Mechanics of Time-Dependent Materials
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RESEARCH

Accelerated thermal-oxidative aging and degradation mechanism of high-density polyethylene butt-fusion welded joint

Ying-Chun Chen[1] · Yan-Feng Li[1] · Jie Yang[1] · Yan Xi[1] · Qiang Li[2] · Xiao-li Fan[2]

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Abstract
High-density polyethylene (HDPE) pipelines are widely used for the transportation of natural gas. The butt-fusion welded joints melt and cool during the welding process, resulting in changes in mechanical properties, molecular chain spatial position microstructure, and functional groups. Herein, we investigate the aging behavior of an HDPE butt-fusion welded joint in accelerated thermal-oxidative aging tests under various temperature gradients. The Vicat softening temperature, oxidation induction time, and infrared spectrum were measured, and the microstructures were observed. The results indicated that the mechanical and chemical properties of the butt-fusion welded joint degraded with incresing aging temperature. Analysis was conducted to identify the molecular chain intersection mechanism in the heat-affected zone and the weld joining mechanism. The findings help understand the aging behavior of HDPE and provide guidelines to reduce the risk caused by butt-fusion welded joint degradation.

Keywords High-density polyethylene · Thermal oxidative aging · Butt-fusion welded joint · Aging temperature

1 Introduction

High-density polyethylene (HDPE) is widely used in industry (Agrawal et al. 2022; Rezakalla and Petrovna 2021). Compared with other raw materials, HDPE has the advantages of non-toxicity, low price, easy processing, and stable chemical properties (Therias et al. 2021; Badia et al. 2012; Hsueh et al. 2020). Besides, the butt-fusion (BF) welding is a common welding method for HDPE pipes. However, aging conditions, such as aging temperature, may affect various properties of the pipe joints due to its particular structure of molecules (Nguyen et al. 2021; He et al. 2021; Zheng et al. 2015; Vijayan et al. 2016; Grabmayer et al. 2014). The aging joint has great potential safety hazard and is prone to leakage and explosion. Therefore, the performance changes and the safe service time of BF welded joints during service have become the focus of many research studies (Colin et al. 2009).

✉ Y. Xi
xiyan@bjut.edu.cn

[1] Beijing University of Technology, Beijing 100124, China

[2] Xinjiang Inspection Institute of Special Equipment, Urumqi, 830011, China

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In order to shorten the experimental period, the accelerated aging experiment is used to achieve rapid aging of materials. At present, scholars' research on polyethylene pipes is mainly based on the body of the pipe, testing the mechanical properties testing under thermal oxidative aging. For example, when different polymer carriers were aged for 6 days at various temperatures under accelerated aging conditions, the result indicated that the tensile properties decreased with increasing aging time (Gholami et al. 2020). PE gas pipes were tested under thermal-oxidative aging conditions controlling different pressures, using an aging time of 0–500 h. It was showed that tensile strength and maximum tensile stress of the aged HDPE pipes decreased with the increase of internal pressure and aging time (Wang et al. 2018).

Currently, there are scholars who, based on optical research in the BF joint, have found that it has a significant change in the polarization of light. This proves that the crystallinity of the BF welded joint increases in the center of the joint, and the crystallinity is low in unheated area during processing (Chen et al. 2022). These illustrate the difference in molecular distribution between BF welded joint and the substrate. It was studied when the thermal oxidative aging temperature was set to 80, 90, and 100 °C, the aging time was 0–384 h. The result showed sample stress-strain curves and oxidation induction time (OIT) curves of the samples decreased with increasing aging time (Wang et al. 2021). There were also scholars who applied notch-tensile and notch-creep tests to study the performance of BF welded joints of buried HDPE pipes. The ductility of the pipe is significantly higher than that of BF welded joint (Kim et al. 2019). When investigating the welding quality of hot gas butt-welded joints, it was found that various degradation phenomena may occur during the heating process, such as hardness or OIT of the sample decreasing with aging time (Nguyen et al. 2021). The above mentioned scholars have not studied the aging mechanism of butt-welded joint in detail. However, a few scholars have researched that the degradation of branched chains predominates during the first 6 h of combustion and after 6 h extensive chain breakage sets in and smaller molecular chain fragments are produced (Salehi and Pircheraghi 2021). A few scholars have carried out research on BF welded joints. However, in these studies, the performance indicators of the joint after aging were not evaluated or the internal factors of aging were not explained from a microscopic perspective.

In this study, the BF welded joint of high polyethylene was taken as the primary research object. The accelerated aging test was carried out and the joint performance changes were analyzed. According to the above results, the aging and degradation effect of BF welded joint was explained from the micro-molecular level. The results of this paper will contribute to a better understanding the BF welded joint and in particular the aging of HDPE pipes.

2 Experimental

2.1 Material

As shown in Fig. 1, a PE100 pipe with a BF welded joint produced by Yada Plastic Products Co., Ltd was used for the experiment. The basic information about the pipe is shown in Table 1.

Figure 2 shows the production process of the HDPE pipe BF welded joint. The information of pipe welding parameter is shown in Table 2. The BF welded joints were made according to the Chinese national standard GB/T 19809-2005 (2005). This standard corresponds to the international standard ISO 11414-1996 (1996). The ends were kept clean and the outer diameter misalignment was less than 0.5 mm before welding.

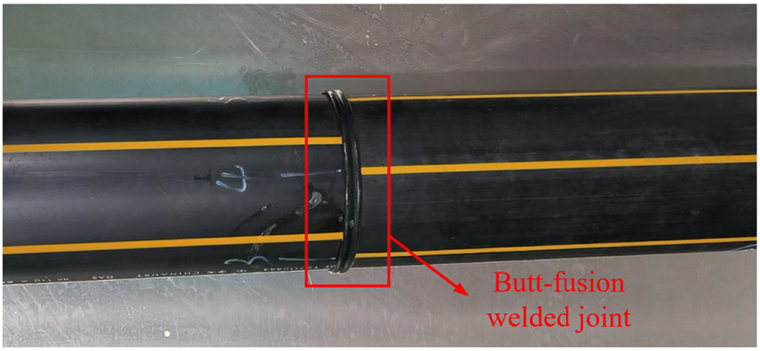

Fig. 1 Experimental PE100 pipe with a butt-fusion welded joint (Color figure online)

Table 1 Information on the PE100 pipe used in the study

Grade	Raw material	Nominal diameter (mm)	Standard dimension ratio	Density (kg/m^2)	Melt flow rate (g/10 min)
PE100	HE3490-LS	110	11	960	0.25

Three different temperatures of thermal-oxidative aging were used in the experiment. The PE100 BF welded joints were aged for 120 h, 240 h, 360 h, 480 h, and 600 h in the drying oven at 60 °C, 90 °C, and 120 °C temperatures. The accelerated aging scheme is shown in Table 3.

2.2 Test method

2.2.1 Tensile testing

In order to test the performance of PE100 pipes with BF welded joint after accelerated thermal-oxidative aging at three different temperatures, the pipe samples were processed according to relevant standards. The tensile test samples were made according to the Chinese national standard GB/T 19810-2005 (2005). This standard corresponds to the international standard ISO 13953-2001 (2001). A microcomputer-controlled electronic universal testing machine produced by Shenzhen Wance Equipment Co., Ltd (Model: ETM204C) was utilized for this tensile test. The tensile test was completed indoors at a room temperature of 23 ± 0.5 °C. The stretching speed was 50 mm/min. The average value of five parallel tests of a sample was selected as the final tensile strength value of that sample. Figure 3(a) shows the photograph of a sample for tensile strength testing.

2.2.2 Impact testing

The samples for mechanical impact testing were prepared as per the Chinese national standard GB/T 1043.1-2008 (2008). This standard corresponds to the international standard ISO 179-1-2010 (2010). A pendulum tester PTM2200 produced by Shenzhen Sansi Zongheng Technology Co., Ltd. was used for mechanical impact testing. The impact test was completed indoors at a room temperature of 23 ± 0.5 °C. When testing the impact strength of

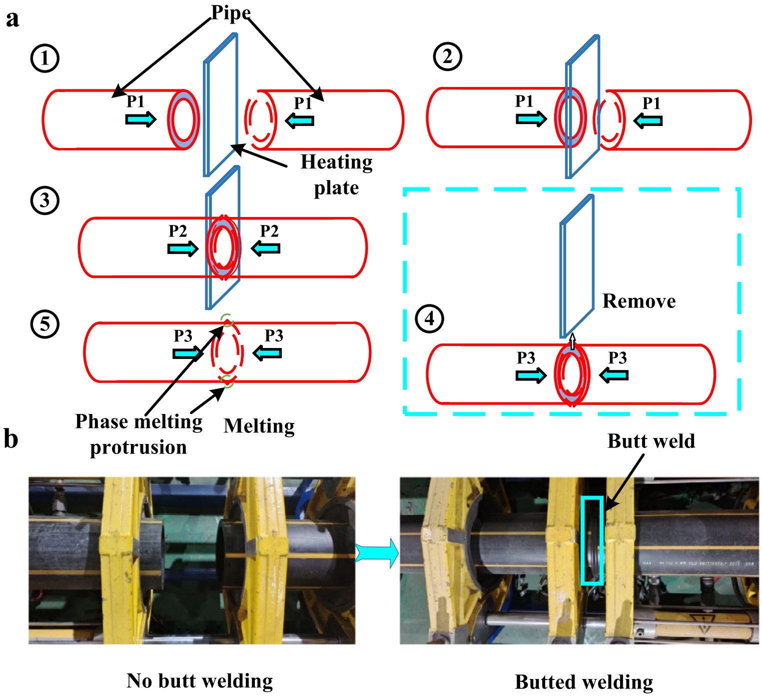

Fig. 2 Schematic diagram of HDPE pipe butt-fusion welded joint manufacturing process and molecular chain reaction mechanism during HDPE butt-fusion welded joint production. (a) Schematic diagram of pipeline butt-fusion welded joint manufacturing process. (b) Photos of pipe butt-fusion welded joint production process (Color figure online)

Table 2 Information of pipe welding parameter

Welding temperature (°C)	Welding pressure (Mpa)	Adsorption time (s)	Cooling time (min)	Switching time (s)
225±10	0.18	100	15	5

Table 3 Accelerated aging scheme

Specimen	Accelerated aging type	Aging time (h)	Temperature (°C)
1	New pipeline		23 ± 0.5
2		0, 120, 240 360, 480, 600	60
3	Thermal oxidative aging		90
4			120

a supported beam, the impact speed of the supported beam was 2.9 m/s and the pendulum energy was 4 J. The average value of five tests was selected as the sample value. Figure 3(b) shows the photograph of samples for mechanical impact test.

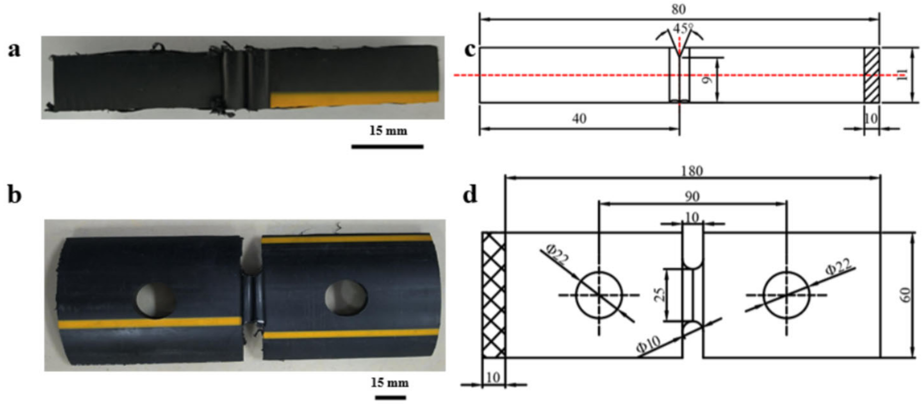

Fig. 3 Test specimens. (a) Photograph of a sample for impact test. (b) Photograph of a sample for tensile strength. (c) Scheme of the sample size for impact test. (d) Scheme of the sample size for tensile strength (Color figure online)

2.2.3 Hardness

The LX-D shore hardness tester produced by SUNDOO Shore Hardness was used to test the hardness of the BF welded joint with reference to the Chinese national standard GB/T 38119-2019 (2019). The diameter of the indenter tip used for hardness test was 0.2 mm. The hardness test was completed indoors at a room temperature of 23 ± 0.5 °C. Six points were selected on the BF welded joint surface. Each point was at least 4 mm away from the edge. The longitudinal distance between the two points was at least 6 mm. The average of six values of six points was taken as the final value for the shore hardness.

2.2.4 Vicat softening temperature

The microcomputer-based Vicat softening point apparatus (HVT302B) produced by Shenzhen Wance Test Equipment Co., Ltd. was used to control deformation. The Vicat softening temperature test was conducted per the international standard ISO 2507-1-1995 (thermoplastic pipes and pipe fittings–Vicat softening temperature measurement) (1995). The weight was selected as 10 N, and the Vicat temperature of the BF welded joint was the temperature at which the standard needle was inserted 1 mm into the sample. The Vicat softening temperature of the sample was the average of three tests.

2.2.5 Oxidation induction time

The differential scanning calorimeter (DSC-500B) produced by Shanghai Yingnuo Precision Instrument Co., Ltd was used to test and characterize the changes of thermal properties of HDPE pipes with BF welded joints after aging. The test was carried out per the Chinese national standard GB/T 19466.6-2009 (2009), which corresponds to the international standard ISO 11357-6-2013 (2013). The material on the convex surface of the thermal BF was selected, and samples were taken in blocks of masses 15 ± 0.5 mg. The average value of three parallel tests was selected as the final value for the oxidation induction times of samples.

Table 4 Operating parameters for the FTIR spectroscopy

Wavenumber range (cm^{-1})	Signal-to-noise ratio	Resolving power (cm^{-1})
400–6000	45000:1	4

2.2.6 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectrometer (model: FTIR-650S) produced by Tianjin GangDong Scientific and Technology Co., Ltd. was used to characterize the chemical structure of the exposed surface of the sample. The sample surface was kept clean before testing. The test parameters of the FTIR spectrometer are shown in Table 4.

2.2.7 Scanning electron microscopy

The change in the surface morphology with respect to tensile fracture was observed by FEI scanning electron microscope (Helios 5 CX). Before the test, the samples were stewed for 2 hours and sprayed with gold. Samples were cut into rectangular pieces of 1 cm $\times$ 1 cm $\times$ 0.5 cm dimensions. Finally, the surface dust was removed before the test, and the sample was sprayed with gold.

3 Results and discussion

3.1 Mechanical properties

3.1.1 Impact properties

Figure 4(a) shows the impact energy of BF welded joints after thermal-oxidative aging at different temperatures. At each aging temperature, the impact energy of the BF welded joint shows a decreasing trend. When aged for 600 h, the impact energy of the thermal BF decreases by 0.158 J after thermal-oxidative aging at 120 °C. The impact energy of the BF welded joint decreases by 0.125 J after thermal-oxidative aging at 90 °C. The impact energy of the BF welded joint decreases by 0.118 J after the thermal-oxidative aging at 60 °C.

Figure 4(b) presents the impact strength of BF welded joints after thermal-oxidative aging at different temperatures. With aging, the impact strength of the BF welded joint decreases. This also precisely confirms that the impact strength of the serviced pipeline decreased with increasing service time in practical engineering (Chen et al. 2023). After aging for 600 h, the impact strength of the BF welded joint decreases significantly, with a total reduction of 1.84 kJ/m^2 after thermal-oxidative aging at 120 °C. The impact strength of the BF welded joint decreases the least, with a total reduction of 1.4 kJ/m^2 after thermal-oxidative aging at 60 °C. When the aging time is the same, a higher temperature breaks up the long molecular chains and increases the inter-molecular cross-linking. As a result, the material becomes brittle and the impact energy required to damage the sample is reduced. Hence, the impact strength of the BF welded joint reduces, ultimately increasing the degree of aging of the BF welded joint.

3.1.2 Tensile properties

Figure 4(c) shows the tensile strength of BF welded joints after thermal-oxidative aging at different temperatures. The tensile strength of the BF welded joint decreases with increasing aging time and temperature. After aging for 600 h, the tensile strength of the BF welded joint decreases by 2.71 MPa after thermal-oxidative aging at 120 °C. The tensile strength of the BF welded joint decreases by 3.80 MPa after thermal-oxidative aging at 60 °C.

The macromolecular chain and part of the short molecular chain in the fiber filament of the BF welded joint gradually becomes easier to break with increasing aging time. Therefore, the tensile strength decreases with increasing aging time. This result is also reflected in the decrease in the tensile strength of the BF welded joint with increasing temperature. The decrease in the tensile strength of the BF welded joint with the temperature and time indicates that the material oxidation and molecular chain fracture reduce the flexibility of the molecular chain. The mechanical properties like impact strength, tensile strength, hardness, and Vicat softening temperature of PE materials decrease with increasing thermal-oxidative aging temperature (Kanegami et al. 2013). This proves that there is a close relationship between the degradation of BF welded joints and oxygen diffusion during thermal-oxidative aging.

3.1.3 Hardness

Figure 4(d) presents the surface hardness of BF welded joints after thermal-oxidative aging at different temperatures. The surface hardness of the BF welded joint increases after the thermal oxidative aging at three different temperatures. Compared with the unaged BF welded joint, the surface hardness of the BF welded joint after aging for 600 h at thermal-oxidative aging at 120 °C increases by 20.67%. In addition, it can be found that the slope of each curve gradually decreases with time. As the aging continues, the degradation rate of the material and the oxidation rate of the matrix gradually decrease.

Some studies showed that the aging process results in a harder and denser sample (Gulmine et al. 2003). PE pipe with BF welded joint is a secondary processing product. The structure of the BF welded joint has a semi-crystalline region and a crystalline region. Compared with the crystalline region, the molecular chain spacing in the semi-crystalline region is large and the void ratio is high, improving oxygen diffusion ability between the molecular chains (Gong et al. 2021). As the thermal-oxidative aging temperature increases, the degree of aging of the BF welded joint increases and the molecular chains break. The microscopic performance is based on crystallization, and the macroscopic performance is based on increased sample hardness. Oxygen diffusion to the semi-crystalline region breaks up the molecular chains and produces short molecular chains in the energetic environment. In high-energy enviroment, small molecules with high fluidity are formed at the ends of the short molecular chains. These small molecules join the main chain of molecules. As a result, the molecular chains in the semi-crystalline region are closely arranged closely and ordered, increasing crystallinity. In addition, the polar free groups introduced by thermal-oxidative aging interact through intermolecular hydrogen bonds, and crystallization occurs again (Dörner et al.1998). However, there is currently no method for detecting recrystallization.

3.1.4 Vicat softening temperature

Figure 4(e) shows Vicat softening temperatures of BF welded joints after thermal-oxidative aging at different temperatures. During the aging process, the Vicat softening temperature

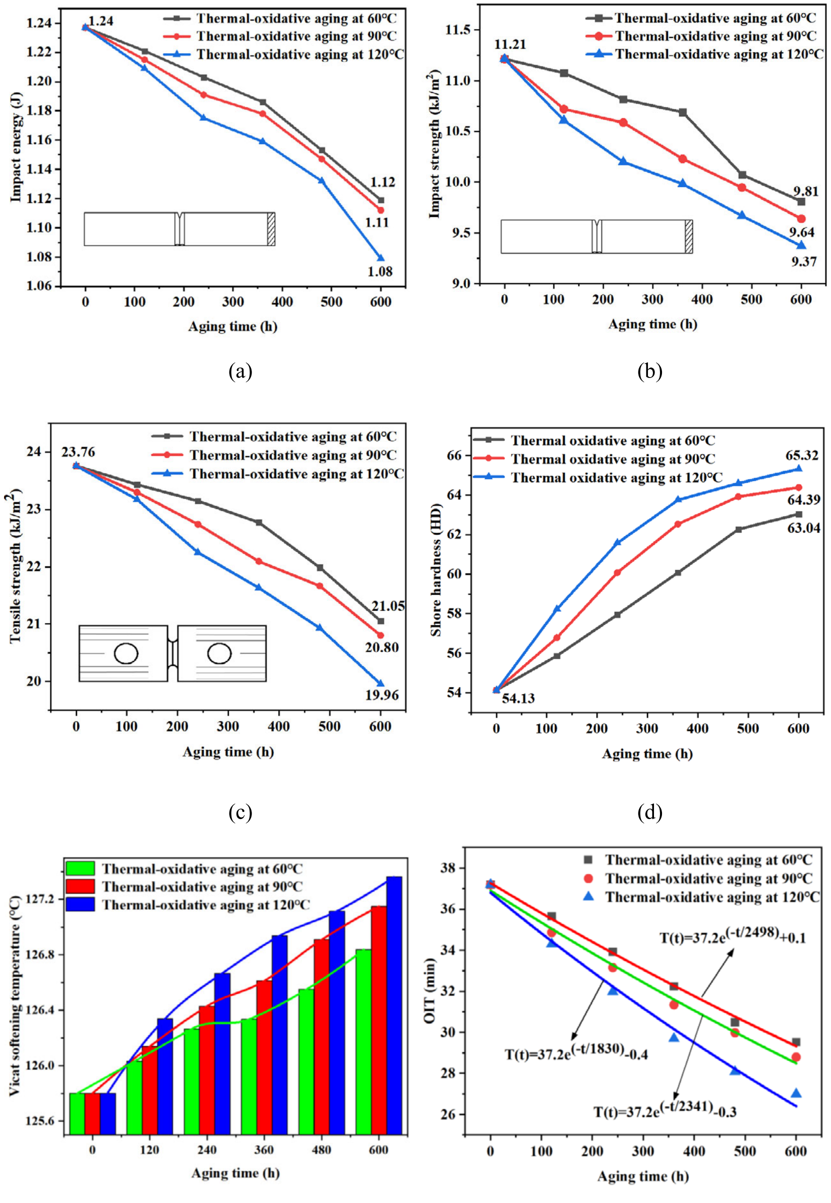

Fig. 4 Mechanical properties test results. a) Impact energy of butt-fusion welded joints after thermal-oxidative aging at different temperatures. b) The impact strength of thermal butt-fusion joints after thermal-oxidative aging at different temperatures. (c) The tensile strength of butt-fusion welded joints after thermal-oxidative aging at different temperatures. (d) The surface hardness of butt-fusion welded joints after thermal-oxidative aging at different temperatures. (e) Vicat softening temperature of butt-fusion welded joints after thermal-oxidative aging at different temperatures. (f) Fitting results of OIT decay index of butt-fusion welded joint after thermal-oxidative aging at different temperatures (Color figure online)

of the BF welded joint increases. After aging for 600 h, the Vicat softening temperature of the BF welded joint after thermal-oxidative aging at 120 °C is up to 127.36 °C. This Vicat softening temperature is 0.21 °C and 0.52 °C higher than that of thermal-oxidative aging at 90 °C and thermal-oxidative aging at 60 °C. After aging for 480 h, the Vicat softening temperature of the BF welded joint after thermal-oxidative aging at 90 °C is up to 127.15 °C. After aging for 480 h, the Vicat softening temperature of the BF welded joint after thermal-oxidative aging at 60 °C is up to 126.84 °C. During the aging process, the Vicat softening temperature of the BF welded joint increases with increasing aging temperature. The degree of molecular chain cross-linking and winding increases with increasing aging time and aging temperature. However, before and after thermal-oxidative aging, the Vicat temperature of BF welded joints do not change more than 1.56 °C. This shows that the thermal-oxidative accelerated aging has little effect on the thermal deformation resistance of the joints.

Moreover, the distance between molecular chains is reduced, so that the molecular chain spacings and their free flow ability decrease. Additionally, the Vicat softening temperature of the BF welded joint increases. The free flow ability of the molecular chains of the BF welded joint is weaker after aging for 600 h than before it.

3.2 Oxidation induction time

OIT is the time spent consuming antioxidants in the sample. Therefore, the OIT value can indicate the degree of antioxidant consumption in the BF welded joint. Relevant researchers believe that the decay rate of polyethylene pipe during OIT follows the following exponential equation:

$$\mathrm{T}(\mathrm{t}) = \mathrm{T}_0 \cdot \mathrm{e}^{(-\mathrm{s}\cdot\mathrm{t})} + \mathrm{A}, \tag{1}$$

where it is the aging time of the pipeline with hot melt joint, $T(t)$ is the OIT of the pipeline after the aging time t in h, T_0 is the OIT of the unprocessed pipeline, s is the antioxidant consumption rate, and A is a constant.

The OIT of the BF welded joint is measured by differential scanning calorimetry (DSC) after aging at different temperatures. After curve fitting, the decay curve and equation of the OIT of the BF welded joint at various temperatures are shown in Fig. 4(f). It can be seen from Fig. 4(f) that after thermal-oxidative aging at different temperatures, the OIT of the BF welded joint from 0–600 h shows a downward trend, indicating the gradual consumption of the antioxidants with an intense degree of aging. Moreover, the OIT of the BF welded joint decreases by 27.42% after thermal-oxidative aging at 120 °C. This decrease in the OIT is greater than the OIT of the BF welded joint after thermal-oxidative aging at 90 °C, which only decreases by 22.58%. The OIT of the BF welded joint after thermal-oxidative aging at 60 °C decreases by 20.62%. These results are similar to those of mechanical properties. When the aging time is the same, the OIT of the BF welded joint gradually decreases with increasing temperature. The antioxidant activity increases with increasing temperature. So, the higher the temperature, the shorter the OIT.

3.3 FTIR spectroscopy

In order to investigate the similarities and differences in the aging mechanism of HDPE BF welded joints after accelerated thermal oxygen aging under different temperatures, the FTIR test was carried out along with the acquisition of the infrared spectrum. It should reflect the changes of the main functional groups during the aging process. In Fig. 5 (a, b, and c), there are unique absorption peaks of methylene at 2913 cm^{-1}, 2846 cm^{-1}, 1461 cm^{-1}, and 717 cm^{-1}. The absorption peaks at 2913 cm^{-1} and 2846 cm^{-1} correspond to the asymmetric and symmetric tensile vibrations of – CH_2. The absorption peaks at 1461 cm^{-1} and 717 cm^{-1} are associated with the swing and swing vibration of –CH_2, respectively. After aging of the BF welded joint, its molecular chain fracture is intensified (Kemari et al. 2019). However, it can be seen from Fig. 5 (a, b, and c) that thermal-oxidative aging does not damage the basic skeleton of the material.

Figure 5 presents the absorption peaks in the 3127–3662 cm^{-1}, 1527–1710 cm^{-1}, and 954–1170 cm^{-1} bands after aging. The absorption peak of the welded joint in the range 3127–3662 cm^{-1} is a representative, separately analyzed, the enlarged view of which is given in Fig. 5 (a, b, and c).

The absorption peak in the 1527–1710 cm^{-1} band is related to forming oxidation-induced esters (Luongo (1960)) and shows the characteristic absorption peak of antioxidants (Maria et al. 2015). The absorption peak in the 954–1170 cm^{-1} band matches the stretching vibration of the oxidation functional group. Oxidative degradation occurs during the aging process of the BF welded joint. The oxidative degradation products include esters (1710 cm^{-1}), ketones (1715 cm^{-1}), aldehydes (1725 cm^{-1}), and carboxylic acids (1705 cm^{-1}) (Gedde and Ifwarson 1990). Esters, ketones, aldehydes, carboxylic acids, and other carbonyl-containing organic compounds are considered to be the products of polyethylene pipe degradation (Gong et al. 2021; Montes et al. 2012). Moreover, the alcohol structure of -OH bonds has vibrational peaks in 1500–1650 cm^{-1} and 3200–3700 cm^{-1} bands, while C-O-C bonds have peaks in the 1000–1200 cm^{-1} band (Gedde and Ifwarson 1990). It should be noted that the -OH bond may originate from oxidation products (Rozental-Evesque et al. 2006). In summary, aging products such as alcohol, phenol, and hydrocarbons are produced on the pipe BF welded joint surface after aging (Luongo 1960; Gedde and Ifwarson 1990). The number of weak -C=C- bonds in the molecular chains gradually increases with aging time at different temperatures. These weak -C=C- bonds continuously absorb energy until saturation or the breakage of the molecular bonds. As a result, new short molecular chains and new oxidized free groups are formed.

Figure 5 (a, b, and c) shows the absorption peak of the BF welded joint in the 3127–3662 cm^{-1} band after thermal oxygen aging at different times. As the aging time increases, the absorption peak value of the BF welded joint increases. It shows that the absorbance of the material increases with aging time. In addition, it was found that the absorption peak appeared in the 3127–3662 cm^{-1} band after the test. This absorption peak is matched with -OH and -C≡C- stretching vibration and water bending vibration. It indicates that the aging products of esters, carboxylic acids, aldehydes, and ketones appear on the surface of the pipe BF welded joint.

3.4 SEM

Figure 6 shows the micro-surface morphologies of fractured surfaces of BF welded joints at different aging times of thermal-oxidative aging at 60 °C. (a) 0 h, (b) 120 h, (c) 240 h, (d) 360 h, (e) 480 h, and (f) 600 h. Compared with the samples after aging, the fiber diameter and length of the BF welded joint without aging are the largest and the longest. The length of the fiber is 38.7 μm. As the aging time increases, the diameter and length of BF welded joint fibers decrease. After 600 h of aging, which is the maximum aging of the pipe joint, the fiber has the shortest length. The shortest fiber length is 26.1 μm, which is a reduction of 32.56%.

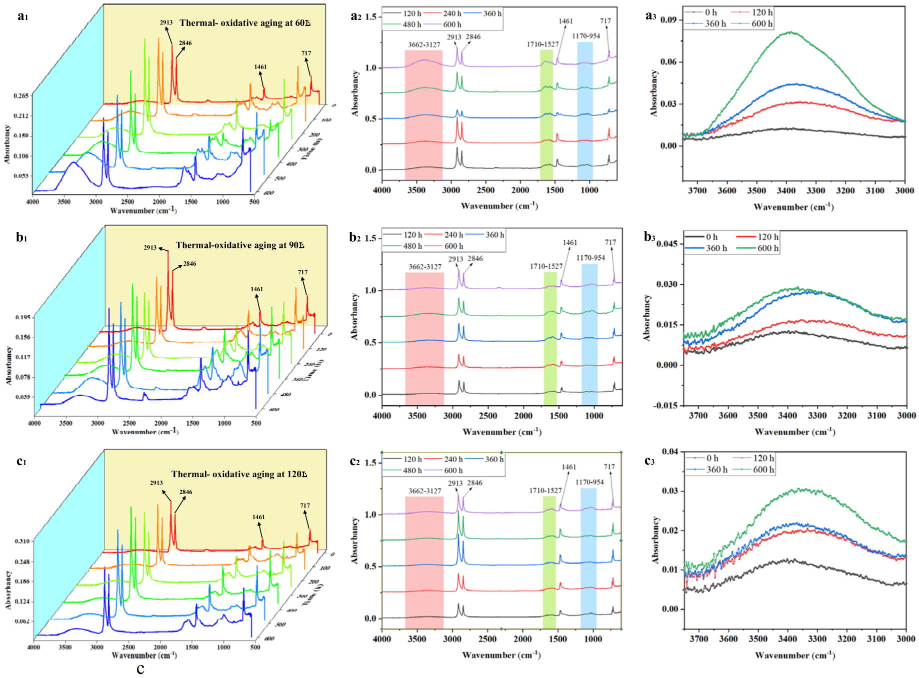

Fig. 5 FTIR absorbance spectra of butt-fusion welded joint after thermal-oxidative aging at different times. (a_j) Thermal oxidative aging at 60 °C. (b_j) Thermal oxidative aging at 90 °C. (c_j) Thermal oxidative aging at 120 °C (j=1, 2, 3) (Color figure online)

Figure 7 shows the micro-surface morphologies of fractured surfaces of BF welded joints at different aging times of thermal-oxidative aging at 90 °C. (a) 0 h, (b) 120 h, (c) 240 h, (d) 360 h, (e) 480 h, and (f) 600 h. The fiber length of the BF welded joint is the longest when it is not aged, and its value is 38.7 μm. After aging for 600 h, the fiber length of the BF welded joint decreases to 24.9 μm. It is a decrease of 35.66%. Therefore, the aging of pipe joints is the most intense after aging for 600 h.

Figure 8 shows the micro-surface morphologies of fractured surfaces of BF welded joints at different aging times of thermal-oxidative aging at 120 °C. (a) 0 h, (b) 120 h, (c) 240 h, (d) 360 h, (e) 480 h, and (f) 600 h. The fiber length of the pipe joint decreases from 38.7 μm to 20.8 μm after thermal-oxidative aging at 120 °C. The length is reduced by 46.25%. The aging of pipe joints is the most intense after 600 h.

The diameter and length of BF welded joint fibers decrease with increasing aging time and temperature. For the aging time of 600 h, there are three different temperatures, 120 °C, 90 °C, and 60 °C. At 120 °C, the fractured surface of the BF welded joint is the roughest. Moreover, the fractured fiber is the largest comprised of the smallest broken fibers. This trend is followed by the fractured surface of the BF welded joint for 90 °C temperatures. The fractured surface of the BF welded joint is the smoothest for 60 °C. The change in the length of these fibers may be related to the carbonyl defects introduced by the molecular chain fractures after aging. It can be concluded that the degree of aging of the pipeline gradually increases with increasing temperature under the condition of thermal-oxidative aging. The degree of aging of the BF welded joint is the most intense when the temperature

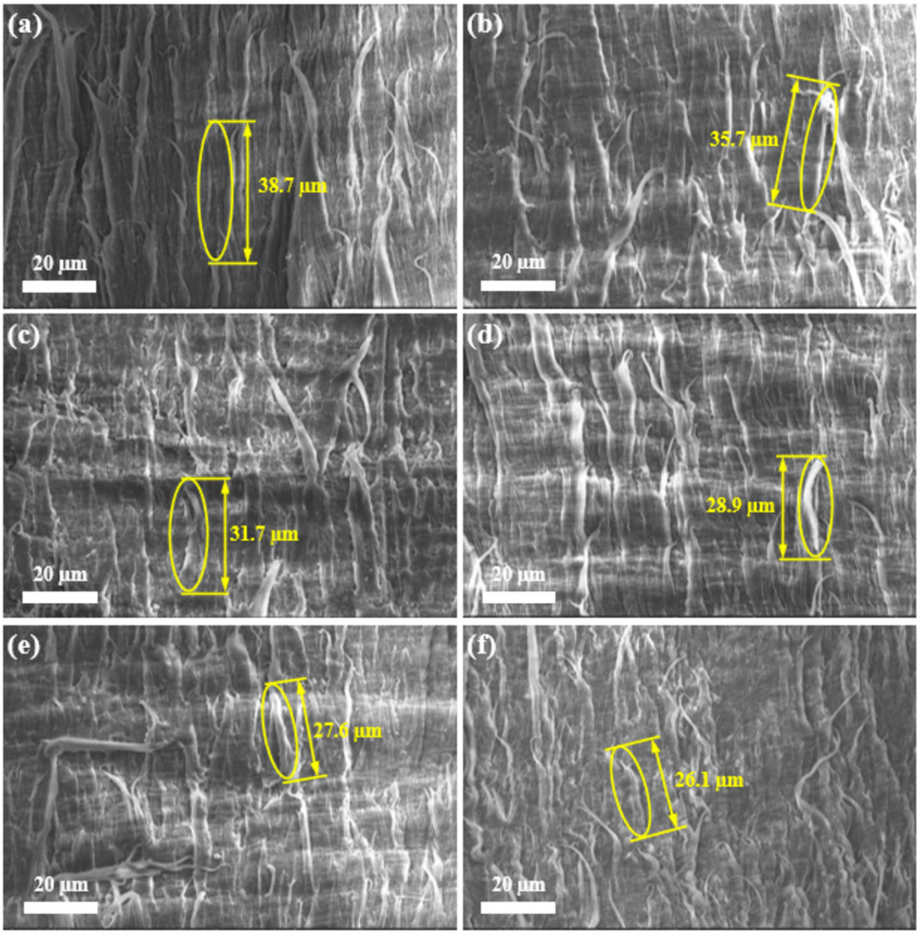

Fig. 6 Micro-surface morphologies of fractured surfaces of butt-fusion welded joints at different aging times of thermal-oxidative aging at 60 °C. (a) 0 h, (b) 120 h, (c) 240 h, (d) 360 h, (e) 480 h, and (f) 600 h (Color figure online)

of thermal-oxidative aging is 120 °C. The degree of aging after thermal-oxidative aging at 60 °C is the lowest.

At the same temperature and with increasing test duration, the antioxidants in the BF welded joint gradually decrease, and the BF welded joint begins to degrade. The macromolecular chains and some short chains break to different degrees. Hence, the number of fibers at the interface of the BF welded joint specimen gradually increases, and the length decreases under the tensile action. The diameter and length of the BF welded joint fiber decrease, which may be due to the decrease in the strength of the molecular bond or the direct fracture of the molecular bond due to the absorption of macromolecular groups and partial molecular chains during the aging process. Combined with the tensile test results (see Sect. 3.1.2), the length of the BF welded joint in the SEM photos decreases with the increase in the aging temperature. In contrast, the fracture roughness of the BF welded joint increases.

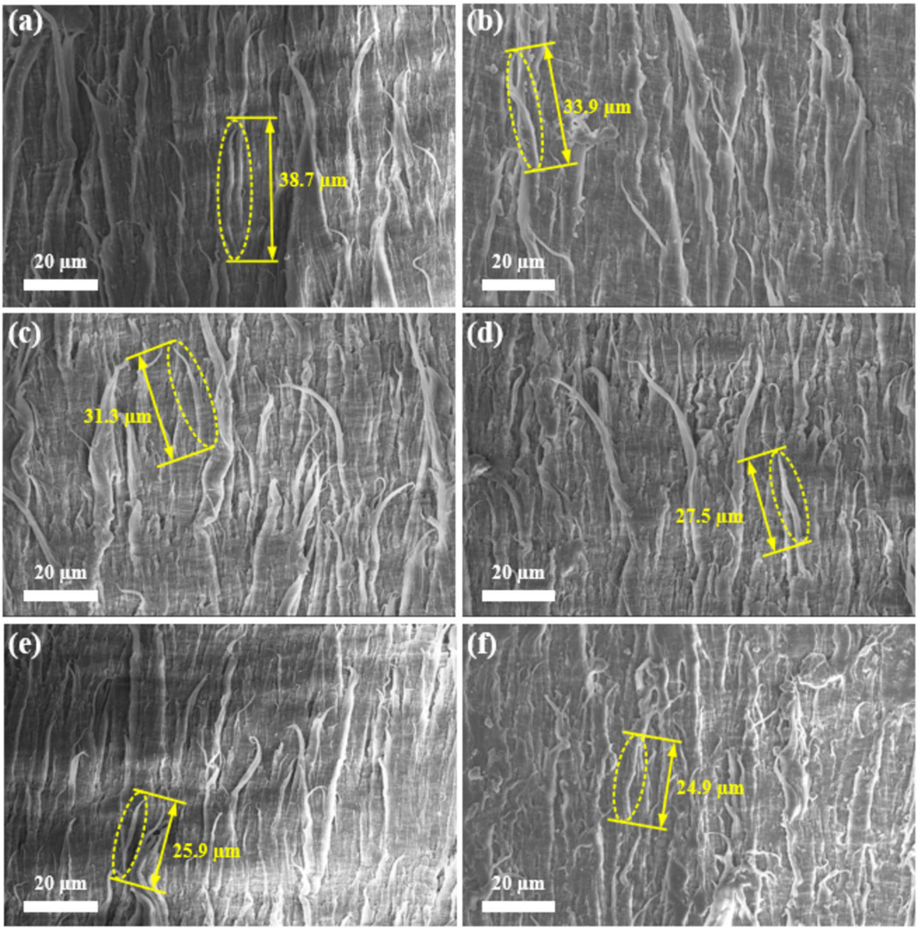

Fig. 7 Micro-surface morphologies of fractured surfaces of butt-fusion welded joints at different aging times of thermal-oxidative aging at 90 °C. (a) 0 h, (b) 120 h, (c) 240 h, (d) 360 h, (e) 480 h, and (f) 600 h (Color figure online)

3.5 Aging mechanisms

For the aging process of high-density polyethylene, a widely accepted mechanism of oxidation and pyrolysis has been proposed in many research studies, as shown in Fig. 9. In the process of thermal-oxidative aging, the weak hydrocarbon bond in the molecule of HDPE BF welded joint is destroyed and free radical R° is generated. These free radicals R° are oxidized in an environment with sufficient oxygen and energy to produce peroxy free radicals ROO°. ROO° reacts with hydrogen peroxide to produce ROOH. A part of ROOH is decomposed into RO° and OH°, and the free radicals after decomposition are oxidized. The final product of pyrolysis is carbonyl, unsaturated group, and conjugated group (Zhang et al. 2020).

The molecular chain of HDPE BF welded joints mainly cross-links and breaks at high temperatures. Therefore, the molecular chain reaction mechanism of oxidative pyrolysis of

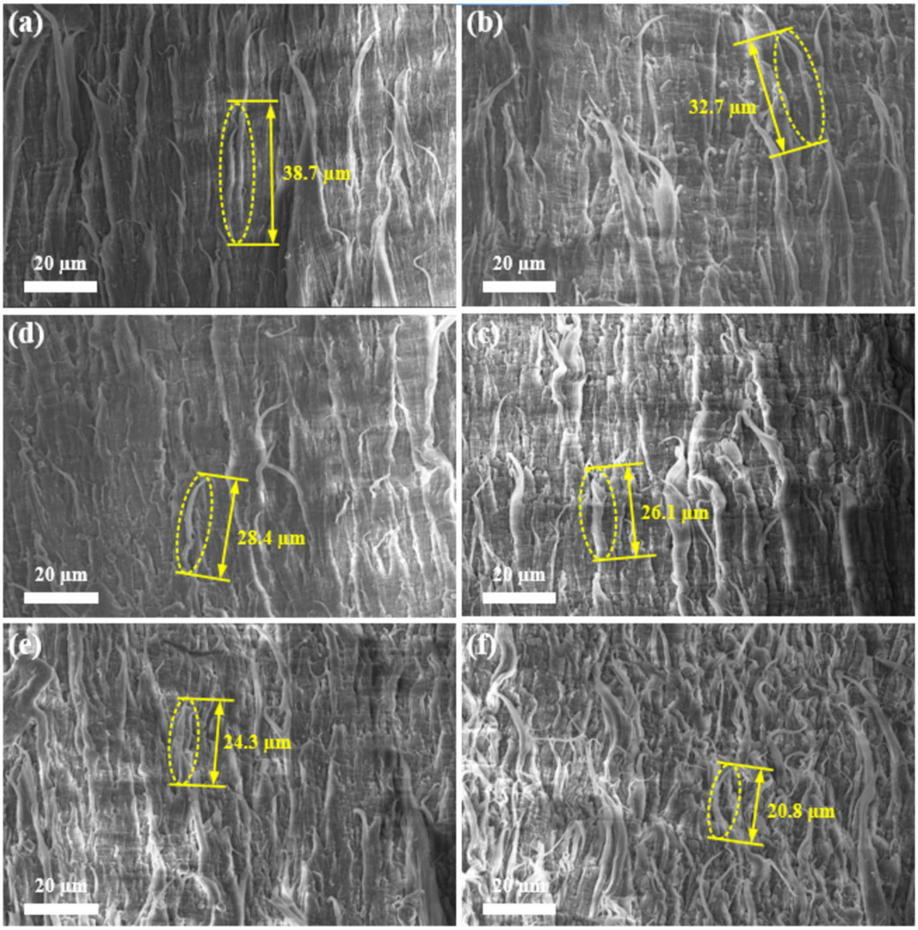

Fig. 8 Micro-surface morphologies of fractured surfaces of butt-fusion welded joints at different aging times of thermal-oxidative aging at 120 °C. (a) 0 h, (b) 120 h, (c) 240 h, (d) 360 h, (e) 480 h, and (f) 600 h (Color figure online)

HDPE, shown in Fig. 9, applies to the accelerated thermal-oxidative aging at these three temperatures only.

As shown in Fig. 10(a), the molecular chain structure of the HDPE pipe BF welded joint is mainly composed of long molecular chains. There are branchy short chains on the main chain. The BF welded joint belongs to the product of secondary processing. Figure 5(i_1) (i=a, b, c) in Sect. 3.3 shows that, when BF welded joints were not aged, polyethylene aging-specific products, ester groups, were present, ketone, aldehyde, and carboxylic acid products of polyethylene aging at 3127–3662 cm^{-1}, 1527–1710 cm^{-1}, and 954–1170 cm^{-1}. As shown in Fig. 10(b), when processing and manufacturing the BF welded joint, the joints of the two pipe bodies are heated to a specific temperature. During the heating process, the -C=C- absorption energy in the molecular chain of the tube body is destroyed, and free hydroxyl and carbonyl groups are produce. The molecular chains are cross-linked and form a grid structure. As shown in Fig. 10(c), when the molten tube body is partially docked, the molecular chains of the two docked tube bodies are cross-linked, producing short chains,

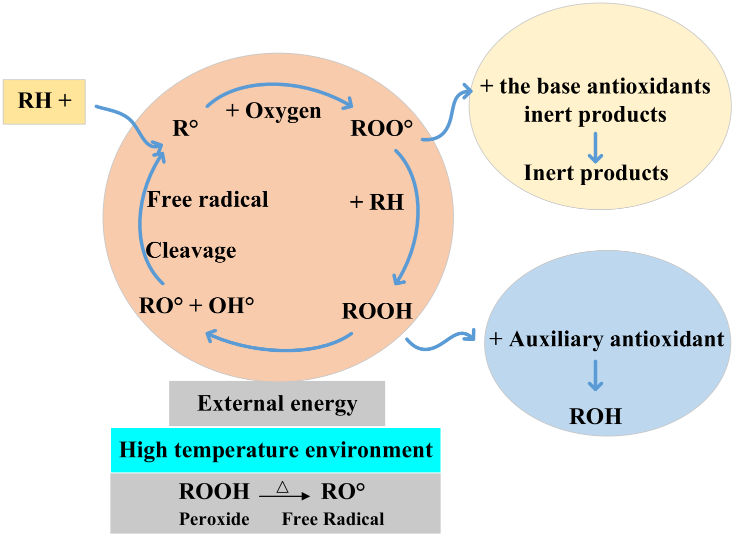

Fig. 9 Oxidative pyrolysis mechanism of high-density polyethylene (Color figure online)

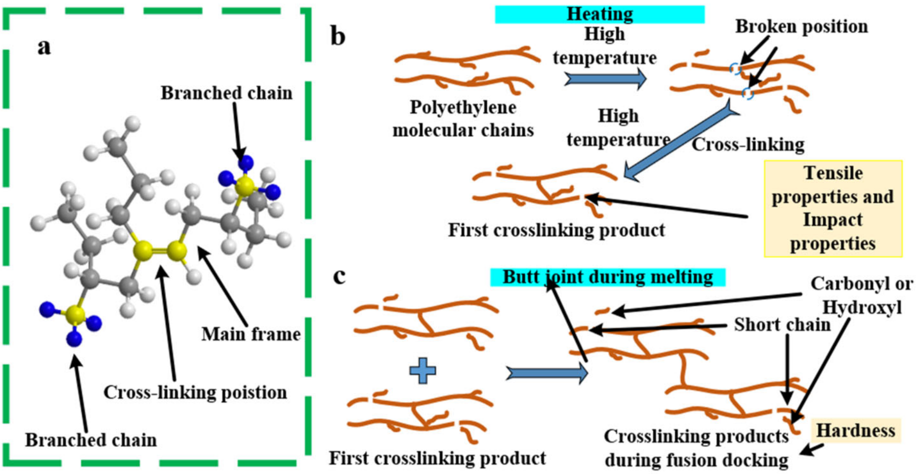

Fig. 10 Molecular chain reaction mechanism during HDPE butt-fusion welded joint production. (a) Molecular diagram of HDPE butt-fusion welded joint. (b) Schematic diagram of molecular chain change after heating of HDPE butt-fusion welded joint. (c) Schematic diagram of change in the molecular chain after HDPE butt-fusion welded joint (Color figure online)

free hydroxyl and carbonyl groups. The increase in hardness, decrease in impact and tensile strength of BF welded joint can be attributed to the molecular cross-linking and fracture. When polyethylene molecule undergoes cross-linking, the intermolecular connections become stronger, leading to an increase in hardness. This also makes the material more brittle, which results in a decrease in impact and tensile strength, as the molecular chains are more prone to breakage under impact and tensile stresses.

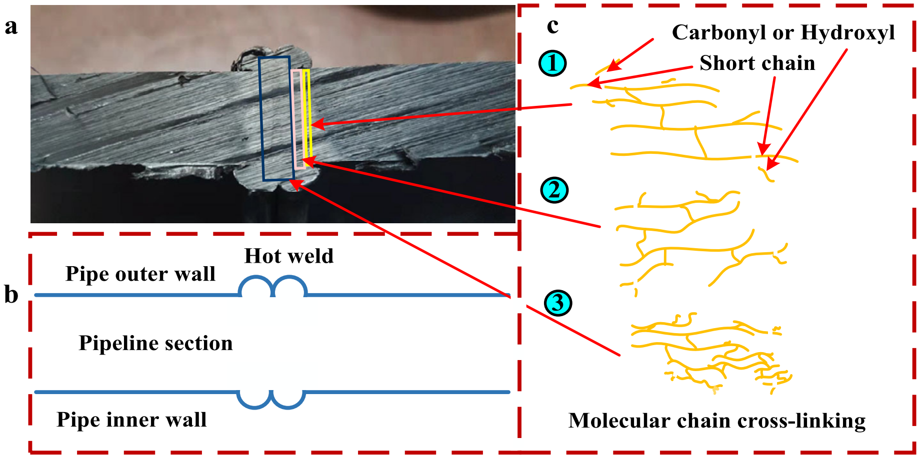

Fig. 11 Schematic diagram of the degree of cross-linking of different areas at the melting point of HDPE pipe butt-fusion welded joint. (a) Sectional photo of HDPE pipe with butt-fusion welded joint. (b) Section diagram of HDPE pipe with butt-fusion welded joint. (c) Schematic diagram of the degree of cross-linking of different areas at the melting point of HDPE pipe with butt-fusion welded joint (Color figure online)

Figure 11 is a schematic diagram of the cross-linking degree of different areas at the melting point of the HDPE pipe with a BF welded joint. From ① to ③ in the heat-affected zone, the degree of molecular chain cross-linking and fracture increase. Moreover, the length of the molecular chain produced by molecular chain cross-linking and fracture decreases, and the mesh complexity increases.

For the different temperatures of accelerated thermal-oxidative aging, the oxidation degree of the BF welded joint is different, and the speed of oxygen diffusion is different. Under the action of high temperature, oxidation occurs on the surface of the BF welded joint. Moreover, free radicals are also generated on the surface of the BF welded joint. These free radicals react with O_2 and produce peroxide and hydroperoxide-type free radicals. As can be seen in Sect. 3.3, the absorption peak intensity of oxidative degradation products, such as alcohol structures containing -OH bonds, increases significantly in the 1500–1650 cm^{-1} and 3200–3700 cm^{-1} bands with increasing aging time. The absorption peak intensity of C-O-C bonds in the 1000–1200 cm^{-1} band also showed a rising trend. In Fig. 5(i_2) (i = a, b, c), there are the unique absorption peaks of methylene at 2913 cm^{-1}, 2846 cm^{-1}, 1461 cm^{-1} and 717 cm^{-1}. The peaks verify that -CH_2 undergoes stretching and oscillating vibrations during the aging of BF welded joint. This creates the conditions for cross-linking and breaking of molecular chains. From Sect. 2.1, the impact and tensile strength of BF welded joint gradually decreases with increasing aging time. This shows that the intermolecular interaction decreases. In Sect. 3.4, the fracture-micrographs of the impact specimens show that the fibre length of the fracture decreases and the number of fractured fibres increases with increasing aging time. This indicates that the external energy of molecular chain can withstand decreases, the number of molecular chains increases, and the complexity of molecular chain structure increases during the aging process. This indicates that the molecular chains of polyethylene molecules undergo chain breakage and an increase in crosslinking degree. The hardness and Vicat softening temperature of BF welded joint increase with aging time. So the material of BF welded joint gradually hardens. In an energy-rich environment, the short chains of molecules produce small molecules at their ends (small molecules are highly

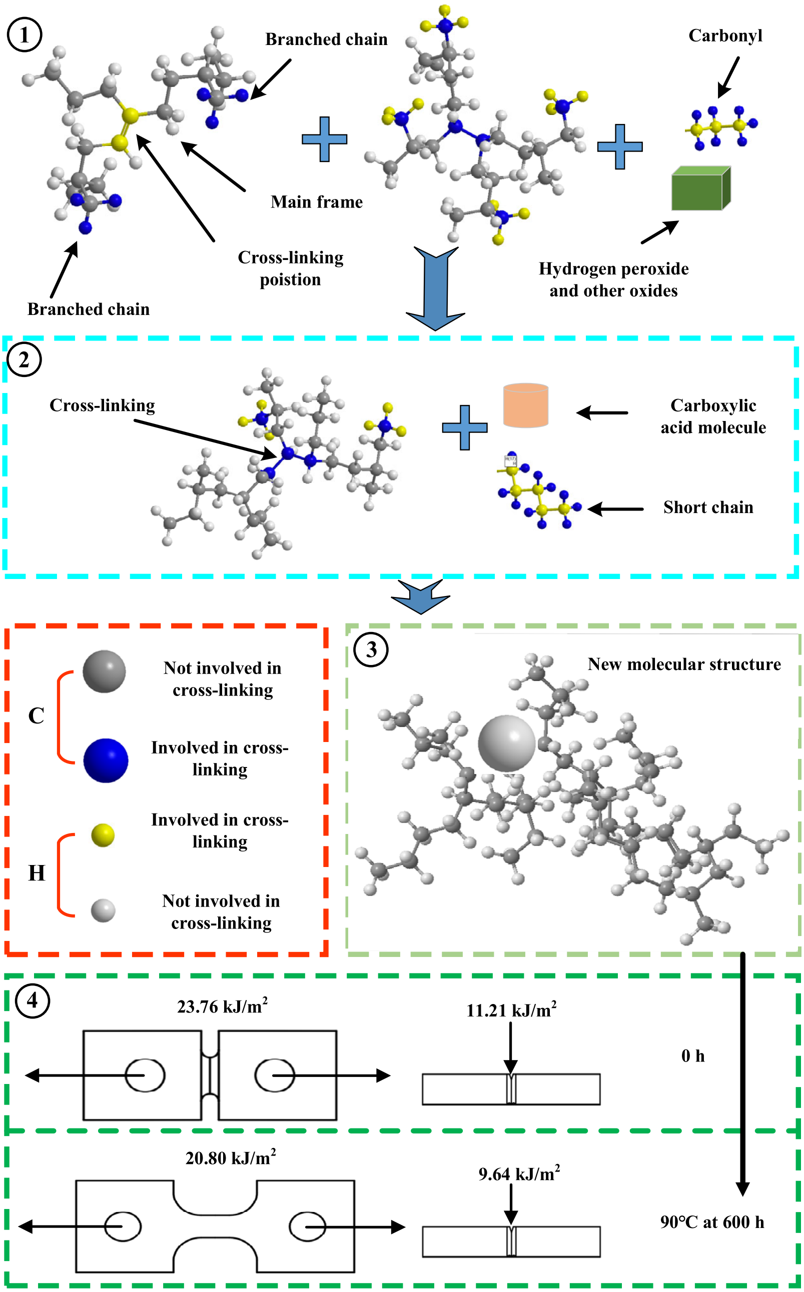

Fig. 12 Molecular chain reaction mechanism of thermal-oxidative aging (Color figure online)

mobile), which join the main chains of molecules, and the molecular chains are tightly and neatly arranged. Therefore, the molecular chain reaction mechanism of thermo-oxidative aging can be derived.

As shown in Fig. 12, during the cross-linking process, dispersed carbonyl groups induced by dispersed peroxides and other free radicals join the main chain of the molecule. This process forms a network structure without shortening the length of the main chain. At high temperatures, the HDPE molecular chain breaks at the weak position formed after processing the BF welded joint and a short chain is produced. The carbon atom at the junction of the carbonyl groups and the main chain is further oxidized to form carboxylic acid, resulting in the molecular chain fracture and increasing cross-linking. This manifests itself directly in the form of an increase in the Shore hardness of BF welded joint and indirectly in its Vicat softening temperature.

Unsaturated fatty acids, carbonyl, and long-chain carboxylic acids are produced by pyrolysis. The carbonyl groups produced by pyrolysis are oxidized to form carboxylic acid, and the final product of pyrolysis is binary acid. It is assumed that oxygen only reacts with carbon-oxygen single bonds to form new bonds. The elimination of oxygen-containing substances leads to the formation of double bonds in the molecular chain of high polyethylene. It forms unsaturated fatty acids. The number of unsaturated fatty acids increases with age. It explains why the last generation of the dicarboxylic acid is due to the further conversion of a long-chain carboxylic acid into dicarboxylic acid (Schwarzinger et al. 2015). Therefore, pyrolysis reduces the impact strength and tensile strength of the BF welded joint with increasing time and temperature.

With increasing aging time, polyethylene molecule undergoes broken chain and cross-linking. The cross-linking makes intermolecular connections become stronger, leading to an increase in hardness. This also makes the material more brittle, which results in a decrease in impact and tensile strength, as the molecular chains are more prone to breakage under impact and tensile stresses.

The accelerated aging of the thermal BF joint significantly impacts its microstructure and crystallinity under the hot oxygen environment of 60 °C, 90 °C, and 120 °C. With the increase in temperature, the crystal structure of HDPE molecules is gradually improved. It also improves the crystallinity of the BF welded joint molecules. At the same time, in the process of thermal-oxidative aging, oxidation takes place on the BF welded joint surface and produces a certain number of free radicals. Cross-linking occurs between molecular chains and interferes with the relative movement of molecules in the BF welded joint, thus reducing the impact resistance of the BF welded joint. With increasing aging time and aging temperature, the crystallinity of the BF welded joint increases, which increases the hardness of the BF welded joint.

4 Conclusion

Accelerated aging tests at three temperature gradients were carried out on PE100 pipe BF welded joints, with a total test period of 600 h. With the process of thermal-oxidative aging, the BF welded joint of the PE100 pipeline has obvious embrittlement, and the mechanical and chemical properties continue to decline. In addition, it was found that the BF welded joint is susceptible to aging temperature. A higher temperature degrades material properties to a great extent. The long chain of -C=C- a molecule in the BF welded joint is more prone to large-scale chain breakage with the external temperature increase. The docking mechanism of the BF welded joint and the molecular chain intersection mechanism of the heat-affected zone are analyzed. During the aging process of the BF welded joint, oxidative degradation occurs, producing the degradation products of polyethylene pipes such as esters, ketones, aldehydes, and carboxylic acids. As the thermal-oxidative aging temperature and the aging time increase, the fracture roughness of the BF welded joint increases. Moreover, the material plasticity decreases and the brittleness increases. The diameter of the filament inside the BF welded joint decreases and the length becomes shorter.

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Declarations

Competing interests The authors declare no competing interests.

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