Aging of polyethylene thermoplastic liner exposed to sulfuric acid corrosive environments

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Abstract. Thermoplastics have been widely used as liners of pressure vessels and pressure pipes to improve corrosive resistance in recent years. During long-term use under complex circumstances of corrosive medium, high temperature and existence of oxygen, gradual aging of thermoplastic was often observed. However, the aging mechanism of thermoplastic under such complex condition is rarely reported. In this study, various methods such as dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and tensile tests were performed to examine the aging mechanism of polyethylene (PE) liner used for different times under various temperatures and concentrations of acid. The results reveal that aging of liner material resulted from swelling due to exposure to acid in low concentrations during long-term use, which will result in surface damage, even leakage of acid and decrease in PE strength. Recrystallization under concentrations higher than 50% is observed, it is accompanied by increase in melting point (T_m), decomposition temperature, tensile strength and change of transparency. With further increase in acid concentration, change of molecular structure was observed in FTIR spectrums, which might be the result of oxidation, dehydrogenation and chain breaking induced by high concentration of acid.

1. Introduction
Thermoplastics have been used as linings for pressure equipment in fields such as chemical industry and petroleum industry due to its advantage that combines high strength of metal materials, excellent corrosive resistance and adhesion resistance property of thermoplastics. Several kinds of thermoplastics can be used as the liner based on the using condition, such as Polyethylene (PE), Polypropylene (PP), Polyvinyl Chloride (PVC), Fluoroplastics, Acrylonitrile-Butadine-Styrene copolymer (ABS), Polyamide (PA) and so on.

Aging of thermoplastics is one of the most important factors that affect safe use of pressure vessels and pressure pipes during long-term use. Several kinds of aging mechanisms were observed in thermoplastics under different use conditions, such as creep, oxidation, physical aging and corrosion [1-2]. However, pressure equipment was often used in a complex condition that usually combines stress, oxygen, high temperature and corrosive medium. The aging of thermoplastics will be more serious compared with exposure to only one of the environmental parameters. For example, PP was found to crack in extremely short time under high concentration of sulfuric acid combined with tensile stress [3]. The crazing damage of PVC was also observed to occur in a short time under a high concentration of sulfuric acid in a tensile study [4]. PE and PP molecules were found to degrade in the...
presence of oxygen under high temperature, result in a decrease of physical properties [5]. When used in moist circumstances, acids, alkalis or microorganisms play a catalytic role in the hydrolysis of amide bond in polyamide, resulting in a decrease of mechanical properties [6].

In chemical industry, PE is often used as a liner material in environments containing hydrochloric acid or sulfuric acid at various temperatures. Failure of PE is often found during long-term use. However, the aging mechanism of PE under such a complex use condition is rarely reported. In this study, samples of PE liner were soaked in different concentrations of acid at different temperatures for a certain time. Several characterization methods were performed to study the mechanical properties, thermal properties and molecular structure change of the PE liner in order to explore its aging mechanism.

2. Methods

2.1. Dynamic mechanical analysis (DMA):
DMA experiments were performed on a TA Q800 DMA instrument. Rectangle samples with size of 10mm×7mm×1mm were used. Samples were tested with frequency of 10 Hz and amplitude of 5 μm in the temperature range of -20 °C to 160 °C with heating rate of 3 °C/min.

2.2. Differential scanning calorimetry (DSC):
The melting temperature (Tm) of the samples were detected by a TA Q200 DSC. Before DSC measurements, Indium was used to calibrate temperature. Empty pan was used as reference. The samples were heated from 0 to 200 °C at the heating rate of 10 °C/min, and Tm was determined as the peak point of the transition.

2.3. Fourier transform infrared spectroscopy (FTIR):
FTIR experiments were performed using a Nicolet 5700 FTIR spectroscope, in attenuated total reflection (ATR) mode. A total of 32 scans was accumulated with an accuracy of 2 cm⁻¹ for signal-averaging each FTIR spectra measurement.

2.4 Thermogravimetric analysis (TGA):
TGA experiments were taken in N2 atmosphere, with a heating rate of 25 °C/min at the temperature range of room temperature to 600°C.

2.5 Tensile test:
Tensile experiments were taken according to GB/T 1040 [7].

3. Results and discussion

3.1. DMA study
PE is a semicrystalline polymer. The crystalline part of PE segments are arranged in a regular order, these segments cannot be re-arranged under stress, which provides strength for PE at effective using temperature, while the amorphous segments of PE molecule arranged in irregular order, these segments can absorb part of energy under stress through segment motion, which provides flexibility for PE. Figure 1 gives the tensile modulus of PE under dynamic stress at various temperatures. With increasing temperature, the tensile modulus of PE decreases continually. At temperatures higher than 70 °C, the tensile modulus decreases with a higher rate. When temperature reaches to 130 °C, the tensile modulus of PE decrease approach to 0, indicated that crystalline segments were melting, and the whole molecule can move freely.
3.2. Long-term use at ambient temperature

Figure 2 shows PE lined pressure pipe used for 7 years in 30% sulfuric acid environment at room temperature. The inserted photo shows a detail of the PE surface after drying. Surface damage of PE after long-term use was observed, which affects the safety for further using.

It was found that liquid or gas molecule will be absorbed and accumulated on the surface of polymeric liner, then gradually penetrate into the liner due to the existence of so called “free volume” in polymer molecules. The polymeric liner becomes softer, which was called “plasticization” effect. Accompanied by liquid or gas flow, the polymeric liner gradually became damaged, which might be the main reason of surface pulverization observed in PE liner. This damage phenomenon would be accelerated by increasing temperature or pressure [8].

When the liquid medium contains gas impurities, the penetration phenomenon becomes more severe. A recent study on penetration behavior of PE lined pipe used in petroleum industry used kerosene to simulate coupled oil and gas compounds, it revealed that kerosene plays a role in swelling and plasticization. The permeability coefficient and diffusion coefficient of methane through PE soaked in kerosene both increase [9].

3.3. Thermal aging at 70 °C

Figure 3 shows the DSC curve of virgin PE and sample that was aged for 1200h at 70 °C. An
endothermic peak at 136°C is found, at which the crystalline part of the PE melted. After thermal treating at 70°C, the melting point of PE is exactly the same compared with the original sample. FTIR experiments were also performed to examine the molecular structure of virgin and thermally-treated samples (Figure 4). The transmittance curve of the two samples is exactly the same. These results indicate that PE is stable at temperatures up to 70°C in the absence of corrosive medium.

3.4 Thermal aging at 70°C combined with sulfuric acid

Figure 5 shows a photo of PE aged with different sulfuric acid concentrations for 480h at 70 °C. The virgin PE is semi-transparent, after treating in sulfuric acid at the concentration of 50% and 70% for 480h, PE samples become completely non-transparent. This might be a result of increasing crystallization degree induced by hot sulfuric acid [10]. When the concentration of sulfuric acid increase to 90%, after 480h treatment, the PE sample became black, indicating the structure of the PE molecules might be affected.

Figure 6 gives the DSC curves of PE samples aged at various concentration of sulfuric acid for 480h. A clear increase in Tm was found after aging at 50% sulfuric acid, which might be due to the increase of crystallization degree induced by hot sulfuric acid. With further increase in the concentration of sulfuric acid, the melting point of PE after treating at 70 oC for 480h gradually decreased, indicating that the molecular structure of PE might be affected by high concentrations of sulfuric acid.
Figure 7 shows DSC curves of PE treated in sulfuric acid concentration of 70% for various times. With increasing treating time, the melting point of PE also increases at a short time, while decreases with further treatment. We summarize the melting temperatures of PE treated at different concentrations of acid, showing in Figure 8. $T_m$ increased at lower concentration, while decreased at higher concentrations. These results further proved that crystallization of PE induced by sulfuric acid concentrations lower than 50% is the main reason for increasing $T_m$. With further increase of sulfuric acid, the crystalize structure of PE was affected, leading to decreasing $T_m$ values.

In order to explore the molecular structure change of PE, FTIR experiments were performed. Figure 9 gives the FTIR spectra of PE treated at sulfuric concentration of 70% and 90%. A new peak near 2330 cm$^{-1}$ was found, which was assigned to unsaturated continues double bonds (C=C=C=C) or triple bond. With the concentration of sulfuric acid increased to 90%, the peak height of unsaturated bond increases significantly, another peak near 1730 cm$^{-1}$ appeared, which was assigned to carbonyl group. Many new peaks were also visible in the fingerprint area. These results clearly demonstrated that the molecular structure of PE was affected by high concentrations of sulfuric acid. The aging mechanism of PE under such condition was speculated to be: breaking of PE chains at some weak point take place induced by sulfuric acid, thus forming the reaction point, dehydrogenation reaction take place at part of the reaction point, leading to the appearance of unsaturated bond, while oxidation or crosslinking reaction take place at the other reaction point.
Thermogravimetry and tensile experiments were performed in order to further check the properties of PE after treating at different concentration of sulfuric acid. Figure 10 shows the weight loss of PE after treating at various acid concentrations for 480h with an environment temperature of 70 ºC. As acid concentration increases, the TGA curve of PE shifts to the higher temperature region. Similar results were found in TGA curve of PE aged at acid concentration of 70% for different times (Figure 11). These results further prove the increase in degree of crystallization of PE at such concentrations as discussed earlier.

Figure 12 gives the tensile strength and elongation at break of PE after treatment at different concentrations of sulfuric acid. After treating at acid concentrations of 50% and 70%, tensile strength of PE increases slightly. The elongation at break decreases significantly, which also resulted from increasing degree of crystallization. When the acid concentration reaches to 90%, the tensile strength shows no further change while the elongation at break increases. This resulted from disintegration of the crystallized region and disintegration of the molecular structure of PE.

4. Conclusion
PE liners were studied under various concentrations of sulfuric acid for different times, at room temperature and at 70 ºC. The results revealed that aging of liner material resulted from swelling due
to exposure to acid in low concentrations during long-term use. This resulted in surface damage, even leakage of acid medium and decrease in strength. Recrystallization induced by acid at concentrations higher than 50% is speculated since change in transparency was observed, as well as an increase of melting point ($T_m$), increase of decomposition temperature, increase in tensile strength. With further increase in sulfuric acid concentration, change of the molecular structure were observed in FTIR spectrums with the appearance of carbonyl group near 1730cm$^{-1}$ and continues double bonds (C=C-C=C) or triple bond near 2330cm$^{-1}$. A change in PE color was observed, the melting point of PE decreases and the elongation at break slightly increases. These might be result of dehydrogenation, oxidation or even chain broken induced by high concentration of sulfuric acid.

Acknowledgments
This study was supported by Shanghai administration for market regulation scientific project (2016-14).

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