Research Article

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Investigations of polyethylene of raised temperature resistance service performance using autoclave test under sour medium conditions

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Abstract: The chapter deals with the performance evaluation of the polyethylene of raised temperature resistance (PE-RT) and polyethylene (PE) using autoclave test under sour oil and gas medium conditions. The analyses of performance changes showed that PE-RT has good media resistance at 60°C. As the temperature increases, its mechanical properties decrease, accompanied by an increase in weight. Comparative analyses showed that no matter what temperature conditions are, PE-RT media resistance is better than PE80. The better media resistance of PE-RT depends on its higher degree of branching. Short branches are distributed between the crystals to form a connection between the crystals, thereby improving its heat resistance and stress under high-temperature conditions. PE-RT forms an excellent three-dimensional network structure through copolymerization, ensuring that it has better media resistance than PE80. However, the mechanical performance will be attenuated due to the high service temperature.

Keywords: plastic, stress, chain, degradation, swelling

1 Introduction

Due to the excellent corrosion resistance, nonmetallic and composite pipes have become one of the most important

solutions to solve the corrosion problem of oil and gas fields (1–3). As the amount addition increases, the trend of using nonmetallic and composite pipes to replace carbon steel pipes is becoming more and more obvious. Thermoplastics can be used directly as pipes or as the inner lining of composite pipes, which has an important position (4,5). Since the thermoplastic is in direct contact with the conveying medium, the media resistance of the nonmetallic composite pipe depends on the thermoplastics. Among them, PE has become the most used thermoplastic due to its high-cost performance (6–8). In the microstructure, the crystalline region formed by the folding of the chain segments and the amorphous region coexist. The tie molecules connecting the crystalline and amorphous regions of the polymer play a key role in the long-term high-temperature creep properties of the PE pipe (9–11).

With the expansion of oil and gas fields, the higher medium transportation temperature puts forward higher requirements on the temperature resistance of thermoplastic, PE-RT came into being. In the service process of various types of pipes, the inner wall of the pipe is chemically corroded by the contacting oil-gas coupling medium under high temperature, high pressure, and other multi-physical field conditions (10). Especially in the oil and gas medium with high acidity (H_2S , CO_2 , etc.), it will cause performance degradation of plastic pipes such as swelling, bulging, and softening (12). The combination of medium and internal hydraulic load will cause pipe cracking failure behavior (13). Although thermoplastic plastic pipes have excellent corrosion resistance, they will experience aging under long-term service conditions and are subjected to the multiple effects of temperature, pressure, and media, simultaneously (14,15). There is a risk of performance degradation or even failure under long-term service conditions. Once pipe failure occurs, it may cause serious casualties and environmental damage. The evaluation is an important link in the development and application of new products. For the new products developed, it is necessary to carry out long-term service performance evaluation

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under simulated working conditions and verify the relevant performance indicators before application. Only in this way can the product be safe and reliable during the service period. However, currently there are few reports on the performance evaluation of thermoplastics under sour oil and gas medium conditions (6,9,11,12,16).

In order to understand the interacting mechanisms involved in this study, it will be necessary to consider all the underlying processes, such as the effects of material structure, the effects of temperature and stress, and degradation in specific environments. In this study, the applicability and aging mechanism of PE-RT for the transportation of sour oil and gas media are also studied.

2 Experimental

2.1 Sample preparation

The PE-RT pipe with the specification of DN100*6 mm produced by SABIC Co. is used for research. The sample is prepared according to type 1 of ISO 6259-3:1997 “Thermoplastics pipes – Determination of tensile properties – Part 3: Polyolefin pipes.” Four specimens were prepared under each condition, three of which were used for tensile tests and one was used for other performance tests. For comparison, under the same conditions, PE80 pipes were also tested.

2.2 Experimental process

Before conducting the exposure test, the specimens of PE-RT and PE80 should be tested. Test items include sample size and weight, tensile properties, thermal stability, composition, and microstructure.

The exposure test is completed with the autoclave system, and the medium selection in the autoclave refers to ISO 23936-1:2009 “Petroleum, petrochemical and natural gas industries Nonmetallic materials in contact with media related to oil and gas production Part 1: Thermoplastics.” The requirements for the test medium are as follows: 30% gas phase (10% CO₂, 10% H₂S, and 80% CH₄) and 70% liquid phase (70% heptane, 20% cyclohexane, and 10% toluene); In this exposure test, the temperature is 90°C, the pressure is 8 MPa, and the test period is 0, 1, 3, 5, and 7 weeks.

The sample is taken out and tested after the exposure test is completed. The test samples are the same as those before the test. Among them, visual inspection of external damage includes but is not limited to the following forms: cracks, delamination, swelling, blistering, etc. Meanwhile, cutting is performed to check the internal structure of the sample.

2.3 Performance test and characterization

2.3.1 Weight change

The weight is tested by electronic analytical balance (CPA225D, Sartorius, Germany), with an accuracy of 10⁻⁴ g. Five groups of samples with different exposure time (0–7 weeks) were subjected to weight test, and the weight change of different exposure time was compared and analyzed.

2.3.2 Macro mechanical performance

The tensile properties are tested by the universal test machine (UH-F500KNI, Shanghai Xinsansi, China) with the accuracy of 1 N and the tensile rate of 50 mm/min according to ASTM D638. The test data included strain and stress.

2.3.3 Vicat softening temperature analysis

The Vicat softening temperature is one of the indexes to evaluate the heat resistance of materials and reflect the physical and mechanical properties of samples under heated conditions. The Vicat softening temperature is tested by the Vicat softening point tester (Chengde Precision, China) under the force of 50 N and the heating rate of 50°C/h refers to ISO 306. The specimen is a square with a side length of 10 mm. The temperature ranges from 25°C to 200°C.

2.3.4 Composition analysis

The composition of functional group is analyzed by the fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet Avator 360, American). FT-IR analysis is performed

by means of attenuated total reflection, with the spectral range of 400 to 4,000 cm^{-1} and the spectral resolution of 4 cm^{-1} .

2.3.5 Microstructure characterization

The microstructure is characterized by Scanning electron microscope (SEM, Hitachi S4800, Japan). In order to avoid the damage to the sample in the process of preparing the sample, the surface of the inner wall of the pipe after cleaning is observed in this test.

2.3.6 Crystallinity analysis

The crystallinity is the ratio of the mass or volume of the crystalline part of the polymer to the total mass or volume, which is one of the important physical quantities. The degree of crystallinity is directly related to the mechanical and heat resistance properties of polymer materials. In this study, the differential scanning calorimetry (DSC) is used to test the crystallinity by measuring the enthalpy of fusion. For recording the crystalline melting curve of PE-RT and PE80, the DSC study is carried out. In the DSC analysis, two heating and cooling cycles were performed at a rate of 10°C/min under N_2 environment protection, and the temperature ranges from 25°C to 240°C.

3 Results and discussions

3.1 Weight change

The test result of weight change rate is shown in Figure 1. A comparative analysis of the weight change rate of PE-RT and PE80 shows that the quality change rate of PE-RT is significantly smaller than that of PE80, and this trend becomes more obvious as the exposure time increases. In addition, the analysis of the weight change of PE-RT under different temperature conditions demonstrates that in the middle period of exposure time (from 1 to 5 weeks), the weight change rate at 90°C is slightly greater than that at 60°C. As the exposure time further increases, that is, when it reaches 7 weeks, the weight change rate of the two samples is relatively close. Through the above analysis, it can be seen that the exposure time and temperature will have a significant effect on the weight

Figure 1: The weight change rate of PE-RT and PE80 after the exposure test.

change rate, and both will promote the increase of the sample quality. However, the temperature has different effects on the different materials. Due to the better temperature resistance of PE-RT, the effect of temperature on PE-RT is not obvious. During the exposure test, owing to the penetration and swelling of the oil and gas medium, part of the medium enters the sample, which increases the weight of the sample (17).

3.2 Macro mechanical performance

The stress-strain curves of PE-RT and PE80 are shown in Figure 2. It can be clearly seen that the yield strengths of all samples decrease with the increase of exposure time. Comparing with the yield strength of the original sample, it can be seen that PE-RT's yield strength is larger than PE80's, and the strength values are 22.6 and 21.8 MPa, respectively. And the tensile performance of the former is better than that of the latter. Comparing with the tensile strengths of the two samples at 60°C, the yield strength of PE-RT after exposure for 7 weeks is reduced to 19.6 MPa, which is still greater than that of PE80 after 7 weeks of immersion (18.8 MPa). At 90°C, after the 7-week exposure test, the yield strength of PE-RT decreases to 18.3 MPa, which was still higher than that of PE80 (16.9 MPa). Through the above analyses, whether it is the original sample or the sample exposed to oil and gas media, the mechanical properties of PE-RT are better than those of PE80. However, after the exposure to oil and gas media, the two types of the samples' mechanical properties still showed a trend of decreasing to varying degrees. This is because during the exposure process, the

Figure 2: The stress–strain curves: (a) PE80-60°C, (b) PE80-90°C, (c) PE-RT-60°C, (d) PE-RT-90°C.

medium penetrates the sample and extracts the small uncured resin molecules and decomposed molecules. Due to extraction, the various defects such as concentrated holes and micro-cracks are formed inside the pipe. The stress on the molecular chain near the cavities far exceeds the average stress of the actual material, causing the mechanical properties of the place to decrease, thereby affecting the overall mechanical properties of the pipe (18–20).

As the temperature rises, the movement unit of the chain segment gradually increases, and the total free volume increases. In this state, the restrictive effect of polymer chain on the molecules' movement is weakened, which makes the medium penetration or extraction easier.

3.3 Vicat softening temperature analysis

The Vicat softening temperature test result is shown in Figure 3. The analysis shows that the Vicat softening temperature of all samples at different immersion

Figure 3: Vicat softening temperature test.

temperatures showed a downward trend. As the exposure time increases, the downward trend becomes flatter. As mentioned earlier, during the exposure test, due to the swelling and extraction of the medium, the temperature resistance of the sample is reduced. As the exposure time increases, this change gradually reaches a steady state, so the Vicat softening temperature change trend is relatively flat. Comparing the Vicat softening temperature at different temperatures (60°C and 90°C), it can be seen that the temperature increase in the test can significantly reduce the Vicat softening temperature of the sample. This is because the temperature accelerates the swelling and extraction. Regardless of the test temperature, the Vicat softening temperature of PE-RT is higher than that of PE80, indicating that the temperature resistance of the former is better than that of the latter under contact with the medium. This is also the result of the unique molecular chain structure of PE-RT. The reason for this change is the unique molecular chain structure of PE-RT.

3.4 Composition analysis

The infrared spectrum is shown in Figure 4. The comparison with the samples under different test conditions and the initial samples shows that the composition between them is basically unchanged, and the characteristic peaks are shown as typical PE types. Therefore, during the exposure test, there was no chemical reaction leading to changes in functional groups and physical phenomena such as swelling and extraction due to the medium entering the inside of the pipe.

Figure 4: Infrared spectrum of PE-RT and PE80: (a) PE-RT-60°C, (b) PE-RT-90°C, (c) PE80-60°C, (d) PE80-90°C.

3.5 Microstructure characterization

The microstructure of the two types of thermoplastic during the exposure test is shown in Figure 5. The surface of the original sample of the two samples is relatively smooth, without obvious erosion. With the increase of exposure time, micro-holes appeared on the surfaces of both, and this phenomenon became more obvious with the increase of exposure time and temperature. The appearance of this feature also shows that the medium extracts small molecules in the amorphous region during the exposure test. Under 60°C, with the increase of exposure time, the microscopic morphology of PE-RT is basically unchanged, showing good resistance to the media. When the temperature of the exposure test was increased to 90°C, island-like micro-cracks appeared in PE-RT as that did in PE80, but the number of micro-cracks was less than that of the latter, indicating that its performance under this condition is better than PE80.

3.6 DSC analysis

The thermal scan curves of the two initial samples and the samples after exposure to the test conditions at 90°C for 7 weeks are shown in Figure 6. Comparing the enthalpy of fusion before and after the test, it can be seen that the enthalpy of fusion after the exposure test has an increasing trend. Since the enthalpy of heat fusion is proportional to the degree of crystallinity, it can be seen that the degree of crystallinity is also increasing, which also proves that the physical phenomenon of the medium extracting substances in the amorphous region does exist during the exposure test.

3.7 Comprehensive analysis

The attenuation of pipe performance is mainly affected by three factors, the conveying medium, temperature, and pressure. The exposure test simulates the service conditions of PE-RT and PE80 pipes under actual working conditions. The reasons of PE-RT service performance changes under this working condition are studied through the comparison of physical properties, composition, and micro-morphology analysis before and after the exposure test. During long-term operation, the medium will enter the inside of the pipe due to penetration. Under microscopic view, the medium molecules entering the inside of the pipe

Continue

Figure 5: SEM micrographs of PE80 and PE-RT: (-0): the original samples, (-1): 60°C for 3 weeks, (-2): 60°C for 7 weeks, (-3): 90°C for 3 weeks, (-4): 90°C for 7 weeks.

Figure 6: Thermal scan of PE80 and PE-RT: (a) the original samples of PE80, (b) PE80-90°C for 7 weeks, (c) the original samples of PE-RT, (d) PE-RT-90°C for 7 weeks.

Figure 7: Molecular structure of PE-RT.

are located at the crystal boundary, causing swelling and appearing as weight gain. In addition, the medium extracts the small resin molecules which are uncured or decomposed inside the pipe, showing weight loss. Since the swelling effect is significantly stronger than the extraction, the final manifestation is that the mass increases with the prolonged exposure time. The degradation on PE or PE-RT, such as other semicrystalline polymers, has almost exclusively shown that degradation is concentrated in the amorphous regions (21–23).

Due to the penetration and swelling of the medium, various defects, such as cavities and micro-cracks are formed inside the pipe, can cause the stress concentration of the molecular chain at this place and are higher than the stress of the molecular chains at other positions. Fracture failure occurs first at this stress concentration, which eventually leads to a decrease in overall mechanical properties. Since the swelling process is only a physical process, no chemical reaction occurs, which can also be proved by infrared analysis. Through microscopic morphology analysis, the existence of micro-crack defects is confirmed (24). However, because the defects are micro-sized morphology, they have little effect on reducing the macro-mechanical properties.

The mechanical and temperature resistance of PE-RT are better than those of PE80; the reason is that its molecular chain is different in the structure. The PE-RT is copolymerized by ethylene monomer and 1-octene monomer to form a longer branched olefin monomer containing 6 carbon atoms in the branch, which has a higher degree of branching. PE-RT in this study is a high-density PE produced by a special molecular design and synthesis process. It adopts a copolymerization method of ethylene and 1-octene monomer and obtains a unique molecular structure by controlling the number and distribution of side chains to improve the heat resistance of PE. Due to the existence of short octene chains, the macromolecules of PE-RT cannot be crystallized in a flaky crystal, but

penetrate through several crystals to form a connection between the crystals. The short branches (the tie molecules) run through several crystals to form the connection between the crystals (see Figure 7), thus forming a “three-dimensional network structure”. The formation of this structure retains the good flexibility of PE and high thermal conductivity and inertness, while making it more pressure-resistant, thereby the PE-RT pipe obtains excellent thermal stability and mechanical properties (25).

4 Conclusion

The results of the high-temperature autoclave test show that PE-RT exhibits good media resistance under the test conditions of 60°C. However, when the test temperature is increased to 90°C, its media resistance slightly decreases. Comparative analysis shows that no matter what temperature conditions are, media resistance of PE-RT is better than that of PE80. The excellent resistance to media of PE-RT depends on its higher degree of branching. Short branches as the tie molecules are distributed between the crystals to form a connection between the crystals, thereby improving its heat resistance and stress under high-temperature conditions.

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