and Its Influence on the Mechanical Properties of Oil Well Cement Pastes

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The surface hydrophilicity of thermoplastic rubber (TPR) is poor, and the effect of using it directly in oil well cement is not good. TPR was modified by different silane coupling agents, and the hydrophilicity of the modified TPR was studied by Fourier-transform infrared (FT-IR) spectroscopy and dispersion stability photography. The application effect of modified TPR in oil well cement slurry was also evaluated. The fracture surface morphology of TPR cement stone was observed by macrophotography and scanning electron microscopy (SEM). The results demonstrated that the hydrophilicity of TPR particles was improved after modification with silane coupling agent 3-methacryloxypropyltrimethoxysilane (KH570), and its application effect in cement slurry was excellent. Compared with the pure cement paste, the compressive strength of the cement paste with addition of TPR modified by KH570 was reduced, but the flexural strength and impact strength of the cement paste were effectively enhanced. Moreover, the modified TPR greatly improved the deformation capacity and decreased the elastic modulus of the cement paste. The modified TPR particles formed a plastic polymer network structure in the cement stone and penetrated the cement hydration products, filling in the cement paste to form a flexible structural center. Thus, it improved the mechanical properties and reduced the brittleness of cement paste.

1. Introduction

Cementing involves injection of cement slurry into the annulus between casing and formation, thus forming cement sheath after solidification. The cement sheath seals the formation effectively and supports and protects the casing at the same time [1]. Oil well cement is the main component of cementing material. As oil well cement is a brittle material, microcracks or microgaps are easily produced under the influence of perforation, fracturing, exploitation, and so on, which will result in the destruction of cement sheath integrity and affect the safe and efficient exploitation of oil and gas wells [2, 3].

Improving the mechanical properties of cement-based composites is helpful to ensure the integrity of the cement sheath. Basically, the three main varieties of flexible materials used to improve the mechanical properties of oil well cement include fiber, latex, and rubber. Among them, rubber has the best effect on the elasticity of cement paste, which is conducive to designing a flexible cement slurry system. Li and Guo [4] showed that the filling effect of rubber particles effectively increases the elastic deformation ability of oil well cement stone through research on the effect of rubber powder in oil well cement. Cheng et al. [5, 6] and Long et al. [7] modified rubber powder using low-temperature plasma technology and added modified rubber powder to the oil well cement. The elastic modulus of cement stone containing rubber particles is lower than that of pure cement, which can improve the plasticity and elastic deformation capacity of cement stone and make the structure of cement paste more compact. Liu et al. [8] studied the microstructure of oil well cement paste with rubber elastic particles and showed that elastic particles could improve the deformation ability of cement paste and reduce the elastic modulus. Agapiou et al.

[9] added waste tire rubber powder to oil well cement and improved the mechanical properties and elasticity of the cement paste. These studies show that the application of rubber elastic particles in oil well cement can decrease the elastic modulus, improve the deformation capacity, and enhance the mechanical properties of cement stone and the ability to resist impact damage. In addition, the application of rubber in concrete cement-based materials has also demonstrated that rubber particles can improve the mechanical properties and deformation capacity of cement paste [10–13].

To the best of our knowledge, the most widely applied modifier in cement-based materials is waste tire rubber, while little work has been reported on the oil well cement with other rubber used as reinforcing materials. Thermoplastic rubber is a type of elastomer material. It has the elasticity of rubber at room temperature and can be softened at high temperature. The structure of thermoplastic rubber consists of different resin segments and rubber segments linked by chemical bonds. The resin segments rely on the interchain force to form physical crosslinking points. The rubber segments are highly elastic chain segments and contribute to the elasticity [14, 15]. Therefore, thermoplastic rubber has the physical and mechanical properties of rubber and thermoplastics and is a new type of elastic polymer material. Thermoplastic rubber is widely used in the manufacture of household products, rubber hose, and adhesive tape and in engineering plastic modification [16–18], but almost no application in oil well cement has been reported.

Due to the poor hydrophilicity and low density of thermoplastic rubber particles, they are not stable when they are added directly to cement slurry. It is difficult for these particles to disperse evenly, and they easily float on the surface of the cement slurry, which affects the performance of the cement slurry. Therefore, if thermoplastic rubber is to be applied to oil well cement-based composites, the problem of hydrophobicity should first be solved. Surface modification of thermoplastic rubber particles can improve the hydrophilicity and application effect of thermoplastic rubber particles. The modification methods for rubber particles include water washing, acid and alkali corrosion, plasma pretreatment, and various coupling agent treatments [19]. Among them, the use of coupling agents for rubber hydrophilic modification is widespread. Silane coupling agents, which have both inorganic and organic functional groups, are commonly used particle polarity modification materials that can improve the interface state of rubber particles [20, 21]. Zhang et al. [22], Xu et al. [23], Ji et al. [24], and Dong [25] used 3-glycidoxypropyltrimethoxysilane and 3-methacryloxypropyltrimethoxysilane to modify the surface hydrophilicity of rubber materials, and then modified rubber was used in cement-based composite. The mechanical properties of cement paste were improved after silane coupling agent modified rubber.

To develop new flexible materials to improve the flexibility and enhance the mechanical properties of cementing stone, thermoplastic rubber is applied in the mechanical properties modification of oil well cement. In view of the defect of the poor hydrophilicity of TPR particles, TPR is modified by silane coupling agents and the effect of modified TPR on the mechanical properties of oil well cement-based composites is studied.

2. Materials and Methods

2.1. Experimental Materials. The cementing materials obtained from Gezhouba Special Cement Co., Ltd., China, were conventional class G oil well cement. A filtration reducer, a retarder, and a dispersant were purchased from Jingzhou Jiahua Technology Co., Ltd., China. A filtration reducer is mainly used to decrease the water loss of cement slurry. The effect of the retarder is to adjust the thickening time of the cement slurry, and the dispersant can improve the fluidity of the cement slurry. An enhancer and a defoamer were produced in the laboratory. The enhancer can improve the strength of cement paste, and the defoamer is used to prevent foaming when preparing cement slurry.

Thermoplastic rubber (TPR) was obtained from Hunan Yueyang Baling Petrochemical Co., Ltd., China. TPR is used as a flexible material. The silane coupling agents (3-aminopropyl) triethoxysilane (KH550), 3-glycidoxypropyltrimethoxysilane (KH560), and 3-methacryloxypropyltrimethoxysilane (KH570) were obtained from Jiangxi Chenguang New Materials Co., Ltd., China. The silane coupling agents KH550, KH560, and KH570 were used to modify the surface properties of TPR and to improve the hydrophilicity of TPR and its application effect in cement slurry.

2.2. Experimental Method

2.2.1. Modification of TPR. According to the structural characteristics of the silane coupling agent, KH550 and KH560 were prepared with water as the solvent and KH570 with ethanol as the solvent. The specific processing methods were as follows:

(1) Modification of TPR with KH550 or KH560. 1 wt.% silane coupling agent solution was prepared by weighing a certain amount of silane coupling agent KH550 or KH560, using water as the solvent, and fully dissolving the coupling agent in water at 50°C. Then, TPR was added into the solution and stirred uniformly at the speed of 300 r/min. Finally, the TPR particles were filtered from the silane solution and placed in a dry environment until the surface of the TPR particles was completely dry.

(2) Modification of TPR with KH570. 1 wt.% silane coupling agent solution was prepared by weighing a certain amount of silane coupling agent KH570 and using ethanol as the solvent at 50°C. Then, TPR was added into the solution and stirred uniformly at the speed of 300 r/min. Finally, the TPR particles were filtered from the silane solution and placed in a dry environment until the surface of TPR particles was completely dry.

2.2.2. FT-IR Spectroscopy of Modified TPR Particles. 1–2 mg TPR modified by a silane coupling agent was mixed with

200 mg pure potassium bromide and then ground evenly. The sample was put into a mold and pressed into a thin sheet. Spectral analysis of TPR particles before and after modification was performed using a Fourier-transform infrared spectrometer (EQUINOX 55, Bruker, Germany).

2.2.3. Hydrophilic Test of Modified TPR Particles. Unmodified TPR particles and TPR particles modified by a silane coupling agent were put into distilled water. The dispersion of TPR particles in water was observed after a period of time, and the hydrophilicity of the particles was judged from the macroscopic observation.

2.2.4. Cement Slurry Preparation. The preparation of cement slurry is based on the corresponding regulations of Chinese standard GB/T 10238-2005. According to the proportions of the experimental formulas, cement slurry samples were prepared using a constant speed agitator (TG-3060A, Shenyang Taige Petroleum Instrument & Equipment Co., Ltd.). The formulas of the cement slurry are presented in Table 1.

2.2.5. Conventional Performance Test of Cement Slurry. The performance test of cement slurry was carried out in accordance with the corresponding provisions of the Chinese standard GB/T 19139-2012.

(1) Rheology Test. After the cement slurry was prepared, the cement slurry was maintained at 90°C for 20 min using a constant pressure thickener (TG1250, Shenyang Taige Petroleum Instrument & Equipment Co., Ltd.), and then, readings of the cement slurry at 300 r/min, 200 r/min, and 100 r/min were obtained by a rheometer (OFITE900, OFITE, USA). According to the test data obtained at different speeds, the fluidity index n and consistency coefficient K of the cement slurry were calculated according to Chinese standard SY/T 5504.3-2008. The formulas for the fluidity index n and consistency coefficient K are as follows:

$$n = 2.096\lg\left(\frac{\Phi_{300}}{\Phi_{100}}\right),$$
$$K = \frac{0.511\Phi_{300}}{511^{n}}, \tag{1}$$

where Φ_{100} and Φ_{300} are the readings at shear rates of 100 r/min and 300 r/min, respectively. The smaller the fluidity index n and the greater the consistency coefficient K are, the thicker the cement slurry is. Qualified cement slurry has $n \geq 0.5$ and $K \leq 0.7$.

(2) Thickening Time Test. The prepared cement slurry was poured into a slurry cup for the thickening time test, and the bottom cover was tightened. The slurry cup was put into a pressurized consistometer (TG-8040DA, Shenyang Taige Oil Equipment Co., Ltd., China) to test the time,; it took for the consistency of the cement slurry to reach 100 Bc under the condition of 90°C × 45 MPa, which was taken as the thickening time of the cement slurry.

(3) Water Loss Test. The prepared cement slurry was poured into the test cup of a constant pressure thickener (TG1250, Shenyang Taige Petroleum Instrument & Equipment Co., Ltd.) and was stirred and maintained for 20 min at 90°C and atmospheric pressure. After being maintained, the water loss of the cement slurry was tested by a HPHT filter press (TG-71, Shenyang Taige Oil Equipment Co., Ltd., China) for 30 min at 90°C and 6.9 MPa.

(4) Free Liquid Test. The cement slurry was maintained for 20 minutes at atmospheric pressure and 90°C by a constant pressure thickener. Then, the cement slurry was poured into a 250 mL transparent cylinder, and the lid was covered to prevent evaporation. The volume of the cement paste for testing was 250 mL. The measuring cylinder was placed in a constant temperature water bath curing vessel (TG-1280A, Shenyang Taige Petroleum Instrument & Equipment Co., Ltd.) at 90°C for 2 h. Then, the volume of the free liquid was tested. The volume fraction of the free liquid was calculated according to the following formula:

$$F = \frac{V_f}{V_s} \times 100\%, \tag{2}$$

where F is the volume fraction of the free liquid, V_f is the volume of the free liquid, and V_s is the volume of the tested cement paste, which is equal to 250 mL.

2.2.6. Test of the Mechanical Properties

(1) Test Sample Preparation. The prepared cement slurry was poured into a curing mold to test the compressive strength, flexural strength, and impact strength, and the mold was then placed into a pressurized curing chamber (TG-7370D, Shenyang Taige Oil Equipment Co., Ltd., China) for a certain period of time at 90°C × 21 MPa. After reaching the curing age, the test mold was removed, and the cement sample was obtained. The size of the compressive strength sample, flexural strength sample, and impact strength sample were 50.8 mm × 50.8 mm × 50.8 mm, 40 mm × 40 mm × 160 mm, and 10 mm × 15 mm × 120 mm, respectively.

(2) Mechanical Property Test. The compressive strength and flexural strength were tested using a fully automatic flexural and compression testing machine (YAW-300C, Ji'nan Zhongluchang Testing Machine Manufacturing Co., Ltd., China). The compressive strength and flexural strength were tested for two samples and three samples, respectively, and the average value of the test results was obtained. The impact strength was measured by a pendulum impact tester (XJJY-50, Chengdeshi Shipeng Detection Equipment Co., Ltd., China). Eight samples were tested, the maximum and minimum values of the experimental results were removed, and the average value was calculated.

2.2.7. Stress-Strain Behavior Test. The cement stone sample was prepared according to the preparation process of a cement stone sample. After curing for 28 d, the stress-strain behavior of the cement stone was tested according to

Table 1: Slurry samples with different TPR contents.

Sample number	Cement (wt.%)	Water (wt.%)	Filtrate reducer (wt.%)	Enhancer (wt.%)	Dispersant (wt.%)	Retarder (wt.%)	Defoamer (wt.%)	TPR (wt.%)
T0	100	44	2	2	0.6	0.4	0.5	0
T1	100	44	2	2	0.6	0.4	0.5	1
T2	100	44	2	2	0.6	0.4	0.5	2
T3	100	44	2	2	0.6	0.4	0.5	3
T4	100	44	2	2	0.6	0.4	0.5	4

Chinese standard GB/T 50266-2013 using a universal testing machine (HY-20080, Shanghai Hengyi Precision Instrument Co., Ltd., China) under a constant speed load of 2 kN/min.

2.2.8. Fracture Surface Morphology Observation of Cement Stone. After curing for 7 d, the cement stone was destroyed under an external load, and specimens with smooth and unpolluted surfaces were selected. The microstructure of cement stone was observed by scanning electron microscopy (SEM) (SU8010, Hitachi, Japan).

3. Experimental Results and Discussion

3.1. Influence of Different Silane Coupling Agents on the Application Effect of TPR Particles

3.1.1. FT-IR Spectra of TPR Particles Modified by Different Silane Coupling Agents. TPR was modified by different silane coupling agents according to the experimental method of TPR treatment in the laboratory. The spectra and changes of the surface groups of modified TPR were analyzed. The results of the experiment are shown in Figure 1.

As shown in Figure 1, C-H bond stretching vibrations on the benzene ring are observed in the samples between 3100 cm^{-1} and 3000 cm^{-1}, and there are characteristic peaks of the benzene ring at 1610 cm^{-1} and 1456 cm^{-1}. This result indicates that the samples contain hydrophobic group benzene rings. Meanwhile, the wavenumbers of 755 cm^{-1} and 692 cm^{-1} correspond to characteristic peaks of single substituted benzene rings. At 2920 cm^{-1} and 2856 cm^{-1}, the wavenumbers correspond to $=CH_2$. After TPR is treated with silane coupling agent, the peak of hydrophilic hydroxyl group (−OH) appeared at 3420 cm^{-1}. When TPR particles are modified by KH550, the other surface groups of the particles do not change significantly. After the modification of TPR with KH560 and KH570, there are obvious characteristic peaks on TPR surface at wavenumbers from 1000 cm^{-1} to 1100 cm^{-1}, and the characteristic peaks of KH560 (1099 cm^{-1} and 1020 cm^{-1}) are stronger than those of KH570 (1089 cm^{-1} and 1018 cm^{-1}), which corresponds to Si-O. Moreover, the hydrophilic group C=O (the wavenumber is 1724 cm^{-1}) appeared on the surface of TPR treated by KH570, which is beneficial to the uniform dispersion of TPR in hydrophilic cement slurry.

3.1.2. Dispersibility of TPR Particles Modified by a Silane Coupling Agent. As shown in Figure 2, the unmodified TPR particles are completely free from water infiltration, floating above the liquid level and aggregating into clusters. The TPR particles modified by silane coupling agent KH550 or KH560 are homogeneous, but they could not be dispersed in water. The modified TPR particles can be well infiltrated by and dispersed in water when using the silane coupling agent KH570. These results show that the hydrophilicity of the unmodified TPR is poor. Polar groups are formed on the surface of TPR particles modified by silane coupling agent KH570, and the hydrophilicity of TPR particles increases significantly.

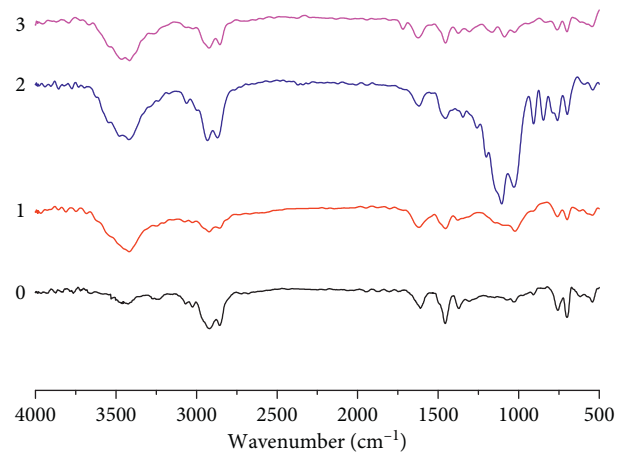


Figure 1: FT-IR spectra of TPR before and after modification (0: unmodified TPR; 1: TPR modified by KH550; 2: TPR modified by KH560; 3: TPR modified by KH570).

3.1.3. Application Effect of TPR Particles Modified by Different Silane Coupling Agents in Cement Slurry. The main purpose of applying TPR in oil well cement is to develop a flexible cement slurry system and improve the mechanical properties of cement paste. Therefore, the evaluation of the application effect is mainly focused on the mechanical properties of cement paste with TPR addition. The compressive strength is the maximum external force that a cement sample can bear when it is destroyed [26]. Cement stone requires good compressive strength to support and protect casing. The flexural strength refers to the ultimate resistance of cement paste to bending moments after being subjected to vertical external forces [27]. It can represent the ability of the cement sheath to bear external shear forces and be calculated based on the three-point bending principle. The impact strength is the energy consumed by the cement specimen after impact fracture, which is used to indicate the capacity of the cement sheath to bear an impact, and its value can directly reflect the toughness of cement stone [28]. In the

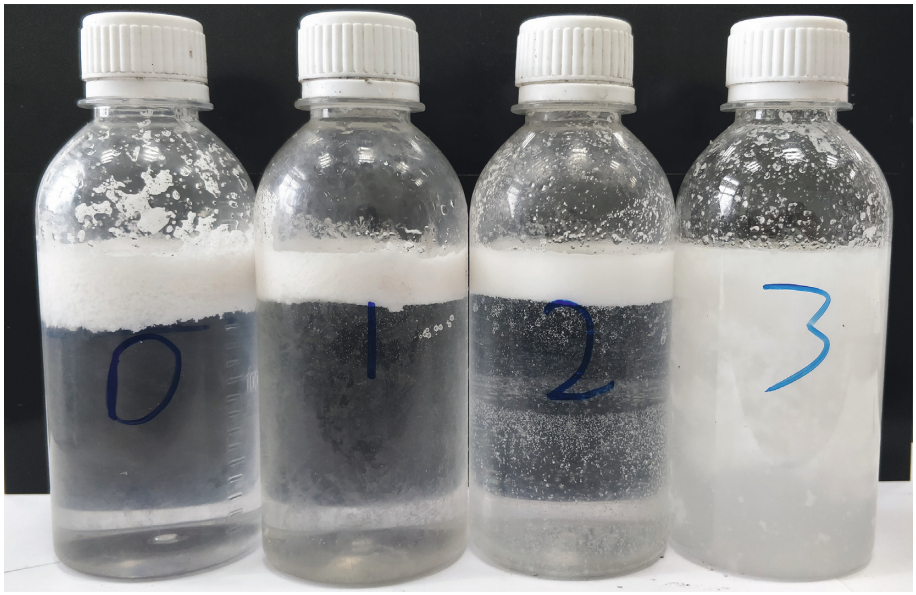


Figure 2: Dispersion stability of unmodified and modified TPR in water (0: unmodified TPR; 1: TPR modified by KH550; 2: TPR modified by KH560; 3: TPR modified by KH570).

laboratory, modified TPR at 2 wt.% was added to the cement slurry system to test the mechanical properties of cement stone after curing for one day and evaluate the application effect of TPR modified by different silane coupling agents in oil well cement.

Figure 3 shows that the compressive strength of cement samples with TPR modified by silane coupling agent KH550, KH560, or KH570 is 10.18%, 6.19%, and 13.12% higher than that of unmodified TPR cement stone. Figure 4 demonstrates that the flexural strength of cement samples with TPR modified by silane coupling agent KH550, KH560, or KH570 is 9.68%, 12.9%, and 24.19% higher than that of unmodified TPR cement stone. Figure 5 shows that compared with the unmodified TPR cement stone, the impact strength of cement samples with TPR modified by silane coupling agent KH550, KH560, or KH570 is increased by 7.05%, 10.26%, and 11.54%, respectively. The experimental results show that the compressive strength, flexural strength, and impact strength of the silane coupling agent modified TPR cement are all higher than those of the unmodified TPR cement stone, indicating that the silane coupling agent modification can improve the application effect of TPR in cementing slurry systems. The reason may be that after the untreated TPR is added to the cement slurry, because of the poor hydrophilicity of TPR, the TPR particles float on the surface of the cement slurry. When the cement slurry is solidified, the upper part of the cement stone consists of undispersed rubber particles, so the mechanical properties are low. When the silane coupling agent is used to modify the TPR, the TPR particles can be dispersed in the cement slurry system uniformly, enabling full utilization of the benefits of the polymer particle material and improving the properties of cement stone.

In addition, the compressive strength, flexural strength, and impact strength of TPR cement paste modified with KH570 are higher than those modified with KH550 and KH560. The molecular formula of the silane coupling agent KH570 is $CH_2{=}C\ (CH_3)\ COO\ (CH_2)_3Si\ (OCH_3)_3$. The organic functional groups of the KH570 molecular formula can form chemical bonds with the surface of rubber particles, and the hydrophilic groups formed on the surface of TPR particles help them disperse in cement slurry [22]. Through this process, rubber particles are well cemented with cement paste.

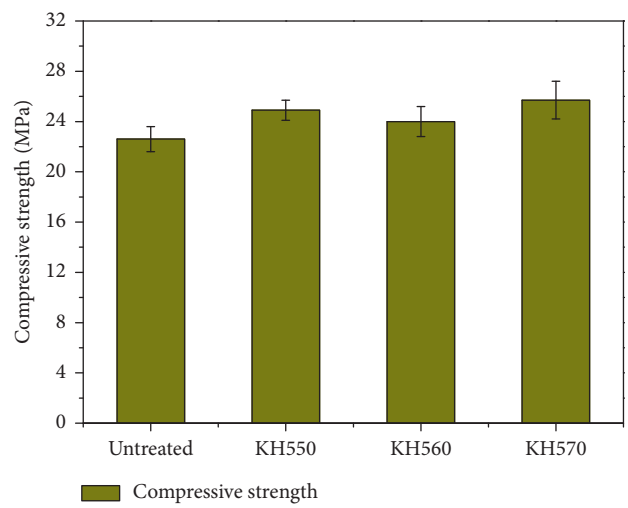


Figure 3: Compressive strength of TPR cement slurry modified by different silane coupling agents.

Subsequent experiments were carried out with TPR modified by silane coupling agent KH570.

3.2. Effect of Modified TPR on the Conventional Properties of Cement Slurry. The conventional properties of cement slurry mainly include the rheology, water loss, free liquid, and thickening time. The rheology determines the pumping

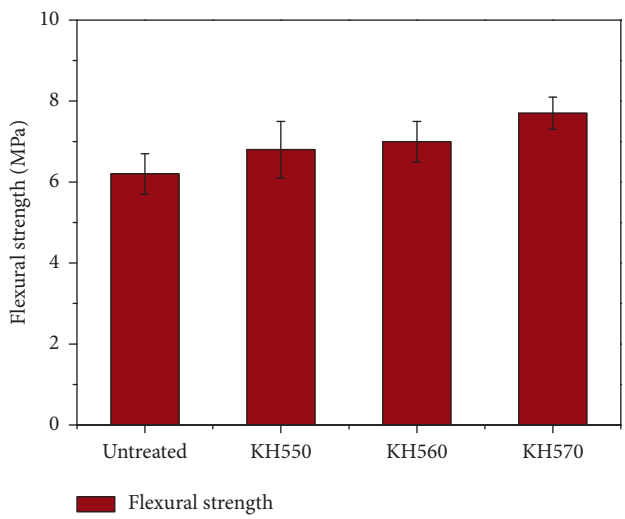


Figure 4: Flexural strength of TPR cement slurry modified by different silane coupling agents.

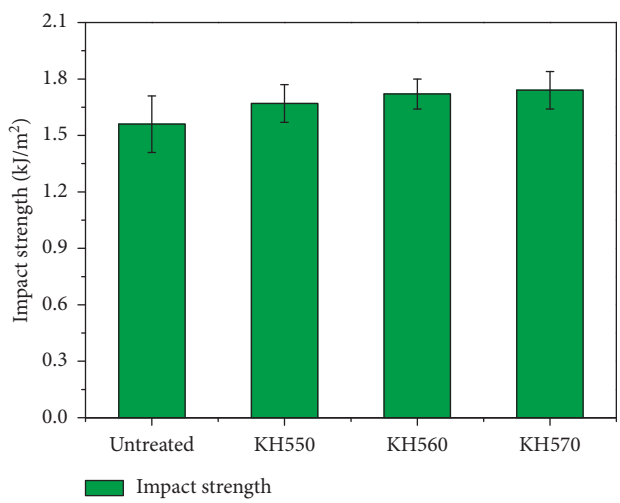


Figure 5: Impact strength of TPR cement slurry modified by different silane coupling agents.

ability and construction safety of cement slurry during cementing operation [29]. The water loss of cement slurry is the free water that can be filtered out through a certain pore area under specified temperature and pressure difference, which is closely related to the cementing quality [30]. The free liquid is an important criterion for evaluating the stability of cement slurry systems [31]. The thickening time of cement slurry is a very important parameter to measure and ensure the safety of pumping and construction [32]. The rheology, water loss, free liquid, and thickening time of cement paste were tested. The rheology and free liquid test results are presented in Table 2. The results of the water loss test and thickening time test are shown in Figures 6 and 7, respectively.

Table 2 shows that the addition of modified TPR has a certain effect on the rheological properties of cement slurry. With the increase of the addition of modified TPR, the flow index n of cement slurry decreases and the consistency coefficient K increases. When TPR is applied to cement slurry, it is necessary to control the dosage or add a dispersant to ensure that the slurry has excellent rheological properties. In addition, after adding modified TPR, the free liquid of cement paste is 0, and the stability of the slurry is improved. As shown in Figure 6, the water loss of the cement

Table 2: Rheology and free liquid of modified TPR cement slurry.

Sample number	Modified TPR content (wt.%)	Rheology		Free fluid (%)
		n	K (Pa·S^n)	
T0	0	0.78	0.37	0.2
T1	1	0.76	0.45	0
T2	2	0.73	0.56	0
T3	3	0.72	0.59	0
T4	4	0.68	0.67	0

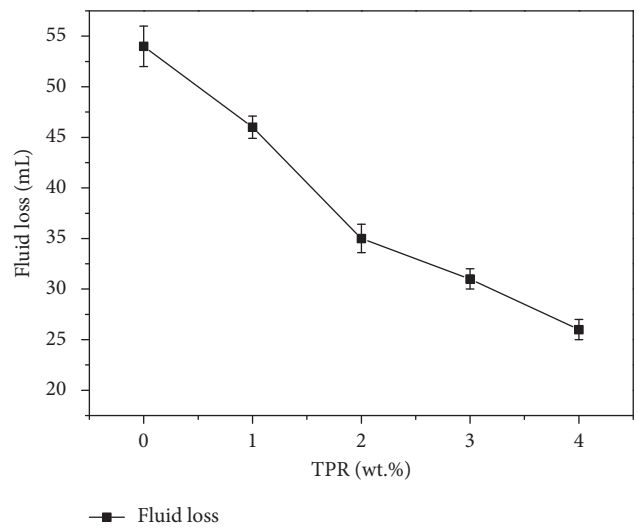


Figure 6: Water loss of cement slurry with different modified TPR contents.

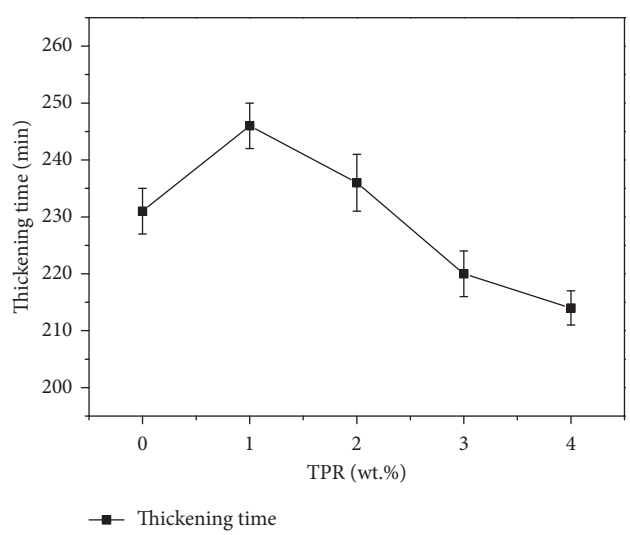


Figure 7: Thickening time of cement slurry with different modified TPR contents.

slurry system with the modified TPR addition of 4% (T4) is 22 mL, which is 59.3% lower than that of pure cement slurry (T0). The addition of TPR can effectively reduce the water loss of the cement slurry. This may be due to TPR filling in the filter cake and forming a polymer bond structure to prevent water loss. From Figure 7, a small amount of modified TPR added to the oil well cement slurry will prolong the thickening time, and the thickening time of the cement slurry is shortened with the increase of the modified TPR addition; however, the thickening time of the cement slurries with different TPR contents changes only slightly and meets the requirements of cementing construction.

3.3. Effect of Modified TPR on the Mechanical Properties of Cement Stone. As a flexible material, the main function of the modified TPR added to the cement slurry system is to improve the mechanical properties of cement paste. The compressive strength, flexural strength, and impact strength of the modified TPR cement samples were evaluated, and the results are shown in Figures 8–10.

The experimental results show that the compressive strength of cement stone is decreased with the addition of modified TPR at different curing ages, but the flexural strength and impact strength of cement paste are greatly improved. The mechanical properties of the modified TPR cement sample increase rapidly within 7 days of curing. With the prolongation of the curing time, the increase of the compressive strength, flexural strength, and impact strength slows down.

As shown in Figure 8, with the same curing time, the compressive strength of cement stone with modified TPR is smaller than that of the pure cement sample, and the compressive strength of specimens increasingly decreases as the TPR content increases from 1% to 4%. After curing for 28 days, the compressive strength of pure cement stone reaches 45 MPa. The compressive strength of cement stone mixed with 1% TPR, 2% TPR, 3% TPR, and 4% TPR is 3.78%, 1.78%, 5.33%, and 10.89% lower than that of the pure cement sample. The reason for the decrease of the compressive strength may be that the flexible TPR particles fill in the network structure formed by cement hydration products, resulting in a reduction in the strength of the hardened matrix. Figure 9 shows that the flexural strength of cement paste is larger than that of pure cement stone when the TPR dosage is less than 3%. When the TPR content is 4%, the early flexural strength of cement paste is lower than that of pure cement paste, but the flexural strength is higher than that of pure cement paste when cured for 28 days. When cured for 1 day, the flexural strength of cement paste with 2% TPR is the largest, reaching 7.7 MPa. With the extension of the curing time, the flexural strength of the cement samples with different amounts of TPR increases. When the curing time is 28 days, the flexural strength of the pure cement sample is 10.2 MPa, and the flexural strength of cement stone with 1% TPR, 2% TPR, 3% TPR, and 4% TPR added is 11.76%, 15.69%, 9.8%, and 3.92% higher than that of pure cement stone, respectively.

As shown in Figure 10, when the curing time is 1 day and 28 days, the impact strength of the cement sample with 3% modified TPR added is the highest, reaching 1.78 kJ/m^2 and 2.23 kJ/m^2, respectively. With the extension of the curing time, the impact strength of the cement samples increases. When the curing time is 28 days, the impact strength of pure cement paste is 2.02 kJ/m^2, and the impact strength of the cement stone mixed with 1% TPR, 2% TPR, 3% TPR, and 4% TPR is 6.44%, 8.91%, 10.4%, and 5.94% higher than that of the pure cement sample, respectively.

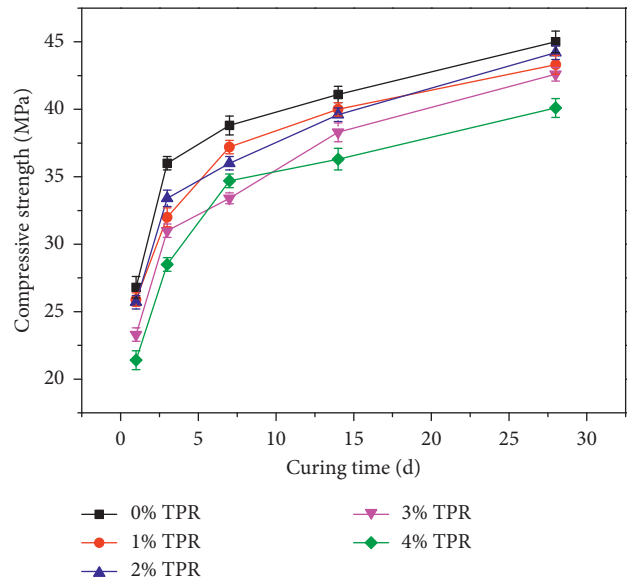


Figure 8: Compressive strength of cement stone with different TPR contents for different curing times.

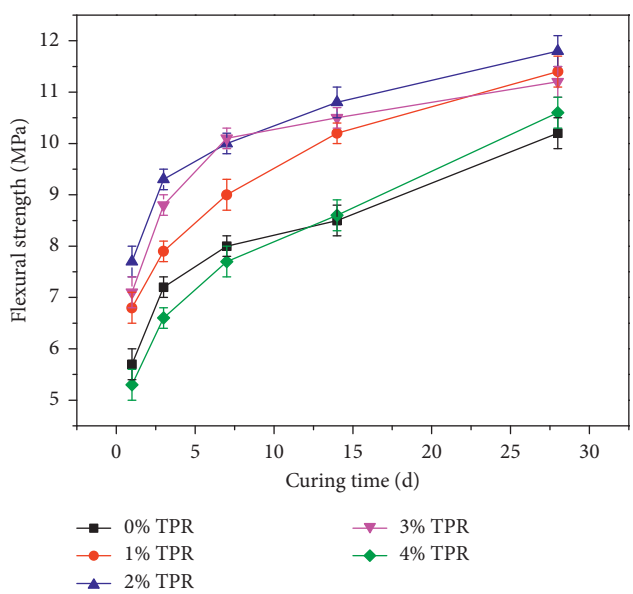


Figure 9: Flexural strength of cement stone with different TPR contents for different curing times.

3.4. Stress-Strain Curve of Modified TPR Cement Stone. To achieve the purpose of long-term cement sealing, cement paste also requires great flexibility and deformation capacity.

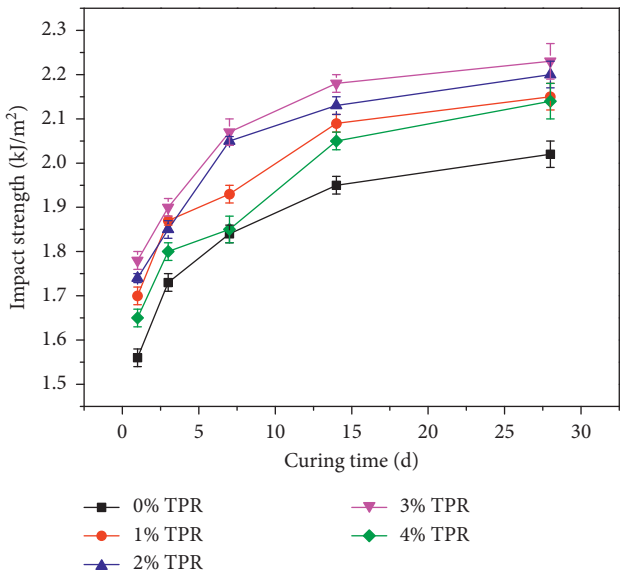


Figure 10: Impact strength of cement stone with different TPR contents for different curing times.

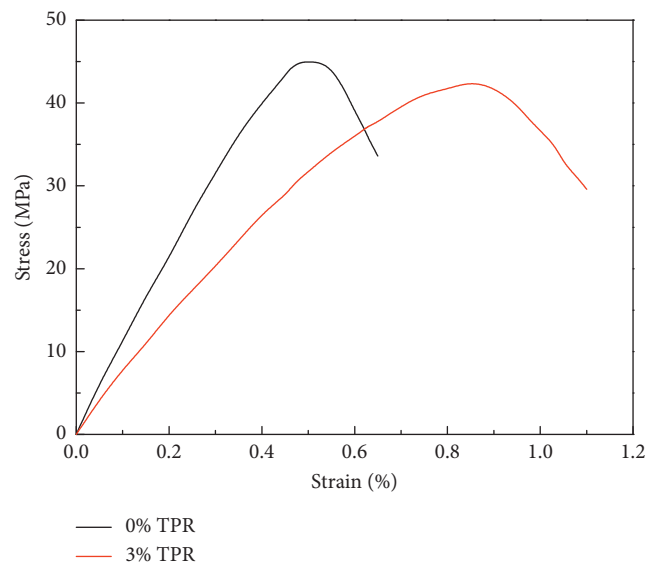


Figure 11: Stress-strain curves of pure cement sample and 3% TPR cement stone.

The stress-strain behavior reflects the deformation rule of cement stone under external stress, and the elastic modulus of cement stone can be obtained from the stress-strain test results. The modulus of elasticity is the standard for measuring the difficulty of deformation of cement stone [33]. The stress-strain behavior of 3% TPR cement paste after curing for 28 d was tested and compared with that of pure cement stone. The results are shown in Figure 11 and Table 3.

As can be observed in Figure 11, the stress-strain behaviors of TPR cement paste and pure cement slurry are quite different under an external load. Under the same load, the deformation of the TPR cement paste is greater than that of the pure cement sample. From the stress-strain curve, it can be seen that the strain increases with the increase of stress when the cement stone is compressed. After reaching the maximum stress, the cement stone is destroyed, and the stress drops. The stress of the pure cement sample rapidly decreases after destruction, while the stress of the sample containing 3% modified TPR decreases slowly. This is because the cement stone is subjected to external compression stress at the beginning and the inner pores of the cement stone are gradually compressed [34]. With increasing load, the stress and strain of the cement stone are nonlinear. When the maximum stress is reached, the cement stone is destroyed. However, the destruction of the cement stone is a gradual process; the cement sample with good flexibility has a certain load bearing capacity after reaching the peak stress, so the stress drops slowly.

The elastic modulus of cement paste can be obtained according to the test results of the stress-strain behavior. The results in Table 3 show that the maximum strain of the cement sample with 3% TPR (T3) added increases by 77.55% and the elastic modulus decreases by 45.16% compared with those of pure cement paste (T0). The TPR significantly improves the deformation capacity of cement paste and reduces the modulus of elasticity. This is of great significance for improving the ability of cement stone to resist damage caused by downhole stress.

Table 3: Test results of stress and strain.

Sample number	Modified TPR content (wt.%)	Peak stress (MPa)	Peak strain (%)	Elastic modulus (GPa)
T0	0	45	0.49	9.3
T3	3	42.6	0.87	5.1

3.5. Fracture Surface Morphology Observation of Modified TPR Cement Stone. The internal morphology of the cement sample with 3% TPR (T3) was observed. The internal macromorphology structure after the destruction of cement paste is shown in Figure 12, and the microstructure is shown in Figure 13. From Figure 12, after specimen T3 was destroyed, a clear TPR coupling structure can be seen in the cement specimen, and the softening of TPR to form a cohesive structure will lead to bonding with the hydration products of cement. From the SEM photo of Figure 13(a), it can be seen that TPR forms a bonded network structure inside the cement paste. The SEM photograph (Figure 13(b)) clearly shows the formation of hydration products in the interior of the reticular structure, and the hydration of cement is closely related to the softening structure of TPR. When the TPR cement slurry solidifies at a certain temperature, the connection structure formed by the softening of TPR particles dispersed in the cement paste penetrates the hydration products of the oil well cement, which improves the structure and properties of the cement matrix. After the cement stone is subjected to an external compression load, a microcrack is produced inside the cement stone. The TPR polymer material filling in the cement stone will cement the surrounding cement hydration products together and bridge the cracks, which prevents the rapid development of cracks

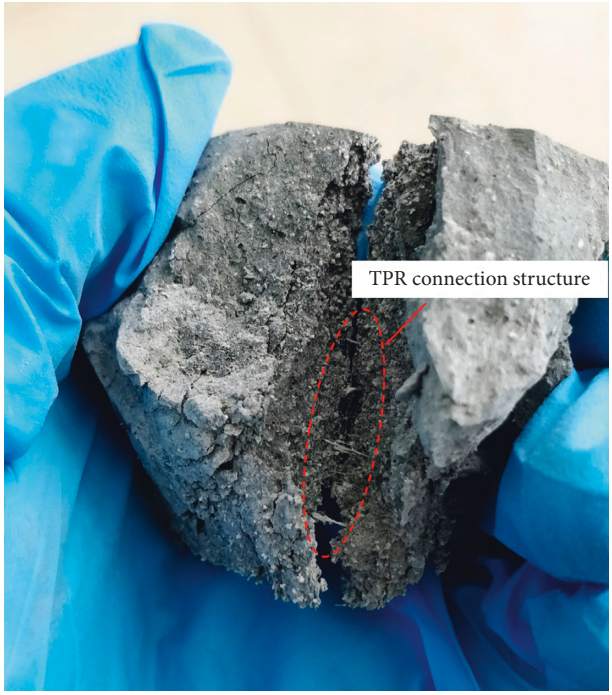
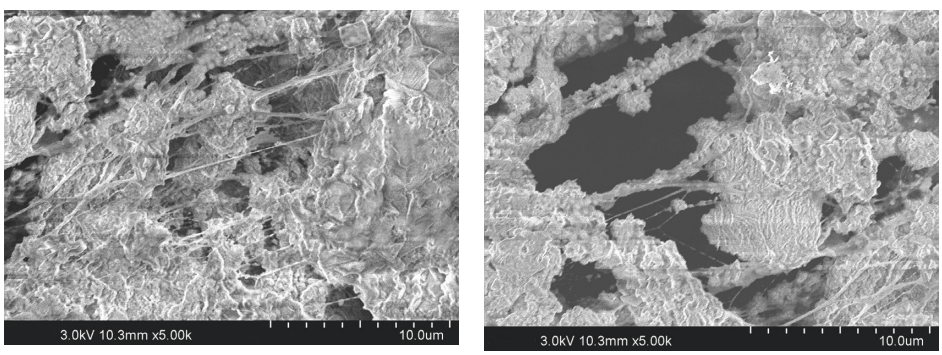


Figure 12: Internal macromorphology of a T3 cement stone specimen.



(a) (b)

Figure 13: SEM photos of T3 cement stone specimens: (a) the overall microstructure of TPR cement stone; (b) the partial microstructure of TPR cement stone.

and thus improves the mechanical properties of cement stone. At the same time, because of its high elasticity, TPR particles filling in the cement stone can form a structural center to absorb external destructive energy. When the cement stone is affected by an impact force, the cement crystal particles are the medium that transfers the impact force, and the force is transferred to the TPR structure filling in the cement stone [35]. The elastic deformation of TPR material has a certain buffer effect on the external load and absorbs some energy, thus increasing the elasticity and toughness of the cement sample.

4. Conclusion

(1) The modification effect of TPR with silane coupling agent KH570 used in the surface treatment is the best. The hydrophilicity of TPR particles is improved, and the dispersion in water is good. Additionally, the compressive strength, flexural strength, and impact strength of modified TPR cement stone are 13.2%, 19.2%, and 10.2% higher than that of the unmodified cement stone, respectively.

(2) After adding TPR, the rheology of the cement slurry system meets the construction requirements. The settlement stability and water loss are better than those of pure cement slurry, and there is no adverse effect on the thickening time.

(3) Modified TPR will slightly reduce the compressive strength of cement paste but effectively improve the flexural strength and impact strength. When the content of modified TPR is 3%, the compressive strength of TPR cement paste decreases by 5.33%

after 28 days of curing, while the flexural strength and impact strength increase by 9.8% and 10.4%, respectively. In addition, the content of modified TPR applied in oil well cement slurry needs to be controlled.

(4) Modified TPR can effectively improve the deformation capacity of cement paste and reduce the elastic modulus. Compared with the pure cement sample, the maximum strain of 3% modified TPR cement paste increases by 77.55% and the elastic modulus decreases by 45.16%.

(5) When the modified TPR cement slurry is solidified at 90°C, the connection structure formed by the softening of TPR particles dispersed in the cement slurry penetrates the hydration products of oil well cement. The structure and properties of the cement matrix are improved, and the brittleness of the cement stone is reduced.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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