Aging behaviour and properties evaluation of high-density polyethylene (HDPE) in heating-oxygen environment

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Abstract. The high-density polyethylene (HDPE) samples aged in heating-oxygen environment were prepared. The mechanical properties were determined by the tensile test and small punch test (SPT), and the chemical properties were determined by Fourier transform infrared spectroscopy (FT-IR) and gel permeation chromatography (GPC). Meanwhile, microscopically morphology of tensile fracture was observed successively. The result showed that tensile strength increasing continuously with the aging time increasing; meanwhile elongation and maximum load in SPT reached the maximum value at the aging time of 28 days. The carbonyl index on the sample surface increased significantly with the aging time increasing. At the same time, the molecular weight increased until the aging time is 28 days, and then changed slightly. This means that the aging behaviours based on cross-linking increased firstly, and then degradation played a more important role in materials properties change. The microscopically morphology of tensile test samples could prove this point with the amount of crazes decrease, and the brittleness of aged samples increase.

1. Introduction
Over the past years, polyethylene (PE) has been widely used for pipe materials of drinking water and gas, and it has been reached 50% in the construction of medium and low pressure pipe network [1-3]. The high-density polyethylene (HDPE) has become the widely used materials in gas or water deliver pipe since 1950s [4-5]. HDPE pipe has many excellent properties, such as corrosion resistance in soil, economic performance and low price. But the other fact is that aging effect in multiple environments was one of the most important limitations to it. Nowadays there were many studies on the aging process in ultraviolet (UV) radiation, but fewer studies in heating-oxygen environment [6,7]. Most scholars think that the process of polymer had a low reaction rate and unsustainable change tendency of early stage in heating-oxygen environment [8-12]. However, the mechanism of the variation was still not clear. Meanwhile, most scholars used the full size samples to determine the polymer aging degree. Some articles noted that the aged layer maybe less than 100 μm, and it is very thin comparing with the original substrate, would result for full size samples not satisfy the evaluation condition of the aged polymer properties [13-15]. Therefore, we want to seek a method replaced full size sample, and it could show more information of the properties on aged layer, that is more suitable for the aged polymer evaluation.
2. Experimental preparation

2.1. Materials preparation
The HDPE raw material is M7600. It is a type of PE 80 and produced by SINOPEC Yanshan Company. Bar-extruded method for all samples. The heating-oxygen environment provided by a heating cabinet. The aging condition making reference to others' research was kept at constant temperature of 90±1°C with air circulating, and 7 days was one cycle for calculating the aging duration. The aging durations are 0 to 8 cycles, and the aging time of 0, 7, 14, 21, 28, 35, 42, 49 and 56 days [16].

2.2. Mechanical properties test

2.2.1. Tensile test. The tensile samples were conducted on dumbbell shape, referring to ASTM D638 (type I), and 5 parallel samples were prepared in each aged case. This experiment was tested in a the universal mechanical tester GWT4503, provide by SANS , and with the extensometer DBX-800, also provided by SANS. Loading speed in this test was 2mm/min, and the room temperature was 25±3°C in test.

2.2.2. Small punch test (SPT). SPT was referred to ASTM F2183. The samples were conducted on disk samples, and 4 parallel samples were prepared in each aged case at least. The SPT sample was 10mm in diameters, and 1.0 mm in thickness. The loading system was similar as the tensile test, and loading speed was 2 mm/min. The structure diagram of SPT test device is shown in figure 1. For this device, it was 2.5 mm in punch diameter, and 4mm in diameter of hole in the base with 0.2 mm chamfer radius.

![Figure 1. Structure diagram of SPT test device.](image)

2.3. Chemical properties

2.3.1. FT-IR measurement. ICarbonyl index of aged HDPE in 28 d and 56 d were detected to evaluate the aging degree of HDPE We use the Bruker LUMOS IR-Microscope with Attenuated Total Reflection (ATR) mode to test it. For surface evaluation, the detection points were random choosed, and for the depth evaluation, the measurement of depth were point-by-point scanning from heated surface to interior on sample fracture surfaces after sanding. In order to calculate the carbonyl index accurately, the carbonyl consumption is derived from 1730 cm⁻¹ to 1765 cm⁻¹.
2.3.2. GPC measurement. The molar mass distribution was determined by the high temperature GPC of Tosoh HLC-8321. The temperature of the injection block and the column compartment making reference to others’ research was set to 145°C [17]. The gel chromatographic columns with dimensions of 7.8 mm I.D. x 30 cm were used, and the flow rate of the mobile phase was 1 ml/min. The polymers were dissolved for 4 h in 1,2,4-trichlorobenzene containing butylated hydroxytoluene as antioxidant at a concentration of 0.5 mg/ml, and a temperature of 145°C, 200 ml of the polymer solution for each injection. The sample was then cut from SPT samples with full thickness.

2.4. Microstructure observation
A scanning electron microscope (SEM) of HITACHI SU 3400 was used to observe microscopically morphology with tensile samples. The observation area was the necking region on the tensile samples’ surface, with gold sputtering first.

3. Result and discussion

3.1. Mechanical properties
Figures 2 and 3 show the results of tensile tests of HDPE at different aging time, and figure 2 is a stress-strain curves.

Figure 2 shows the tensile curves performed very similar at different aging time. There are no obvious yield platform in this curves, and tensile strength (Rm) almost equals to yield strength. The range of plastic deformation is very wide in all of the tensile curves, which show a viscoelastic fracture characteristic.

Figure 3 shows the variation tendency of Rm and elongation at break (A). According to the results, tensile strength (Rm) increased continuously with the increasing of aging time, and it reached 23.33 MPa at the aging time of 49 days and 56 days, which increased about 16% than the original value of 20.04 MPa at 0 day. The variation tendency of elongation was not consistent with the increasing of aging time. At first it was increased, and then decreased slightly with the increasing of aging time at 28 days. The maximum value of the elongation was 112.82% at the aging time of 28 days, which increased about 15% than the 0 day. The minimum value was 87.66% at the aging time of 56 days, which was about 10% decreased. The results show clearly that heating-oxygen environment could cause HDPE aging, with loss of ductility to a certain extent.

Figure 4 shows the load-displacement curves in SPT of aged HDPE samples, and figure 5 shows the maximum load of HDPE with increasing aging time.
It can be seen that the load-displacement curves had similar characteristics for all samples, and the variation tendency of maximum load was regular with increasing aging time.

In this case, the maximum load in SPT increased rapidly firstly, and then declined with the increasing of aging time. The maximum value of maximum load occurred at 28 days, which was 217.5 N, increased about 21% than the 0 day. It must be noted that, the variation tendency of maximum load in SPT is very similar to the elongation in tensile test, and the SPT changed more significantly than tensile tests. It indicated that the SPT might be a more susceptible method to evaluate the HDPE aging degree than the traditional tensile tests in heating-oxygen environment.

**Figure 4.** Load-displacement curves in SPT at different aging time.

**Figure 5.** The change of maximum load in SPT at different aging time.

### 3.2. Chemical properties

Figure 6 shows the number-average molecular weight (Mn) and weight-average molecular weight (Mw) of HDPE at different aging time.

**Figure 6.** The number-average molecular weight (Mn) and weight-average molecular weight (Mw) at different aging time.

According to the results, HDPE had a high macromolecular chain structure. Mn and Mw performed similar variation tendency with increasing of aging time, and the variation value almost change in the same level. Firstly, the Mn and Mw increased rapidly until the aging time of 28 days, and then basically kept stable. In the stable-stage, Mn kept the value within a range of 3.6-3.9 x 10^3, and Mw kept in 4.5-5.0 x 10^6. The results indicated that molecular chains of HDPE may have been broken in this heating-oxygen environment, but not significantly. For the samples made by raw materials without additives, the raise of Mn and Mw may be attributed to the slight cross-linking reaction [18].

Figures 7 and 8 show carbonyl index of HDPE surface at 28 days and 56 days, respectively.
The results showed that carbonyl occurred both on the two HDPE samples’ surface with different aging time, and the carbonyl index with 56 days aging (1.53-1.70) was much higher than the 28 days (0.61-1.03). It is well known that carbonyl index can be used as a quota to judge the state of polymer degradation, and is associated with chain scission. So the results indicated that the degree of oxidation and chain scission on HDPE surface would be more and more with the increasing of aging time. As the result shown, the oxygen degradation only occurred on the sample surface, and it could increase the susceptibility of slow-crack-grow, so that elongation was reduced. But for the tensile strength, the force appeared on the cross section, and the sample is hardening for cross-linking all the time. So it increased.

![Figure 7](image1.png)  ![Figure 8](image2.png)  ![Figure 9](image3.png)

**Figure 7.** Carbonyl index of HDPE surface at the aging time of 28 days. **Figure 8.** Carbonyl index of HDPE surface at the aging time of 56 days. **Figure 9.** Carbonyl index from surface to interior at the aging time of 56 days.

Figure 9 shows carbonyl index from surface to interior at the aging time of 56 days at HDPE surface.

It can be learned that the maximum carbonyl content location occurred on the sample surface after aging experiment. The carbonyl index declined from the surface to the interior linearly, and nearly disappeared at the center of sample interior. It indicated that the chain scission reaction almost occurred only on a very thin surface layer.

Figure 10 shows the microscopically morphology in necking region of HDPE sample surface in tensile test.
It can be seen that HDPE absorbed energy by an elastic shrinkage perpendicular to the direction of stress at original situation [19,20]. At the same time, it can be seen that a lot of crazes formed in microfibers and cavities, which is perpendicular to the tensile direction, and arranged closely. The density of crazes decreased with the increasing of aging time, and disappeared completely at the aging time of 56 days. At this time the tensile stress causes a brittle fracture on HDPE surface.

Figure 10. The microscopically morphology in necking region of HDPE surface in tensile test, (a) 0 day aging, (b) 7 days aging, (c) 28 days aging, and (d) 56 days aging.

3.3. Discussion

There are three stages of HDPE aging in the heating-oxygen environment, and the properties changes due to the competition of strengthening and degradation in this environment, as shown in figure 11.

Figure 11. The three stages of HDPE aging in the heating-oxygen environment with the increasing of aging time.

At the aging time of 0 day, HDPE possessed original properties, with low strength and more craze initiation characteristic. After that time, the HDPE aging reaction began in the hot-oxygen environment. For the low thermal activation energy of environment, reactions dominated by radical combination, and cross-linking reaction began in this stage [21]. For the same temperature in the aging process, the reaction had essentially the same strong from sample surface to interior, because it is only
relative to the reaction temperature of environment. At the aging time of 28 days, the cross-linking reaction reached the limit in the heating-oxygen environment. Mechanical properties such as elongation at break and maximum load in SPT reached the maximum at this stage, and HDPE possessed properties of high strength and ductility. At the aging time of 56 days, the degradation reactions became explicit on the results. The process of HDPE degradation in heating-oxygen environment can be divide into three stages relating to the reactions of free radical production, bond broken, and recombination., and they were named the radical initiation stage, propagation stage, and termination stage. The chemical reaction show as equations(1)-(6) [22]. The aged layer just situated at the surface, and covered on the original HDPE sample substrate. It could prevent the oxygen degradation spreading into the interior, so that the aged layer was very thin, about only micro-scale. Meanwhile, the aging degree was gradually weakened from the surface to interior of the sample. This phenomenon has been proving by the previous experiments in this article. The chain scission reacted on the thin aged layer, and GPC results came from full thickness samples, so that there was no significant decrease in molecular weight results.

Initiation stage:

\[ RH \rightarrow R^\cdot \]  \hspace{1cm} (1)

Propagation stage:

\[ R^\cdot + O_2 \rightarrow RO_2^\cdot \]  \hspace{1cm} (2)
\[ RO_2^\cdot + RH \rightarrow ROOH + R^\cdot \]  \hspace{1cm} (3)

Termination stage:

\[ R + R \rightarrow R - R \]  \hspace{1cm} (4)
\[ RO_2^\cdot + R \rightarrow ROOH \]  \hspace{1cm} (5)
\[ RO_2^\cdot + RO_2^\cdot \rightarrow ROOH + O_2 \]  \hspace{1cm} (6)

The result also shows that SPT changed more significantly than tensile tests. The reason of it can be illustrated in figure 11, which shows the effective regions of SPT samples and tensile samples in the test. The aged layer was very thin, which is about micro-scale. As for the SPT test, the thickness of samples is only about 1.0 mm, much thinner than the tensile test samples. The maximum deformation occurred on the aged layer in SPT test, and increased the susceptibility of the material crack growth, and its’ value decreased rapidly than the traditional tensile test.

4. Conclusion

Mechanical properties of HDPE changed regularly in heating-oxygen environment with increasing of aging time. Tensile strength increased continuously with the increasing of aging time, meanwhile elongation and maximum load in SPT reached the maximum value at the aging time of 28 days for cross-linking reaction. Then degradation of aged layer on the sample surface played a more important role in materials properties, causing it to decrease.

The mechanical properties of aged HDPE varied more significantly in SPT than the traditional tensile test, and it might be a more susceptible method to evaluate the HDPE aging degree than the traditional tensile tests in heating-oxygen environment.

Acknowledgments
The authors thank the China Special Equipment Inspection and Research Institute (CSEI, Government-affiliated institutions of China) and General Administration of Quality Supervision, Inspection and Quarantine (AQSIQ, Government-affiliated institutions of China) for the financial support through projects T2015-CSEI-0003.
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