

General Degradation

Degradation and characterization methods for polyethylene gas pipes after natural and accelerated aging

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ARTICLE INFO

Keywords:

Polyethylene pipes
Aging
Nanoindentation
Time-dependent properties
Heterogeneous oxidation

ABSTRACT

How to solve the divergence between natural and accelerated aging behavior is the core for the lifetime prediction of polymeric materials, so special attention should be paid to the degradation mechanism and fitness of engineering-based characterization methods of materials in various conditions. In this paper, the degradation of polyethylene (PE) pipes was evaluated by accelerated tests with exposure time up to 10,000 h. Meanwhile, the aging behavior was also evaluated for PE pipes in operation after a long-term service. To characterize the effect of thermo-oxidative aging on PE pipes, commonly used methods were performed such as tensile testing, scanning electron microscopy, differential scanning calorimetry, infrared spectroscopy, as well as a new method- nano-indentation. The results reveal that the degradation of polyethylene PE pipes under oxidative conditions possesses time-dependent properties and spatially heterogeneous oxidation profiles. Due to diffusion-limited oxidation, PE pipes shows more distinct heterogeneous oxidation process in high temperature than that in service condition. In addition, indentation depth is a useful parameter to characterize the long-term aging in samples, especial the heterogeneity. Moreover, the result also elucidates that thermal oxidation stability of PE100 high density polyethylene (HDPE) gas pipes is greater than that of PE80 medium density polyethylene (MDPE) gas pipes. Furthermore, the current engineering-based prediction of PE pipe failure or lifetime lacks consideration of diffusion-limited oxidation and in-depth discussion of degradation mechanism, which indicates it is too early to estimate the lifetime or the remaining lifetime of the PE pipes in operation.

1. Introduction

During recent decades, the lifetime prediction of polymers has always been a key concern for researchers, material manufacturers and consumers [1–3]. The lifetime of polymers is closely related to the long-term stability which is usually assessed by accelerated aging tests such as exposure to ovens [4], disinfected water [5], and high oxygen pressures [6]. Due to well-known specific properties, such as excellent corrosion resistance, high flexibility, easy maintenance, etc. [7], the polyethylene (PE) pipes are prevailing in transportation of the medium in lifeline engineering, such as urban water supply and drainage system, gas supply system and so on. Some studies indicate that PE water pipes will be degraded by chlorinated water [5,8,9] and PE gas pipes will undergo thermo-oxidative degradation [10,11]. Incidentally, in terms of the PE pipes for gas, the focuses should be predominantly laid on thermo-oxidation under the internal pressure rather than photo-oxidation or radiation degradation, since sunlight, as reported in

the literature [12], is not generally involved when the PE pipes are buried underground. Thereinto, the thermo-oxidative aging tests for PE pipes rely on the fact that the degradation follows Arrhenius relationship which has a strong temperature dependence [2,13,14]. To shorten the test time, it is generally carried out by heating the oven to a temperature close to the melting point of the PE material, such as 110°C. However, excessive temperature will not only lead to alterations in the morphology as well as in oxidation kinetics of polymer compared to the operating temperatures [6,15,16], but also accelerate the evaporation, migration, extraction of antioxidants or reduce their efficiency which results in significant performance degradation in structures [6,17–21]. Furthermore, high temperatures might lead to the diffusion-limited oxidation (DLO) of polymer which results in the inhomogeneous degradation of materials [22–24]. So it is better to conduct aging tests in relatively lower temperatures, but it means to take a longer time. Although accelerated aging tests of PE materials at high oxygen pressure can effectively shorten the aging time, they are mostly used for ranking

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Received 28 August 2022; Received in revised form 24 December 2022; Accepted 28 December 2022

Available online 29 December 2022

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materials and limited in significance of lifetime predictions [6,8,25]. As a consequence, accelerated aging tests require an environmental factor other than temperature or high oxygen concentration to provide sufficient aging acceleration. Increasing the internal pressure of PE pipes might be one possibility. Actually, relevant studies also show that it has a great impact on the brittle fractures and thermo-oxidative degradation of PE pipes [26–29]. One reasonable explanation is that there is a chemo-mechanically coupled process in the aging of polymers, where aging reactions lead to the deformation of polymers and conversely the increased free energy caused by force increases the affinity which speeds up chemical reactions [30–32]. Another explanation might be the crack tip aging- the effect of material aging will be significantly enhanced near the crack [33,34].

To characterize the thermo-oxidative behavior of PE pipe, commonly used methods include infrared spectroscopy (FT-ATR), differential scanning calorimetry (DSC), high-performance liquid chromatography (HPLC), or tensile tests [5,6,35,36]. Commonly evaluated performance parameters include elastic modulus, elongation at break, strain-hardening modulus, carbonyls or its derivatives, carbonyl or hydroxyl index, relative molecular mass, oxidation induction time (OIT) or oxidation onset temperature (OOT), micromorphology of sample surface, etc. [5,6,37,38]. The measurement of OIT by DSC is one of the most popular methods to characterize the oxidation resistance because of its simplicity [39–42], which can monitor the antioxidant consumption of polymer. Besides, infrared spectroscopy (FT-ATR) is perhaps another most widely used method due to its versatility in determining composition, tacticity, conformation, crystallinity, among others, and then can be used to characterize the thermo-oxidative degradation of polymers [43–45]. Moreover, material performance will decay undoubtedly with the aging time and accurate measurement or characterization of its changes under different conditions will determine the precision of lifetime prediction of polymers. Evaluating a method or series of methods that can be used to characterize the performance of pipes in operation will be of great significance to estimate the lifetime or

the remaining lifetime of the PE pipes.

The main objective in this paper is to investigate the aging behavior of two PE pipes under elevated temperatures and ambient aging conditions, and evaluate the fitness of characterization methods for in-service PE pipes. Based on considerations of reducing test time and DLO behavior, which aggravate with the temperature, aging tests were carried out in the air at 80 °C. Additionally, to simulate the actual PE pipe in operation and for safety considerations, 0.4 MPa air is applied into PE pipes. For comparison, the aging behavior of two categories PE pipes with various service life (15 and 25 years) was also evaluated. The time of the hot air exposure was more than 12 months (over 10,000 h), during which the test specimens were periodically sampled and measured for the mechanical, physical properties and the chemical characteristics to evaluate the extent and trend of aging or degradation. It is worth noting that nanoindentation was chosen as a new method to characterize the micro-mechanical properties of aged PE materials. Furthermore, the degradation mechanism of PE pipes under high temperature and actual operating environment was emphatically analyzed, as well as the feasibility of these methods in lifetime prediction.

2. Experiment

2.1. Aging device

To study the thermo-oxidative aging of PE pipes under accelerated conditions, a unique aging experiment setup was designed referring to the previous investigation [46]. The basic structure of the setup is briefly shown in Fig. 1(a). The setup is used for a parallel thermo-oxidative aging test of multiple groups of PE pipes in high temperatures and high pressures, which can shorten the aging time greatly. Aging media for outer and inner surfaces are both heated air. The temperature can be regulated to a set value (0~100°C) when pipes are exposed to the oven. Otherwise, to control the internal pressure of PE pipes, an arithmetic program is compiled. Stable pressures in pipes can be attained through

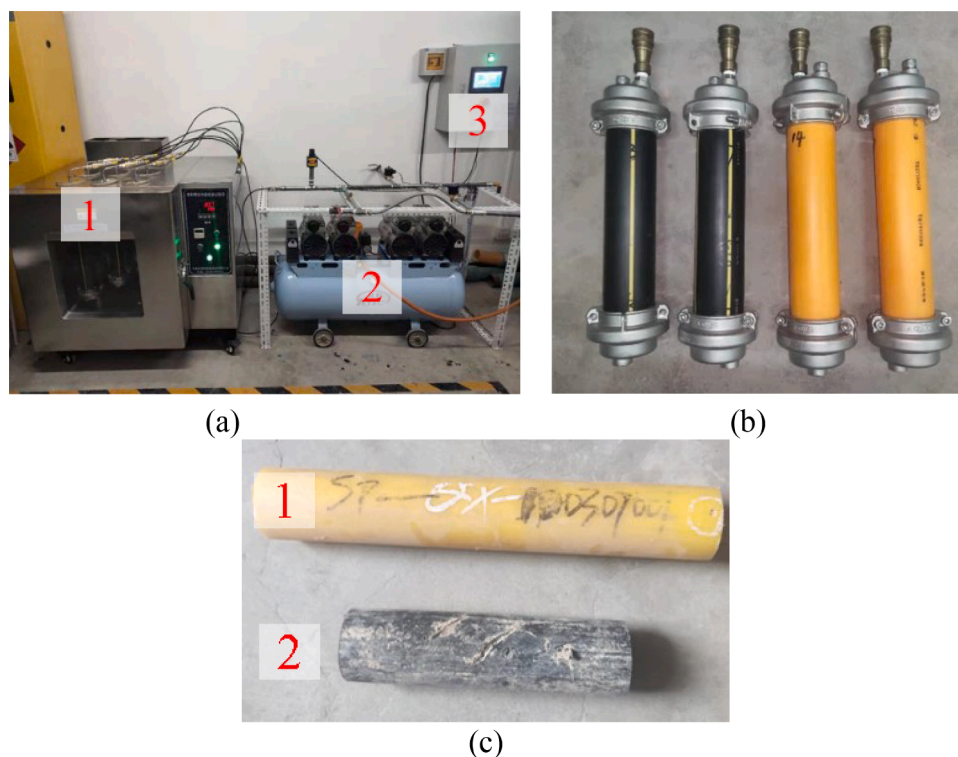


Fig. 1. (a) Structure of the aging device consist of ①heating oven, ②air compressor, ③programmable controller, (b) PE80 and PE100 pipe samples with end caps, (c) two categories of PE pipes with service life of ① 15 years and ② 25 years.

the cooperation between the sensor and the solenoid valve, whose maximum value is 1.0 MPa. After the start of each operating cycle, all parameters (temperatures and pressures) reach the specified value within 5 min and stay at a constant level. These results confirm the ability to adjust the equipment.

2.2. Materials

Two PE grades used for pipes were supplied by Nam Sok Building Material & Plastic Products (Shenzhen) Co, Ltd. Material properties of PE pipes in unaged conditions are summarized in Table 1. The ratio of pipe diameter to wall thickness, i.e. the standard dimension ratio (SDR) is 11 in this paper. Both PE materials were presumably stabilized with 0.1 wt.% Irganox 1010 and 0.1 wt.% Irgafos 168. Additionally, PE80 material also contained 5 wt.% carbon black and the polymeric material might include 0.1 wt.% calcium stearate [47].

Referring to ISO1167–2006 [48], the type B end caps were fixed to the ends of the PE pipe. The free length of the pipe between the end caps was set as 400 mm, which is bigger than three times the pipe diameter in accordance with ISO1167 as shown in Fig. 1(b). In addition, two categories PE pipes with various service life (15 and 25 years) was obtained from Shenzhen Gas Group Limited, as shown in Fig. 1(c).

2.3. Aging test procedure

PE80 pipes were aged 672 h, 1344 h, 2352 h, 3024 h and 10,104 h at 80°C and 0.4 MPa in a hot air circulating oven, and for PE100 pipes aged 672 h, 1344 h, 2016 h, 2688 h and 10,104 h. The internal pressure of pipe was selected according to the pressure rating of the urban gas pipeline system in China (GB/T 50,028–2008). Due to the potential accident caused by the high temperature and long-term operation of the oven and the discussion in the introduction - lower temperature aging, the heating destination was set as 80°C. The relatively lower temperature might cause lower aging rate, therefore, the higher pressure than the standard operating pressure of city gas was applied to pipes for saving time.

3. Characterization tests

3.1. Scanning electron microscopy

Surface morphology was characterized with scanning electron microscopy (SEM) ZEISS EVO18 (Carl Zeiss AG, Germany) equipped with the energy dispersive spectroscopy (EDS) of Oxford. The outer surfaces of the aged PE pipe samples were observed in this paper, as well as the natural aged PE pipes. An approximate cubic block of 1 cm × 1 cm wall thickness was cut for testing from unaged, aging 10,104 h PE80 and PE100 pipes, as well as two kinds of PE pipes in service, respectively. Owing to the lack of electrical conductivity of PE material, the outer surfaces to be measured of the pipe must be sprayed with platinum for scanning tests to observe the microscopic morphology. Additionally, the composition of the surface products of some specimens was also analyzed.

3.2. Tensile test

Tensile tests were performed at 23(±2)°C on a MTS CMT4000 (MTS,

USA). Specifically, the tensile tests were carried out on standard dumbbell-shaped pipe samples using a crosshead speed of 50 mm/min, in general accordance with ISO 6259–3 [49]. The corresponding control program is programmed by a numerical control lathe to cut the pipe sample into the tensile sample. The stress was measured based on the initial pipe cross-section and the strain was measured relative to the original parallel length. The extensometer measured the variation in specimen length under the applied stress. The variation in tensile strength (TS) and elongation at break (ϵ_b) was calculated by using relative equations [50,51], of which the test results were the average of three parallel specimens.

3.3. Nanoindentation

Nanoindentation testing was conducted at room temperature of 23 (±2)°C on PB1000 (NANOVEA, USA) equipped with a Berkovich tip. One set of nanoindentation experimental schemes was designed: the target load is set as 1000 μ N, loading and unloading rate remained at 2000 μ N/min. Typical load versus time curves of the nanoindentation test (peak load equals 1000 μ N, loading rate 2000 μ N/min) would be obtained. The pipe segments were taken at each scheduled aging time, then, a 0.5 cm fan-shaped piece was cut out along the radial direction of the pipe.

The cross section of the pipe specimen was continuously sanded with sandpaper from p200 to p5000 eventually. To prevent rounded corners on the inner and outer surfaces, the polish should be along the tangent of the cross section. For each sample to be measured, seven points arranged from the inner surface to the outer surface were test twice time, and the distances from inner surface are 0 μ m, 100 μ m, 200 μ m, 2660 μ m, 5520 μ m, 5620 μ m and 5720 μ m, sequentially.

3.4. Differential scanning calorimetry

The samples were subjected to oxidation tests with a differential scanning calorimeter (DSC) of the type DSC 200F3 (NETZSCH Group, Germany). To take their oxidation onset temperature (OOT), the samples were continuously heated up from 25°C to 300°C with a heating rate of 20°C/min in a synthetic air atmosphere until they reached the onset of the oxidation [5]. The calculation of the OOT was carried out by shifting the baseline with 0.2 mW [52]. Moreover, the oxidation induction times (OIT) were also determined, to confirm the correlation between OOT and OIT in case of aging [5,53]. The OIT measurements were carried out according to ISO 11,357–6:2018 at 200°C [54]. The testing results of OIT or OOT were the average of three parallel specimens. In addition, the material with 1 mm inner wall, middle layer, and outer wall of the pipe specimen were cut and made into chips to facilitate the test, sequentially.

3.5. Infrared spectroscopy

IR spectra were collected with an ATR-FTIR spectrometer, using a 4 cm^{-1} spectral resolution and 30 scans per specimen [55]. To characterize potential changes in the chemical structure during the exposure time, FTIR spectroscopy measurements were completed with a device of the type Bruker VERTEX 70 (Bruker Corporation, Germany). The sample preparation method is consistent with the dynamic oxidation test, moreover, samples were wiped and cleaned properly before the

Table 1
Material properties of the reference samples.

| | Nominal outside diameter [mm] | Density [g/cm ³] | SDR [-] | Oxidation induction time [min] | Oxidation onset temperature [°C] | Elongation at break [%] |
|--------------|-------------------------------|------------------------------|---------|--------------------------------|----------------------------------|-------------------------|
| PE80 (MDPE) | 63 | 0.932 | 11 | 72 | 257 | 840±50 |
| PE100 (HDPE) | 63 | 0.961 | 11 | 79 | 261 | 870±20 |

carbonyl index was measured. The ATR-FTIR for ranges from 400 to 4000 cm^{-1} was used to analyze the variation in functional groups of pipe samples due to exposure to heated air [56]. The growth of the carbonyl index as a function of exposure time was used as a measure of the degree of oxidation. The carbonyl index was calculated from the ratio between the integrated band absorbance of the carbonyl (C = O) peak from 1650 to 1850 cm^{-1} [5,51,57] and that of the methylene (CH_2) scissoring peak from 1330 to 1500 cm^{-1} [5,51] (method 1) or from 1420 to 1500 cm^{-1} [57] (method 2).

4. Result and discuss

4.1. Time-dependent properties

Variations in stress-strain curves of the PE pipes exposed to high temperature and pressure environments are illustrated in Fig. 2. There is no doubt that the extent of aging increases with exposure time, where the value variations can also be extracted from the specific value shown in Fig. 3. Compared to the unaged sample, stepwise reductions in tensile strength and strongly decreased elongation at break were observed after aging 10,104 h. Specifically, the PE80 showed more noticeable decreases in tensile strength and elongation at break as compared to the PE100 pipe materials. Two types of PE materials show 10.5% and 6.1% losses in tensile strength, however, 49.7% and 46.7% in elongation at break respectively. It is noticeable that elongation at break is more susceptible to the effects of thermo-oxidative aging than tensile strength, and the material changes from tough to brittle gradually. In addition, as shown in Fig. 3, the lower values in tensile strength and elongation at break can also be seen in the actual operating pipes compared to unaged samples, and their ϵ_b are only larger than that of the aging 10,104 h pipe. Therefore, after a long period of operation, the strength of the PE pipe may still be able to withstand the internal pressure of pipes and the pressure of the soil, but its resistance to deformation is significantly reduced. It may be more prone to fracture due to large deformation loads, e.g. mechanical excavation, and the possibility of large-scale failure and serious consequences increases.

The SEM surface images of the PE80 and PE100 samples are shown in Fig. 4. Surface microfissures or voids are clearly visible in the surface of PE80 after aging 10,104 h, highlighting material degradation to a certain extent. However, surface cracks and voids were not detected in the PE80 sample with 25 years of service and the PE100 sample after aging 10,104 h or with 15 years of service, which indicates a relatively smaller extent of degradation. Furthermore, the surface roughness increases visibly and tiny particles after aging approximately 10,000 h, thus there might be some oxidation product formation. But the origin of the tiny particles is necessary to be confirm by other method. Fig. 5(A) and (B) present some other SEM images and their EDS mapping results of

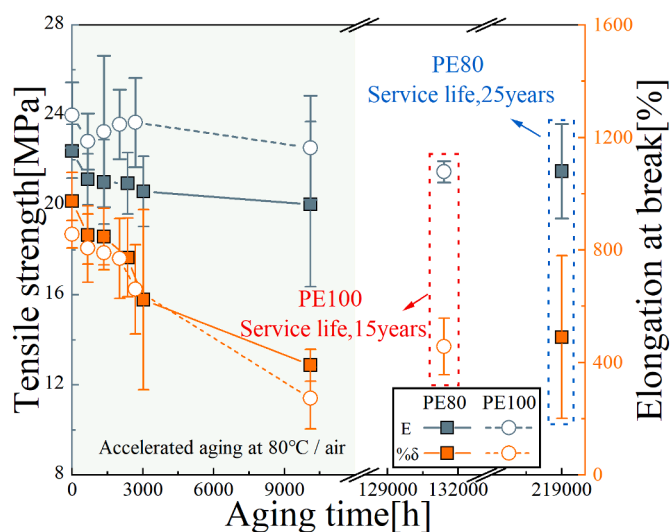


Fig. 3. Changes in tensile strength and elongation at break of PE80 and PE100.

PE80. It can be seen that after one year of exposure the PE80 surface is degraded and it shows obviously microfissures, voids and particles (Fig. 5(A)). Only the carbon and oxygen atom present in the mapping, likely proving surface of sample to be rich in oxidation products content and there is no calcium stearate. Nonetheless, it cannot rule out the possibility that the oxygen atom originates from antioxidants rather than oxidation products. Additionally, due to the existence of calcium and silicon atom in Fig. 5(B), the appearance of spherical pulverized or agglomerated particles are more likely some deposits which originate from stabilizer (e.g. calcium stearate), soil or from carbonates in the water. Thus, it seems not a feasible way to determine the degree of degradation of PE pipes by surface composition analysis. At least, it is difficult to determine the presence of oxidation products in particles without exact knowledge in the initial concentration of stabilizers and other additives in the pipe material. This is especially true for pipes that have been buried for many years and where the original information of material may be lost.

Combined with the previous tensile test results, the discovery of microfissures and voids provides a plausible explanation for the significant decrease in elongation at break of the PE pipe samples under tensile loading. It may be the stress concentration appears at the cracks or voids of the PE pipe samples. Overall, thermo-oxidative aging resulted in a significant decrease in elongation at break, confirming the occurrence of degradation of the polyethylene material. However, this degradation needs to be confirmed in combination with other

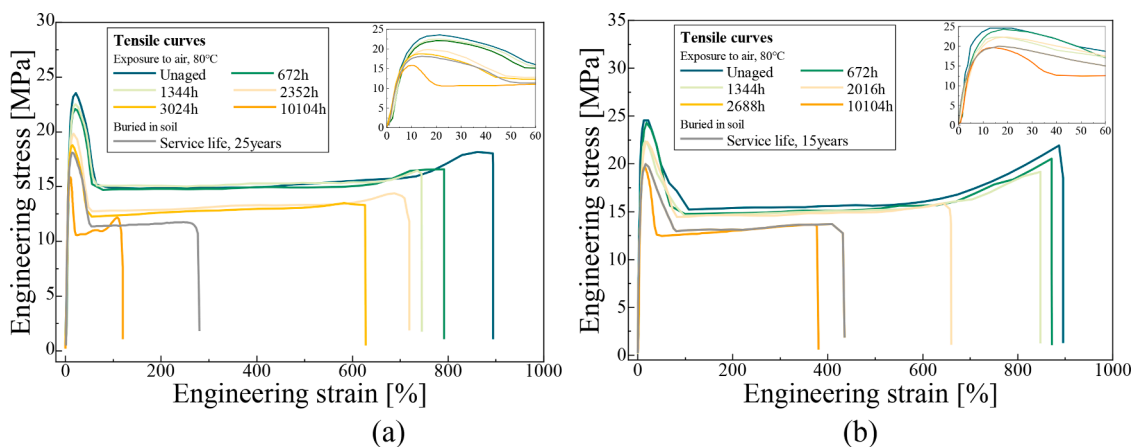


Fig. 2. Effect of exposure time on typical stress-strain curve of PE80 (a) and PE100 (b).

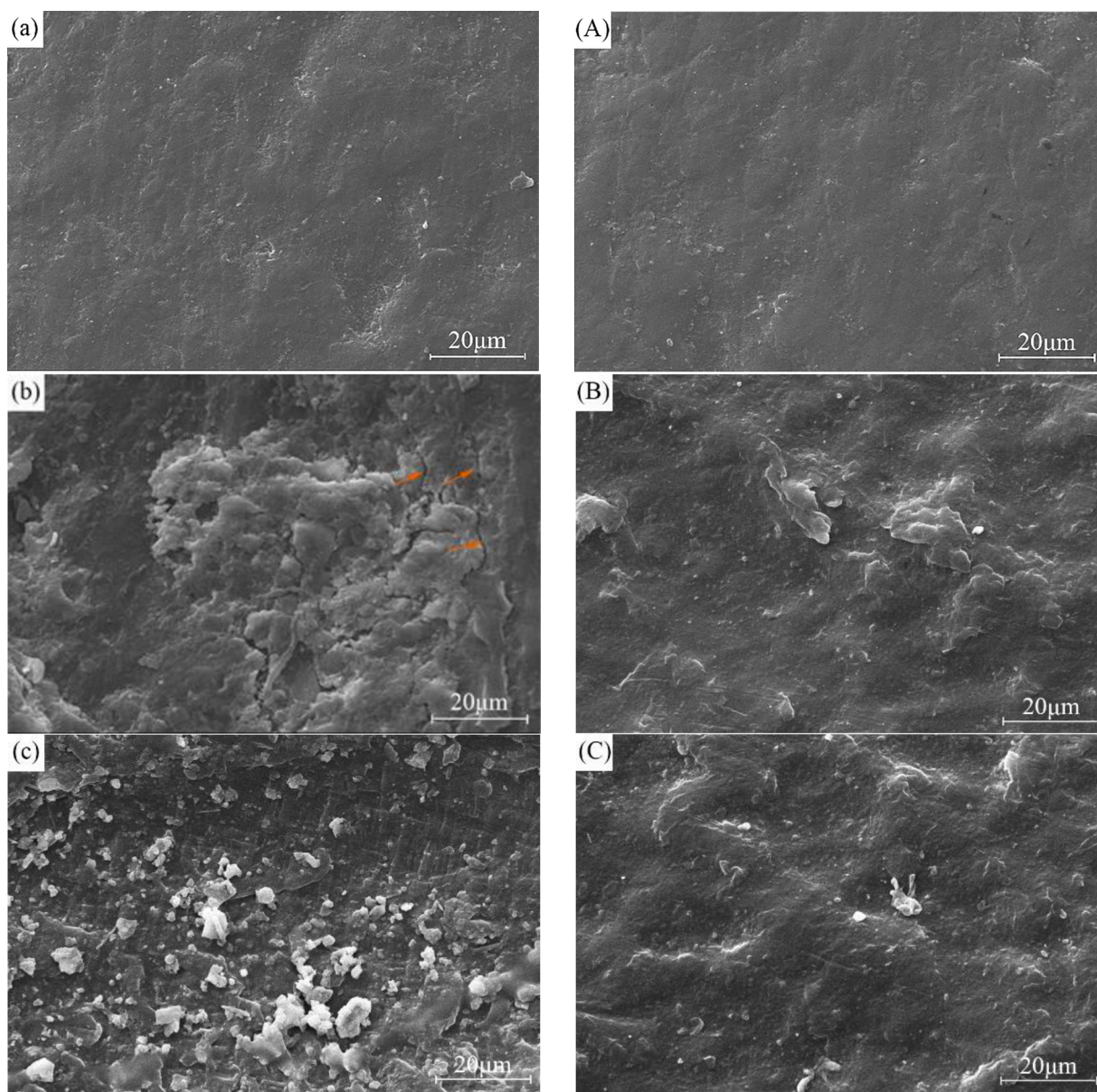


Fig. 4. SEM surface images of PE pipes: unaged PE80 (a), after 10,104 h (b), service 25 years (c) and unaged PE100 (A), after 10,104 h (B) and service 15 years (C).

characterization methods. In terms of lifetime prediction of PE pipes, as analyzed above, the tensile test results contain information on potential material defects and heterogeneous aging, which might lead to a decline in the accuracy of lifetime prediction methods based on the elastic modulus or tensile strength. The calibration of oxidation products on the surface of PE pipes by SEM and EDS is also susceptible to external impurities and its own antioxidants, stabilizers and other substances.

Fig. 6(a) and (b) show typical nanoindentation loading and unloading curves of the PE80 and PE100 samples at different exposure times, respectively. The test position is located in outer surface of the pipe wall. The depths at the peak loading (<1000 nm) were small enough to eliminate the effect from the substrates ($<10\%$ of the thickness of the sample which equals 0.5 cm) [58]. As shown in the indentation test results, the PE samples show delayed response to indenter unloading due to creep, hence, causes uncertainties in the measurement of surface mechanical properties during the conventional indentation [59]. Therefore, quantitative analysis of the hardness and the elastic modulus would not be conducted in this paper. Instead, the maximum indentation depth is selected as a parameter to characterize the aging behavior of PE pipes. The indentation depth (displacement in the

indenting direction) decreased with aging time for all samples, which indirectly elucidates the increment of the material hardness. In the macroscopic scale, these changes in hardness suggest that the aging process leads to a closer packing of the material, resulting in harder and denser products [60]. As a semi-crystalline polymer, the structure of PE consists of amorphous region (semi-crystalline region), the crystalline region and the interzonal region. Many research indicated that thermal oxidation only occur in the amorphous region, because the lower degree of chain packaging and higher degree of voids in the semi-crystalline region compared to the crystalline region increase the penetration and diffusion of oxygen [12,61]. Therefore, the changes in the hardness of the PE pipes presented in this paper should also be originated from some kind of modifications in the amorphous region. In one respect, chain scission caused by aging and degradation of the material can lead to chemi-crystallization, which results in the reduction of indentation depth [62]. The calculation of the crystallinity will be completed in the section of IR spectra, and the change of crystallinity will be a strong explanation for the reduction of the indentation depth. Moreover, due to the penetration of oxygen into the amorphous region, the breakage of molecular chains during thermo-oxidative aging at high temperatures

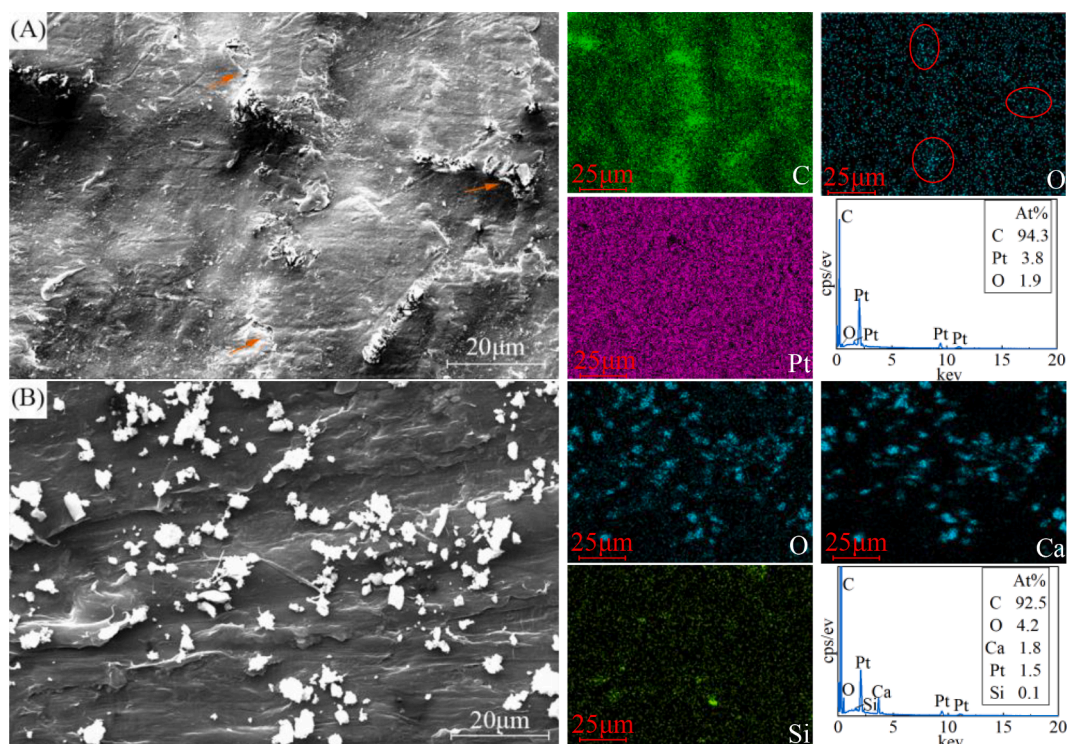


Fig. 5. SEM surface images and EDS mapping of PE80 pipes: aged 10,104 h (A) and service 25 years (B).

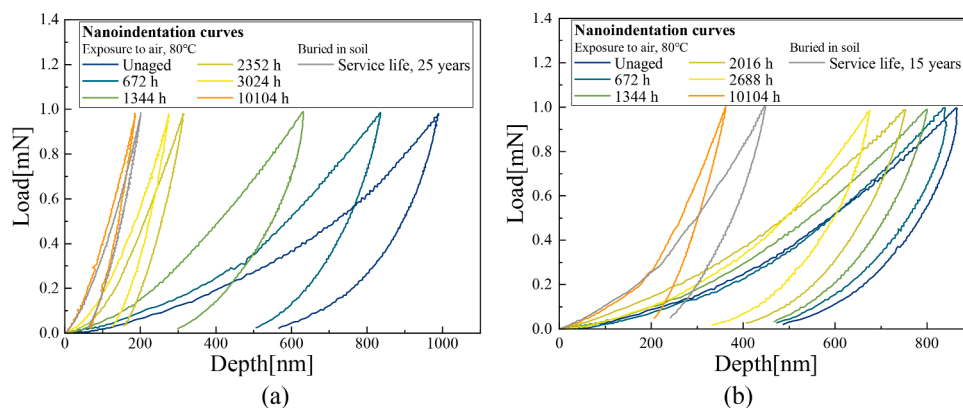


Fig. 6. Effect of aging time on load-depth curve of outer surface of PE80 (a) and PE100 (b) pipe.

destroys the entanglement network and produces small molecules with strong mobility at their ends, which will occur along the outer edge of the original grain for secondary crystallization, resulting in increased crystallinity. Besides, the polar groups introduced by thermal oxidation can interact through intermolecular dipolar forces or hydrogen bonds, which allows further crystallization processes to take place [60,63]. But up to now, secondary crystallization and re-crystallization have not been detected in a measurable way, probably the increase in material crystallinity is originating from chemi-crystallization. On the other hand, cross-linking reactions also might lead to increases in hardness, which may be triggered by free radicals at high temperature. In general, the result of decreasing indentation depth may be related to the competition between oxidation and cross-linking processes. In addition, it can be seen from Fig. 6 that the loading and unloading curves for the PE80 sample with 25 years of service and PE100 sample with 15 years of service in actual operation are relatively close to those of the pipes after aged 10,104 h. But it does not prove that the both aging belongs to the same level, which is due to the lack of raw data of the actual operating

pipes. Moreover, other testing methods are needed to further confirm the both aging profiles.

Previous research indicates that the measurements of OIT and OOT to monitor the loss of antioxidant have advantage and disadvantages in case of accelerated aging experiments, respectively [5]. By contrast, a further advantage of applying OOT instead of OIT is significantly shortening testing time. In this context, both OIT and OOT tests were carried out to result in a better resolution of the oxidative resistance of aged samples over exposure time. Fig. 7(a) and (b) show the curves of OIT and OOT values with aging time for two types of PE pipes, respectively, including different test positions. Notably, the dotted line in the figure represents the values of some parameter of the two pipes after their service life, while the intersection point has no real meaning and is only artificially added for comparing relative aging levels with the aged pipes. Moreover, similar expressions are adopted in the subsequent data plots. It is clear that the antioxidants in two categories of PE pipe samples were gradually consumed during the thermo-oxidative aging test, and therefore the resistance to oxidation degradation of materials is

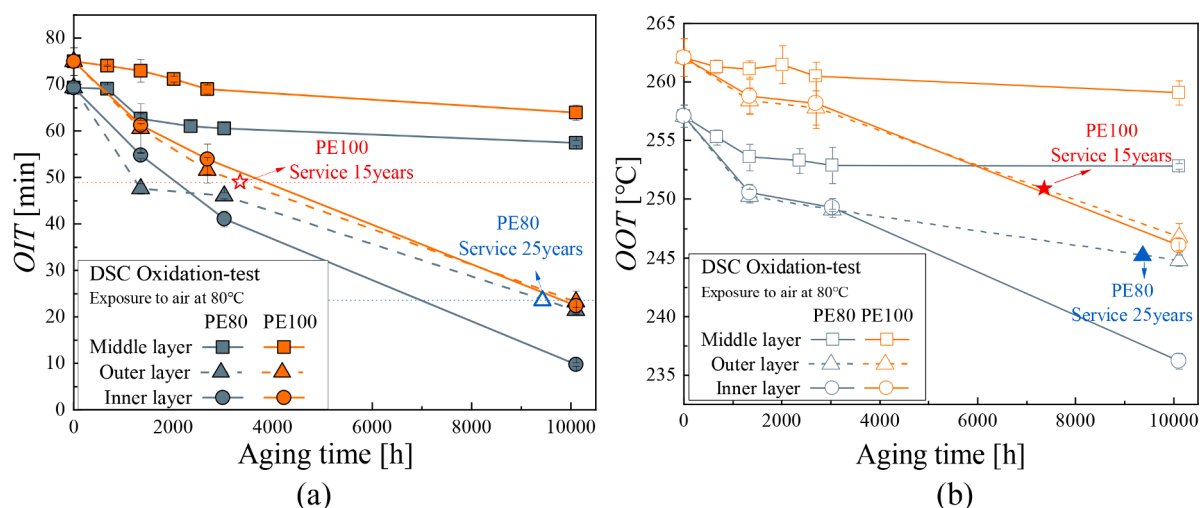


Fig. 7. Comparison of OIT (a) and OOT (b) evolution over exposure time.

gradually decreased. In more detail, in terms of outer surface, Fig. 7(a) shows a decrease of OIT by 69.12% and 68.93%, (b) shows that OOT decreases from 257.1°C to 244.8°C and from 262.1°C to 246.8°C, which is observed for the PE80 and PE100 pipe exposed to the oven after aging around 10,000 h, respectively. Except for the OIT value on the outer surface of the PE100 pipe with 15 years of service which is closer to the result after aging 2688 h, other results including OIT of PE80 and OOT of PE80 and PE100 are closer to the result after aging 10,104 h. In our case, the oxidation temperature was determined through dynamic scans of temperature. Also in this case the data indicates that the PE100 pipe has stronger resistance against aging than the PE80 pipe. It should be noted that the OIT did not decrease to zero even with an accelerated aging time of more than 10,000 h, which might be related to the influence of sample thickness for DSC tests and the migration of the antioxidant from the middle layer to the surface of the pipe. In addition, the following analysis from the infrared spectrum also can obtain the speculation that the antioxidant diffuses from the inside to the outside of the materials.

The FTIR spectra of the outer surface of the PE pipes with different aging times are shown in Fig. 8. In addition, the aging degree of the two PE materials was characterized using the two carbonyl index calculation methods mentioned earlier, and the results are shown in Fig. 9(a). The degree of crystallinity was calculated by using the method proposed by Zerbi et al. [64], and the results are listed in Fig. 9(b). In Fig. 8(a) and (b), it is noted that all curves present the same similar absorption peaks, varying only in terms of intensity, which can be attributed to differences in quality of sample [65]. As the general characteristics of the infrared spectrum of high density polyethylene, all the infrared spectrum curves obtained have two absorption peaks around 2900 cm^{-1} and one strong absorption peak at 1460 cm^{-1} and 720 cm^{-1} respectively. From Table 2, the two peaks around 2900 cm^{-1} are formed by asymmetric stretching and symmetric stretching movement of CH_2 . The absorption peak of about 1464 cm^{-1} is formed by $-\text{CH}_2-$ bending motion and bending deformation. The absorption peak of about 720 cm^{-1} indicated the existence of $-(\text{CH}_2)_n-$, which was caused by rocking deformation and $n \geq 4$ [26]. As the PE pipes are oxidized under high temperature and pressure, some new groups or new absorption bonds are gradually generated on the outer surface of the pipes, and these groups are listed in Table 3.

It can be seen from the Fig. 8(a) and (b) that the intensities of the three wide bands around the wavenumbers of 950~1225 cm^{-1} , 1500~1800 cm^{-1} and 3200~3700 cm^{-1} gradually increase from the virgin sample to the aged samples, which represents the increase in hydroxyl, carbonyl group and C—O—C bond, respectively. Table 3 shows the corresponding peaks of the carbonyl and OH bond in detail and Fig. 9(c)~(f) show zoom-in view of the aging-related absorption peak region (carbonyl region and C—O—C region). Based on free radical theory, PE

pipes primarily undergo the chain scission reaction and oxidation reaction when subject to thermo-oxidative aging conditions, where the majority of the oxidation degradation products are the carbonyl-containing organics, including ester (1720~1770 cm^{-1} , mainly 1740 cm^{-1} [67]), ketone (commonly, 1715 cm^{-1} [67]), aldehyde (1725 cm^{-1}) and carboxylic acid (1705 cm^{-1} [67]). In addition, alcohol structure including OH bond (1500~1650 cm^{-1} and 3200~3700 cm^{-1}) and C—O—C bond (1000~1200 cm^{-1}) have already been reported as a degradation indicator [12,66]. In this paper, the intensities of the three wide bands around the wavenumbers of 1740, 1650 cm^{-1} and 1040 cm^{-1} , which represent the stretching vibration of the C = O of ester, the C = C stretching vibration and the C—O stretching vibration in the alcohol structure [12], respectively, gradually increase with aging time. This phenomenon testifies the degradation mechanism of oxidation for the PE pipes during the thermo-oxidative aging test, and the extent monotonically increases with the aging time [12,69]. However, it is worth noting that the main peak at approximately 1740 cm^{-1} might not only be associated with the oxidation-induced formation of esters [70], but also exhibits a characteristic absorption of antioxidant (e.g. the absorption of Irganox 1010 is 1739 cm^{-1} [61]). Thus, if the band near 1740 cm^{-1} is correspond to C = C on the aromatic ring of the additive Irganox 1010, the migration of the antioxidant would be confirmed. In addition, the OH bond might be generated by the following two aspects, the first is a product of oxidation [71], the second possibility is that there is water in the sample. The broad absorption band between approximately 1550 cm^{-1} and 1650 cm^{-1} is attributable to liquid water bound within the samples since liquid water shows IR absorption bands between approximately 1550 cm^{-1} , 1680 cm^{-1} , 3000 cm^{-1} , and 3600 cm^{-1} [72]. A broadband peak of about 3400 cm^{-1} was found, but the intensity was not strong, which also confirmed the existence of water to a certain extent. In addition, the C—O—C bond appeared at 1100 cm^{-1} and its intensity increased obviously with the aging time. It can also be speculated that the carboxylic acid, which may be the oxidation product, was heated to produce anhydride and water. However, the proportion of the OH bond caused by the oxidative degradation of the material and originating from the impurity water is not easy to distinguish. In addition, the above speculation can also be corroborated by the gradually flattening carbonyl index curve as shown in Fig. 9(a), and it is due to the above mentioned chemical reactions that lead to the slow growth of the relative carbonyl group. It is worth noting that the carbonyl index keeps small in the PE80 or PE100 pipes with many years of service in natural condition, and this is probably due to the transfer of some oxidation products from the pipe surface to surrounding soil. Anyway, the great variety of these oxidative relative products and containing some impurities make it problematic to identify them precisely. Therefore, it is

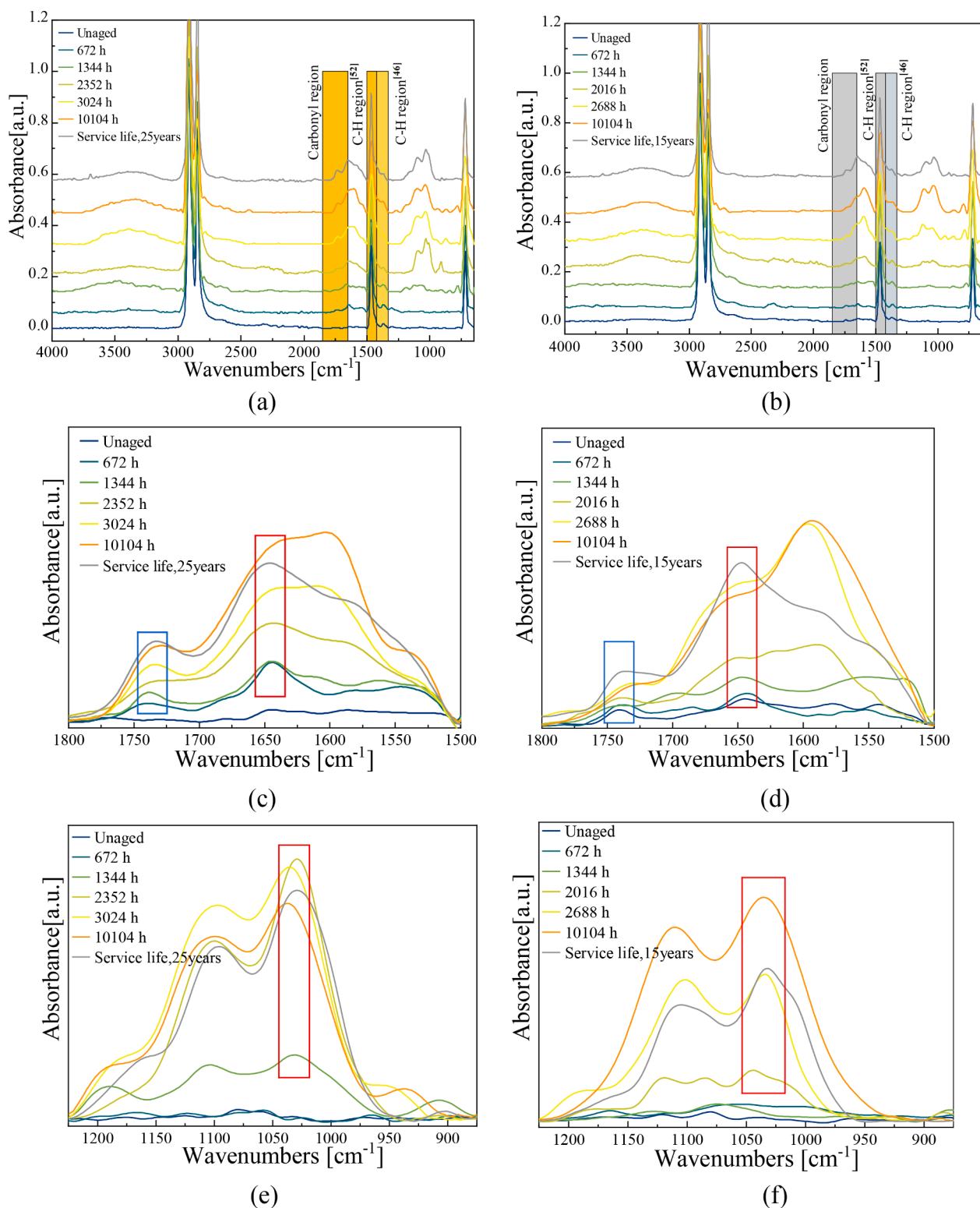


Fig. 8. FTIR spectrums of PE80 and PE100: (a) and (b) full range, (c) and (d) magnification of the band of $1500\text{ cm}^{-1}\sim 1800\text{ cm}^{-1}$ of PE80 and PE100, respectively, (e) and (f) magnification of the band of $850\text{ cm}^{-1}\sim 1225\text{ cm}^{-1}$ of PE80 and PE100, respectively.

more difficult to use these parameters to estimate the lifetime of PE pipes in operation.

4.2. Spatially heterogeneous properties

Fig. 10 shows typical loading and unloading curves at different locations in the cross-section of the PE80 pipe aged 2352 h and the PE100

pipe aged 10,104 h at 80°C . It can be seen that the indentation depth in the middle layer of PE80 and PE100 pipe is significantly larger than the inner and outer surface of the pipe. Combined with the specific values in Fig. 11(a) and (b), it can be found that the maximum indentation depth in the middle layer, the inner and outer surfaces of the PE80 sample decreases from the unaged to the aged 10,104 h, by 7.97%, 81.55% and 81.26% respectively, while the maximum indentation depth of the

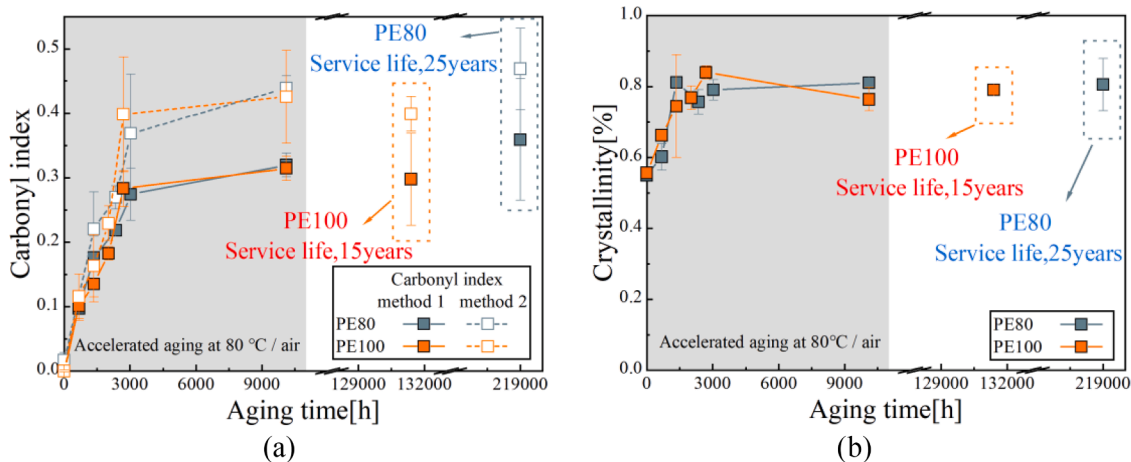


Fig. 9. Carbonyl index (a) and crystallinity (b) change as a function of PE grades and aging time.

Table 2

IR adsorption frequencies of unaged PE80 and PE100.

| Vibration(cm^{-1}) | Phase | Assignment |
|-------------------------------|-------------|----------------------------------|
| ~2912 | Crystalline | CH_2 Asymmetric stretch |
| ~2843 | | CH_2 Symmetric stretch |
| ~1464 | Crystalline | CH_2 bend |
| ~720 | Crystalline | CH_2 rock |

Table 3

IR adsorption frequencies of aged PE80 and PE100.

| Observed (cm^{-1}) | Published data | Assignment |
|-------------------------------|-----------------------|------------|
| ~3200–3700 | 3700 and 3200 [66,67] | OH |
| ~1650–1800 | 1650–1850 [5,57] | C = O |
| ~1500–1650 | 1500–1660 [66,67] | OH |
| ~950–1200 | 1000–1200 [68] | C-O-C |

PE100 sample decreases from the unaged to the aged 10,104 h, by 1.13%, 65.14% and 58.45% respectively. It can be seen from the above data that the maximum indentation depth of the PE pipes during exposure to hot air reflects a strong spatial non-uniformity. The aforementioned non-uniformity can be further clearly seen by plotting the corresponding data into cloud plots as shown in Fig. 11(c) and (d). The greater decrease of indentation depth is concentrated close to the inner and outer surfaces of the pipe as the color gets darker. And as aging

proceeds, its red area representing the smaller indentation depth does not expand rapidly toward the center of the material, but stays more or less within 200 μm of the inner and outer surfaces. In addition, the indentation depth profiles of the PE80 and PE100 pipes aged for 25 and 15 years in actual operation are also plotted in(c) and(d) using the same legend. It can be visually seen that the red area representing the smaller indentation depth of both actual operating pipes (PE80 and PE100) are smaller than the corresponding area of the aged 10,104 h pipes, which indirectly indicates the smaller degree of aging of operating pipes for many years than that of pipes aged over one year. Overall, the whole cross-section shows a clear DLO profile on the inner and outer surfaces, and the degree of oxidative aging shows a higher increasing rate when the inner and outer surfaces are exposed to more oxygen concentration.

It is well known that the thermo-oxidative aging of polymeric materials is controlled by the diffusion and the consumption rate of oxygen. The generation of diffusion-controlled oxidation processes inevitably leads to higher oxidation levels closer to the material surface, which in turn results in heterogeneous aging described above. For accurate life-time prediction, the heterogeneous degradation process must be characterized by parameters. Compared with tensile tests, nanoindentation can reduce the error caused by defects and is more promising to characterize the heterogeneous oxidation of PE materials.

In terms of the spatial distribution of OIT and OOT, Fig. 7 also shows the dynamic oxidation test results for the middle layer, inner and outer surface of the two PE pipes compared to the results for the unaged pipes. As can be seen in Fig. 7, the OOT and OIT near the inner and outer walls

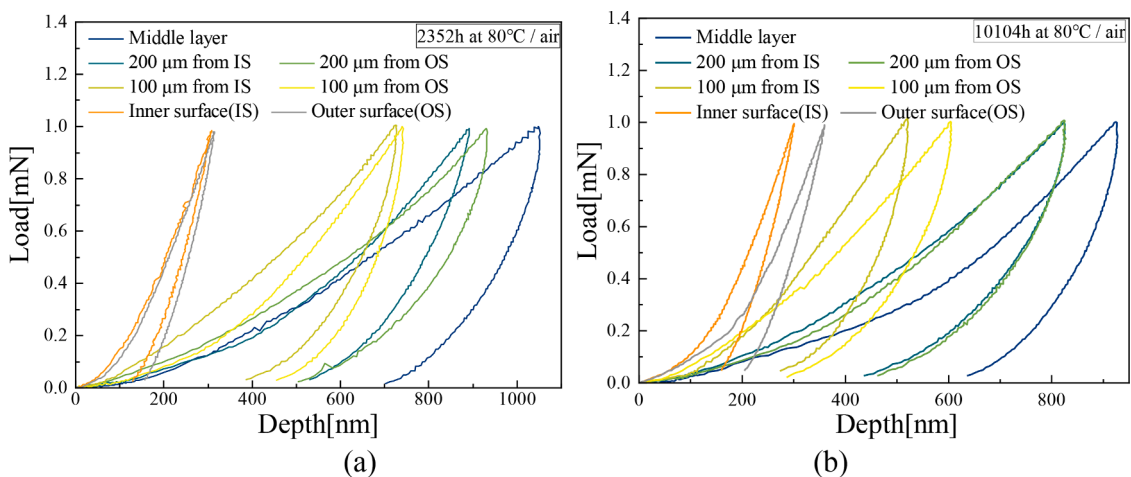


Fig. 10. Effect of position on load-depth curve of PE80 aged 2352 h(a) and PE100 aged 10,104 h(b).

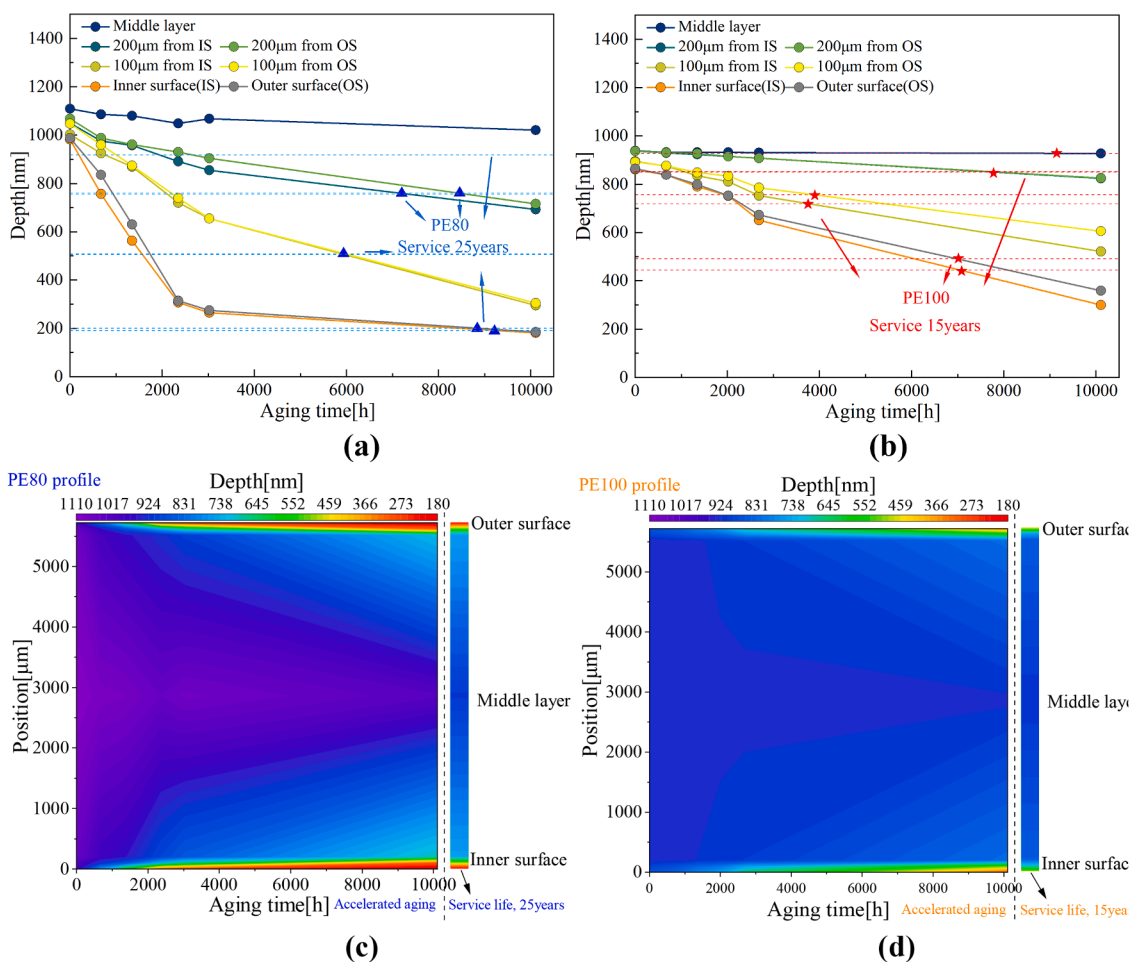


Fig. 11. Correlation of maximum depth and position (a) PE80 and (b) PE100, contour plot (c) PE80 and (d) PE100.

of the pipes decrease very significantly compared to the middle layer of the material. Statistically, on the middle layer, outer and inner surface, the OIT of the PE80 pipe decrease by 17.03%, 69.12% and 85.86%, respectively, while for the PE100 pipe, they decrease by 14.67%, 68.93% and 70.13%, respectively. The OOT of the PE80 pipe decrease to 252.8°C, 244.8°C and 236.2°C, respectively, while for the PE100 pipe, they decrease to 259.1°C, 246.8°C and 246.1°C, respectively. In more detail, compared with the fact that the OIT and OOT decreases slightly

and gradually of the middle layer, the decrease extent of the OIT or OOT of the inner or outer surface is four or five times, and reaches the maximum rate in aged 10,104 h. Besides that, there is no visible difference in OIT or OOT values between the inner surface and the outer surface, and no matter PE80 or PE100 pipes. In the past, OIT was chosen as an attribute parameter to import equations based on Arrhenius relations to estimate lifetimes [14,27,28], but lacks consideration for spatially heterogeneous properties. Therefore, the method of predicting

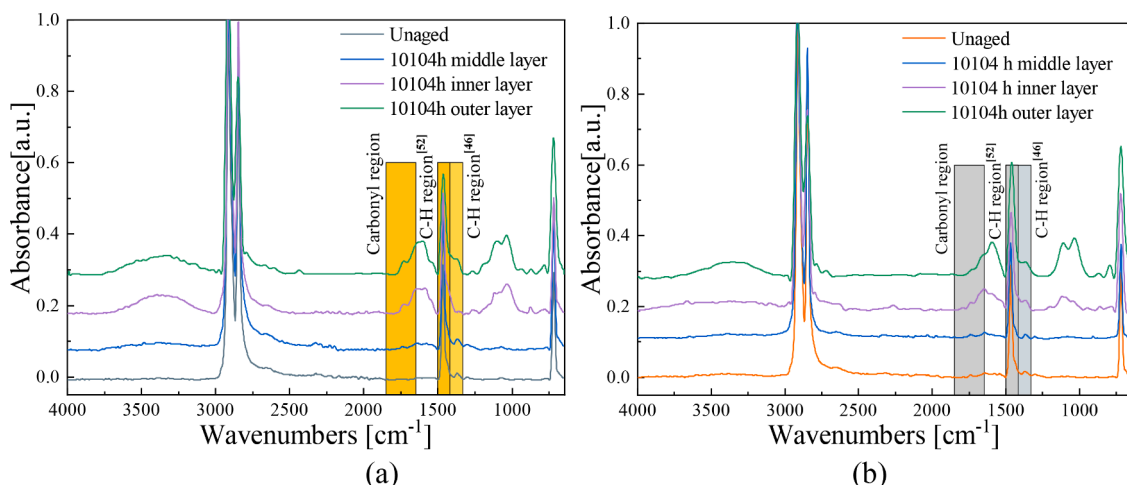


Fig. 12. FTIR spectra of PE80 (a) and PE100 (b) in different position.

the lifetime of PE pipes based on the OIT of the outer surface of the pipe will be non-conservative and the results will be smaller than the actual operating results.

Fig. 12 shows the IR spectra of the inner and outer surface of the PE pipes after aged 10,104 h. The testing is performed by taking samples from few μm of the inner or outer wall of the specimen, as the general thickness of the oxide layer is less than 1.2 mm [8]. Similar to the spectra in Fig. 8, it is evident that a series of oxidation products are formed from the PE material under accelerated aging conditions. The materials closer to the surface of the pipes exhibit increased absorption and have peaks that broaden significantly and shift towards longer wavelengths. In contrast, the IR spectral profile of the intermediate layers of the material did not change significantly with aging. Both PE grades used for pipes exhibit heterogeneous aging characteristics, with the degradation layer extending from the inner and outer surface to the middle layer. The carbonyl indexes of both materials were also calculated and plotted in Fig. 13. It can be seen from Fig. 13 that the carbonyl index near the inner and outer surface of the pipe increases significantly as the aging progresses. It is worth noting that the carbonyl index variation at the inner and outer surfaces of the pipe is significantly higher than that of the middle layer, which also indicates the non-uniformity of aging degradation due to DLO. Research indicates that internal pressure speeds up the aging process [14,27,28], but there is no definite evidence that the pressurized side of the pipe will degrade more than the non-pressurized side and vice versa because the location, as well as intensity of the absorption peaks, are similar on both inner and outer surfaces. The heterogeneous aging makes it difficult to predict the lifetime of in-service PE pipes. At least, infrared spectroscopy (ATR-FIR) is no longer a non-destructive testing method because the middle layers need to be detected for PE pipes.

4.3. Discussions

On the basis of the materials characterization results presented above, the extent and trend of degradation of the PE80 and PE100 pipes under the heated air exposure and natural conditions could be basically acquired. On one hand, with the increase of the aging time, the mechanical properties including the tensile strength, the elongation at break and the maximum indentation depth, as well as the thermal stability indexed by the oxidation induction time and oxidation onset temperature decreased obviously and monotonically, but the carbonyl index was markedly increased. On the other hand, PE pipes in operation after a long-term service (PE80 in operation for 25 years and 15 years for PE100) also show obvious aging, even if they do not reach the result of the pipes after aged 10,000 h in the accelerated condition. If the original parameters of the actual operating pipes are the same as those of the

accelerated test pipes at 0 h, then it is entirely possible to conclude that under the accelerated aging conditions of this paper (80 °C air and 0.4 MPa internal pressure), aging for 10,000 h is approximate equivalent to operate 25 years for PE80 pipes and 15 years for PE100 pipes, separately. However, using a few data points and relying on linear Arrhenius-type extrapolations are too early to extrapolate the lifetime of actual operating pipes.

So far, we have been working on exploring methods and selecting key parameters to characterize performance for the lifetime prediction applicable to in-service PE pipes [14,27,28]. However, the previous extrapolation model seems to be less accurate and lacks in-depth discussion of the aging or degradation mechanism. In this paper, in terms of tensile testing, the results of tensile test contain information on potential material defects. The large decreases in elongation at break are not the result of uniform aging of the material, but rather the result of stress concentration at micro-cracks subjected to external loads due to non-uniform aging. According to the results of other testing methods, it is obvious that the material is subjected to the heterogeneous aging process under thermo-oxidative aging. Therefore, it is apparently unreasonable as well as crude and unscientific to use these macroscopic indicators and simply extrapolate the lifetime of the pipe in combination with Arrhenius theory.

According to the previous analysis, the nanoindentation can be used to characterize the heterogeneous aging profile by testing the micro-mechanical properties of the PE material. But the indentation test requires flat and smooth testing surface of the specimens which cut from the pipe, so it is not possible to perform non-destructive characterization of aging on pipes in-service. The OIT, OOT, carbonyl index and crystallinity can characterize the oxidation resistance and the thermo-oxidative degradation of polyethylene respectively, but it is difficult to establish their time- and spatially dependent oxidative profile because of the requirement for large number of replicate tests and the high testing costs. Therefore, using the OIT or carbonyl index of the outer or inner surface to predict lifetime will make the results non-conservative because of the high oxidation resistance and low extent of degradation inside the pipe material.

All characterization methods cannot be used in operating PE pipes because the characterization of heterogeneous performance parameters affected by DLO cannot be performed without destructive experiments. The current prediction of PE pipe life lacks consideration of DLO behavior and the relationship between the characterization methods and the aging mechanism, which indicates it is too early to estimate the lifetime or the remaining lifetime of the PE pipes in operation. A growing number of studies have shown that finite element methods based on the coupling of oxygen diffusion, dissolution, antioxidant diffusion, depletion, and material chemo-mechanically are a potential

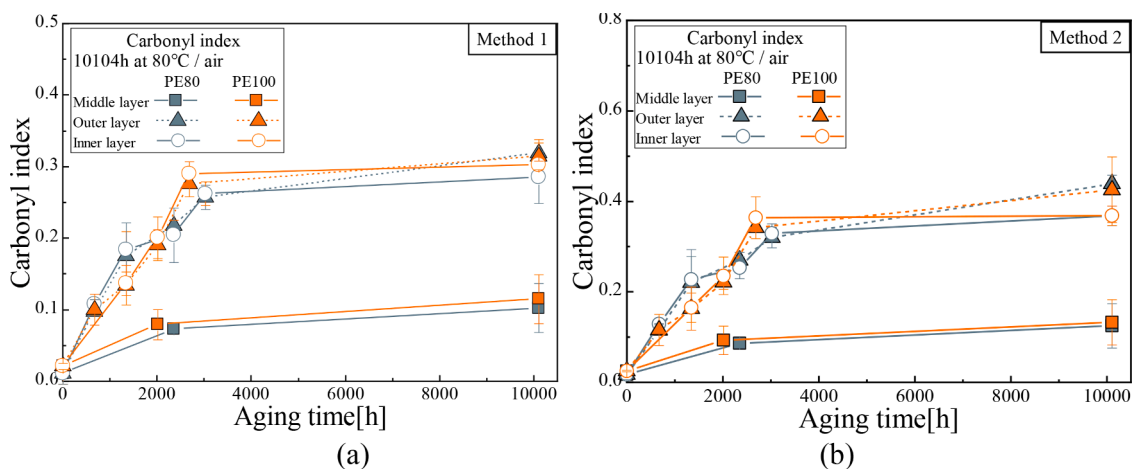


Fig. 13. Carbonyl index change with the position of PE80 and PE100 by using method 1 (a) and method 2 (b).

solution [29,30]. It not only solves the difficulties caused by DLO from high-temperature aging tests for analysis but also reduces the time of aging tests and the tediousness of parameter characterization tests. It is conceivable that in the future, the accelerated aging test may become a validation of the effectiveness by finite element calculation method rather than all content of the prediction methods. As the review stated, with the increasing modeling capabilities and suitable model calibration parameters, it will be possible to predict local oxidative aging failure [2].

5. Conclusion

The degradation of PE pipes under oxidative conditions possesses time-dependent properties and spatially heterogeneous oxidation profiles. Both PE grades used for pipes exhibit heterogeneous aging characteristics, with the degradation layer extending from the inner and outer surface to the middle layer. Moreover, the non-uniform aging mentioned is caused by diffusion-limited oxidation (DLO), which still occurs even at a lower temperature of 80°C. The actual operating PE pipes are also subject to non-uniform degradation, while the accelerated aging of the PE pipes is more pronounced in the oxidative depth of 200 µm near the surface layer due to DLO. In other words, PE pipes show more distinct heterogeneous oxidation process in high temperature than that in service condition. Furthermore, the results also elucidated that thermal oxidation stability of the PE100 was greater than that of the PE80 under high temperature and pressure regardless of the duration. There is no definite evidence that the pressurized side of the pipe will degrade more than the non-pressurized side and vice versa. The heterogeneous aging makes it difficult to predict the lifetime of in-service PE pipes.

All characterization methods cannot be used on operating PE pipes because the characterization of heterogeneous performance parameters affected by DLO cannot be performed without destructive experiments. The current prediction of PE pipe failure or lifetime lacks consideration of DLO behavior and in-depth discussion of the aging or degradation mechanism, which indicates it is too early to estimate the lifetime or the remaining lifetime of the PE pipes in-service. A possible approach, however, is to use accurate modeling capabilities to simulate the aging process of PE pipes based on increased large-scale computing capabilities, and to use data from engineering-based characterization methods for parameter correction.

CRedit authorship contribution statement

Sixi Zha: Conceptualization, Methodology, Data curation, Characterization, Formal analysis, Investigation, Methodology, Validation, Software, Writing original draft. **Hui-qing Lan:** Investigation, Data curation, Methodology, Experiment, Writing - review & editing. **Nan Lin and Tao Meng:** Investigation, Resources, Experiment, Review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

This work was supported by National Key Research and Development Program of China (No. 2021YFC2203601).

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