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Thermal Air Aging and Lifespan Prediction of PVC-P Geomembranes: An Arrhenius Equation-Based Approach

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Abstract: This study explores the durability of plasticized polyvinyl chloride (PVC-P) geomembranes in hydraulic engineering anti-seepage structures, particularly under varying operational temperature conditions. Employing accelerated thermal air aging tests on three distinct PVC-P geomembrane variants, the study assesses their mechanical properties, specifically axial tensile strength, using an electronic universal testing machine. A comprehensive thermal air aging model, based on the Arrhenius equation, has been developed, offering insights into the lifespan prediction of these geomembranes. Results demonstrate that factors such as annual average temperature, plasticizer content, and membrane thickness significantly influence the geomembranes' service life. Post-aging observations include a notable yellowing and increased brittleness of the geomembranes, coupled with a decline in tensile strength and elongation. Elongations exhibit a decreasing trend, aligning with a first-order degradation kinetics equation. Under conditions of 50℃ over a period of 120 days, the elongation of polyvinyl chloride (PVC)-HX, PVC2.0-JT, and PVC2.5-JT geomembranes was reduced to 255.88%, 430.11%, and 434.58%, respectively. Predictions indicate that at an operational temperature of 20℃, the expected lifespans for these geomembranes are 19, 45, and 48 years, with material failure correlating to plasticizer loss rates of 58.2%, 32.5%, and 24.8%, respectively. These findings offer valuable guidance for the selection of geomembrane materials in hydraulic engineering projects, considering various designed service durations.

Keywords: Plasticized polyvinyl chloride (PVC-P) geomembrane; Accelerated thermal air aging; Arrhenius equation; Aging model

1 Introduction

PVC-P geomembranes, primarily composed of high-polymer polymers, have been extensively utilized in anti-seepage structures of water conservancy projects. These geomembranes, known for their robust adaptability to variations in water head, commendable ductility, and exceptional impermeability, were predominantly used in Chinese engineering projects from the mid-1980s to the 1990s. This period saw a gradual transition to polyethylene (PE) geomembranes [1]. The Chinese "Fourteenth Five-Year Plan," aligning with objectives of carbon neutrality and peak carbon targets, envisages the construction of numerous pumped-storage power stations. Given the complexity of geological conditions, traditional concrete and asphalt concrete panels, while used in these structures, present limitations in anti-seepage adaptability and pose challenges in underwater repairs, leading to potential failures in the seepage system due to panel voids and extrusion damage. This vulnerability underscores the importance of PVC-P geomembrane technology for ensuring the safe operation of such projects [2, 3].

The durability and performance of these geomembranes have been the subject of various studies. Zhang et al. [4] advocated for PVC-HX and thermoplastic polyolefin (TPO) geomembranes, particularly those exceeding 1.0mm in thickness, after a detailed mechanical analysis of commonly used geomembranes in membrane-faced rockfill dams. While the international research community has delved deep into the durability of high-density polyethylene (HDPE)/PE geomembranes [5, 6], there has been a notable gap in developing aging models for PVC-P geomembranes, crucial for predicting their service life in dam engineering.

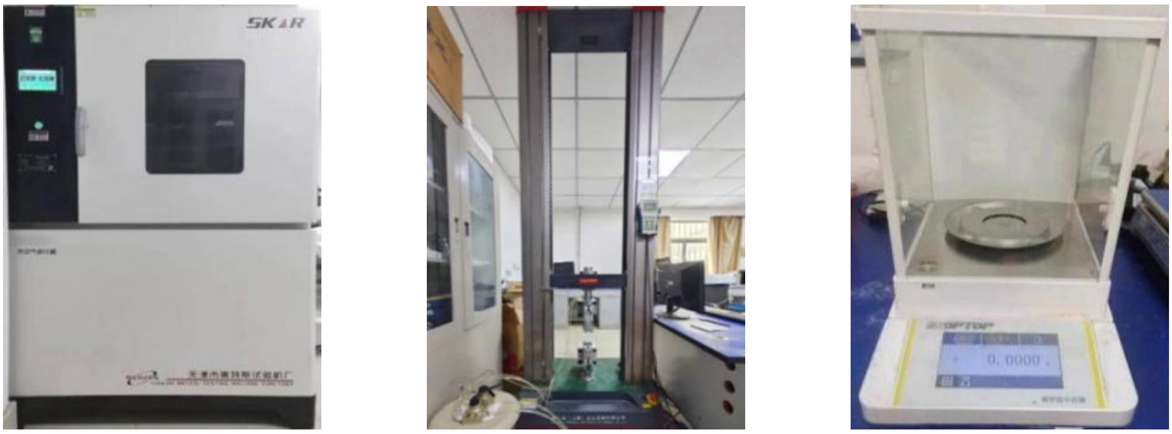
Several international studies have shed light on the aging process of PVC-P geomembranes. Geng et al. [7] indicated that factors like light exposure, temperature variations, and mechanical load can diminish the mechanical properties of composite geomembranes, thereby impacting their durability. Yang and Ding [8] emphasized that aging in geosynthetics is primarily a process of polymer degradation and crosslinking reactions. Rogestedt and Hjertberg [9] discovered that PVC undergoes dehydrochlorination upon heating, with the released hydrogen chloride (HCL) gas further accelerating this reaction. Usman and Galler [10], through infrared spectroscopy, confirmed that the increased brittleness in aged PVC-P geomembranes in tunnels was predominantly due to substantial plasticizer loss. Yu and Chen [11] identified both artificial accelerated aging and atmospheric exposure aging as viable test methods for these materials. Chen et al. [12] conducted indoor accelerated aging tests on PVC films, analyzing the effects of aging on their inelastic and viscoelastic properties. Cazzuffi and Gioffrè [13] examined exposed anti-seepage geomembranes from six Italian dams, suggesting the use of plasticizer loss rate as a metric for assessing geomembrane lifespan. Further, Carreira and Tanghe [14] tested PVC-P geomembranes from various global dam sites, concluding that the remaining plasticizer content should not fall below 20%. Dobilait et al. [15] developed a model for accelerated aging of PVC-coated films, investigating the impact of wear, high temperatures, and humidity on tear resistance.

In conclusion, while artificial accelerated aging tests have been a primary method for life prediction, and substantial progress has been made in understanding the aging mechanisms of PVC-P geomembranes, a reliable model for accurately predicting their service life is yet to be established. This study addresses this gap by conducting indoor accelerated thermal air aging tests on three types of PVC-P geomembranes. Utilizing the Arrhenius equation, a thermal aging model is constructed, determining the threshold of internal plasticizer loss at material failure, thereby enabling prediction of their service life under actual working conditions, which can inform the selection of geomembranes in hydraulic engineering projects with varying service year requirements.

2 Experiment

2.1 Experimental Equipment

Figure 1 delineates the primary equipment employed in this study. The ZSY-32 thermal air aging box, selected for conducting accelerated thermal air aging tests, is suitable for thermal aging examinations on various materials including plastic substances (waterproof materials, rubber, plastics), and electrical insulation. The device circulates thermal air to evenly distribute heat, achieving the requisite temperature for the tests. It features a digital display and a Proportion Integration Differentiation (PID) automatic adjustment instrument for temperature control, enabling the setting of operational temperatures ranging from ambient room conditions to 200℃/250℃. This equipment is characterized by its capability for maintaining a constant temperature automatically, sensitive and uniform temperature control, and stable performance, thereby meeting standard experimental requirements.



(a) (b) (c)

Figure 1. Experimental equipments (a) ZSY-32 thermal air aging box, (b) CMT4304 electronic universal testing machine, (c) AE124 electronic balance

For the axial tensile tests, the CMT4304 electronic universal testing machine was utilized. Integrating electronic technology with mechanical transmission, this apparatus offers a wide spectrum of loading speeds and force measurement ranges. It is capable of accurately measuring and controlling load, deformation, and displacement, with high precision and sensitivity. The testing process is microcomputer-controlled, facilitating real-time display of load values, displacement, deformation, testing speed, and curve data. The machine's maximum tensile load capacity is

30.0kN, and it has a maximum travel distance of 2.1m. Its displacement measurement capability ranges from 0.2% to 100% of the maximum travel, with a measurement error margin within ±0.5%.

To measure the rate of plasticizer loss, the AE124 electronic balance was employed. Given the minimal loss of internal plasticizer in PVC-P geomembranes over brief periods, ordinary mechanical balances were deemed insufficient for the required measurement precision. Therefore, an electronic balance with an accuracy of 0.0001, operating on the principle of electromagnetic force balance, was chosen. This balance replaces the traditional pointer display with a digital one and is known for its stable performance, high sensitivity, and ease of operation. It also offers high precision and the capability to output mass electrical signals, enabling connections to computers and printers for automated weighing, recording, and calculation processes.

2.2 Experimental Materials

In this study, three types of PVC-P geomembranes were evaluated, each measuring 45.0m in length and 2.0m in width. The PVC-HX geomembrane, produced by Shandong Hongxiang New Material Co., Ltd., was tested alongside PVC2.0-JT and PVC2.5-JT geomembranes, manufactured by Shandong Jiantong Geomaterial Co., Ltd. PVC-HX represents a traditional formulation, potentially falling short in meeting the longevity requirements of anti-seepage structures. In contrast, PVC2.0-JT and PVC2.5-JT are advanced formulations, with their physical, mechanical properties, and durability yet to be fully ascertained. To assess whether these newer products offer marked improvements in durability over traditional variants, a comparative analysis of these geomembranes was undertaken. The axial tensile mechanical properties of the three geomembranes were measured in accordance with the Geosynthetic Materials Testing Procedures [16] (SL235-2012) (hereinafter referred to as "procedures"), as summarized in Table 1. Additionally, the composition and mass proportion of each geomembrane type are detailed in Table 2.

Table 1. Main parameters of geomembranes

Index	PVC-HX	PVC2.0-JT	PVC2.5-JT
Average Thickness (mm)	2.00	2.00	2.50
Mass per Unit Area ($g.cm^{-2}$)	0.275	0.260	0.362
Tensile strength (MPa)	23.67	31.15	38.20
Yield strength (MPa)	0.51	0.97	1.18
Elongation at Break (%)	289.68	450.93	452.14
Elongation at Yield (%)	1.03	5.21	7.61

Table 2. Main composition and mass proportion of geomembranes

Composition and Proportion (%)	PVC-HX	PVC2.0-JT	PVC2.5-JT
PVC Resin	56.28	56.67	56.67
Plasticizer (DOP ①)	21.53	30.49	30.49
Filler	19.04	8.37	8.37
Heat Stabilizer ②	1.27	2.36	2.36
Antioxidant	1.20	1.33	1.33
Ultraviolet absorber	0.53	0.78	0.78
Others	0.15	-	-

Note: DOP refers to dioctyl phthalate; thermal stabilizers mainly include calcium-based stabilizers.

2.3 Experimental Procedures

Sample Preparation: Preliminary tests revealed that all three types of PVC-P geomembranes experienced dimensional changes in their longitudinal, transverse, and thickness dimensions following thermal air aging. Consequently, samples slightly larger than the standard tensile specimens were subjected to aging in the thermal air aging box. After reaching the designated aging duration, larger sections of the membrane were retrieved and cut into 200mm×50mm strips, in line with the specifications outlined in the procedures [15], for subsequent tensile testing.

Temperature determination for testing: The TGA2 type thermogravimetric analyzer, manufactured by Mettler Toledo of Switzerland, was employed for the thermogravimetric analysis of the PVC-P geomembranes. The geomembrane samples were finely shredded to dimensions less than 0.2mm, with around 20mg of sample prepared for each test. Prior to testing, samples underwent a drying process in an oven at 60℃ for 24 hours. The test environment was maintained under an N2 atmosphere, with a gas flow rate set at 20mL/min, and a heating rate of 10K/min, escalating from 25℃ to 950℃. Given the identical material properties of PVC2.0-JT and PVC2.5-JT geomembranes, Figure 2 only includes the thermogravimetric curves for the PVC-HX and PVC2.0-JT types. Below temperatures of

162℃ and 240℃, there was a gradual decrease in the residue ratio (TG) of both types of geomembranes, attributed to minor losses of plasticizer. Above these temperatures, a pronounced decline in the residue ratio was observed due to the decomposition of PVC resin, signifying molecular structural damage. To avoid breaking the chemical bonds of the polyvinyl chloride molecules during testing, temperatures exceeding 160℃ were not employed. The test temperatures were established at 50℃, 90℃, and 110℃, following the guidelines of the thermal aging test method for plastics (GB/T7141-2008).

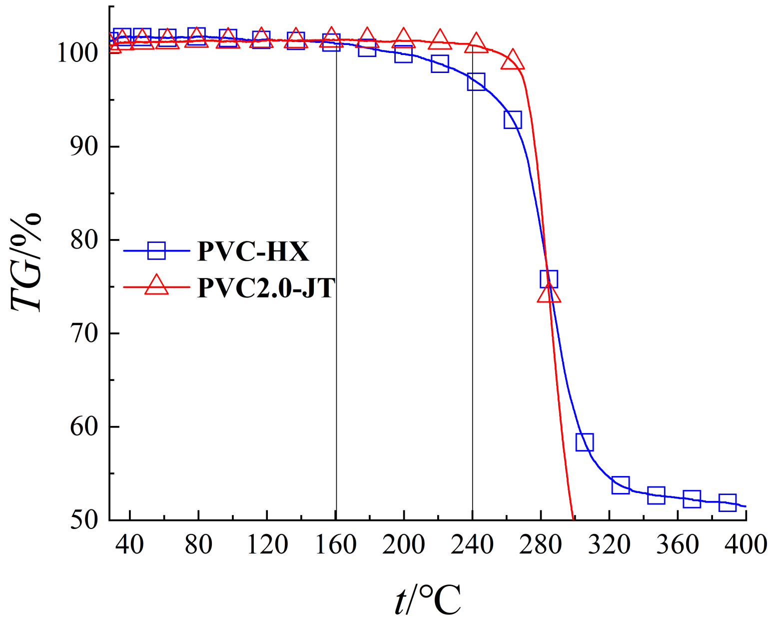


Figure 2. Thermogravimetric analysis of PVC-P geomembranes

Accelerated thermal air aging testing: Three series of thermal air aging tests, each lasting 120 days, were conducted. At 15-day intervals, sections of the aged membrane were removed from the aging box. These were then allowed to rest at room temperature for 24 hours before being cut into 200×50mm strips for axial tensile testing, conducted at a stretching rate of $10\ \mathrm{mm} \cdot \mathrm{min}^{-1}$. Six samples were tested in each stretch test series. Preliminary tests had indicated that the PVC-HX geomembrane, being of lower quality, experienced brittle failure at 110℃ after 60 days. Thus, its testing cycle was reduced to 45 days, with sampling and testing occurring every 5 days, following the same methodology used at other temperatures.

Plasticizer loss measurement: For each set temperature, five strips measuring 200×50mm and of identical thickness were cut from each geomembrane type and placed in the aging box. The weight of each sample was recorded before the commencement of the test. Prior to each weighing, the electronic balance was calibrated using a 100g standard weight. The weight of the samples was measured every 5 days, and the rate of mass loss was calculated accordingly.

2.4 Anticipated Outcomes

Under identical test temperatures, it is anticipated that the mechanical properties of the three PVC-P geomembranes will exhibit deterioration over time. Following thermal aging, the geomembranes are likely to undergo shrinkage and exhibit increased hardness. With consistent testing durations, these alterations are expected to become more pronounced with rising temperatures.

3 Experimental Results and Preliminary Analysis

3.1 Changes in Physical Properties

Throughout the testing period, dimensional and thickness alterations were recorded in all three variants of PVC-P geomembranes. The PVC-HX geomembranes, notably, exhibited considerable shrinkage in both longitudinal and transverse directions, characterized by wrinkling and curling at the sample edges, alongside a minor reduction in thickness. An increase in brittleness was also observed in these membranes. In contrast, PVC2.0-JT and PVC2.5-JT geomembranes demonstrated a slight initial increase in longitudinal dimensions, followed by progressive shrinkage in both directions, with no significant wrinkling or curling, and maintaining consistent thickness without notable brittleness. A gradual yellowing of all three types of PVC-P geomembranes was observed, intensifying at elevated temperatures (Figure 3).

Figure 3. Comparative analysis of PVC-P geomembranes pre- and post-test (a) PVC-HX: ①original material, ②50℃ for 120d, ③110℃ for 120d: (b) PVC2.5-JT: ①original material, ②50℃ for 120d,③110℃ for 120d

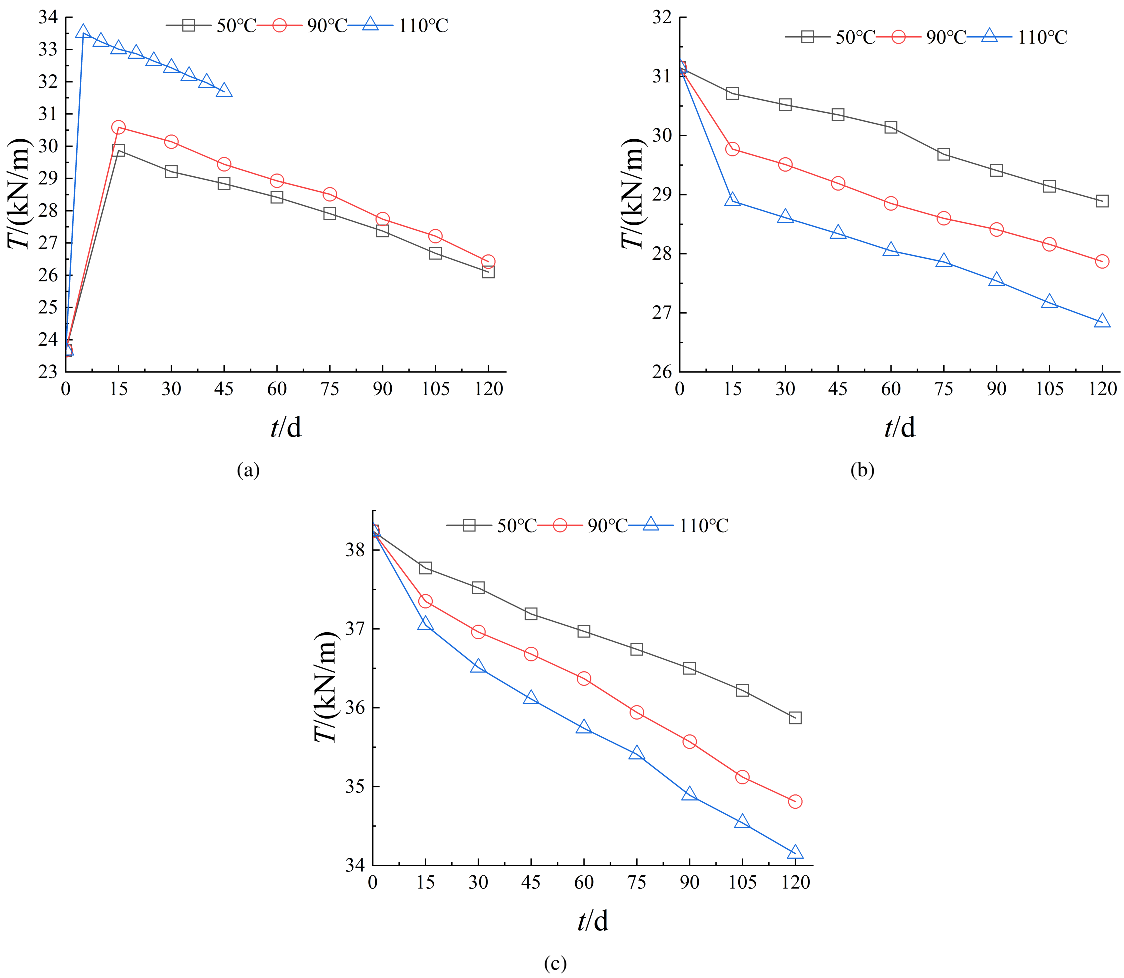


Figure 4. Tensile strength of PVC-P geomembranes (a) Tensile strength of PVC-HX geomembranes, (b) Tensile strength of PVC2.0-JT geomembranes, (c) Tensile strength of PVC2.5-JT geomembranes

3.2 Tensile Strength

Figure 4 demonstrates the relationship between tensile strength, testing duration, and temperature for the geomembranes. An initial marked increase in tensile strength was observed in PVC-HX geomembranes at all testing temperatures, more pronounced at elevated temperatures. This was followed by a consistent decrease over time. Both PVC2.0-JT and PVC2.5-JT geomembranes exhibited a continuous decline in tensile strength with extended testing duration, experiencing the most rapid decrease at 110℃.

3.3 Elongation

Figure 5 depicts the elongation trends over time for all samples. The elongation of all three types of PVC-P geomembranes decreased progressively, generally adhering to an exponential decay pattern. The rate of elongation decrease was accelerated at higher testing temperatures. The variance in the rate of elongation decline can be attributed to the differing aging rates of the three geomembrane materials, indicating that increased temperatures expedite the aging process, thus hastening the decline in elongation.

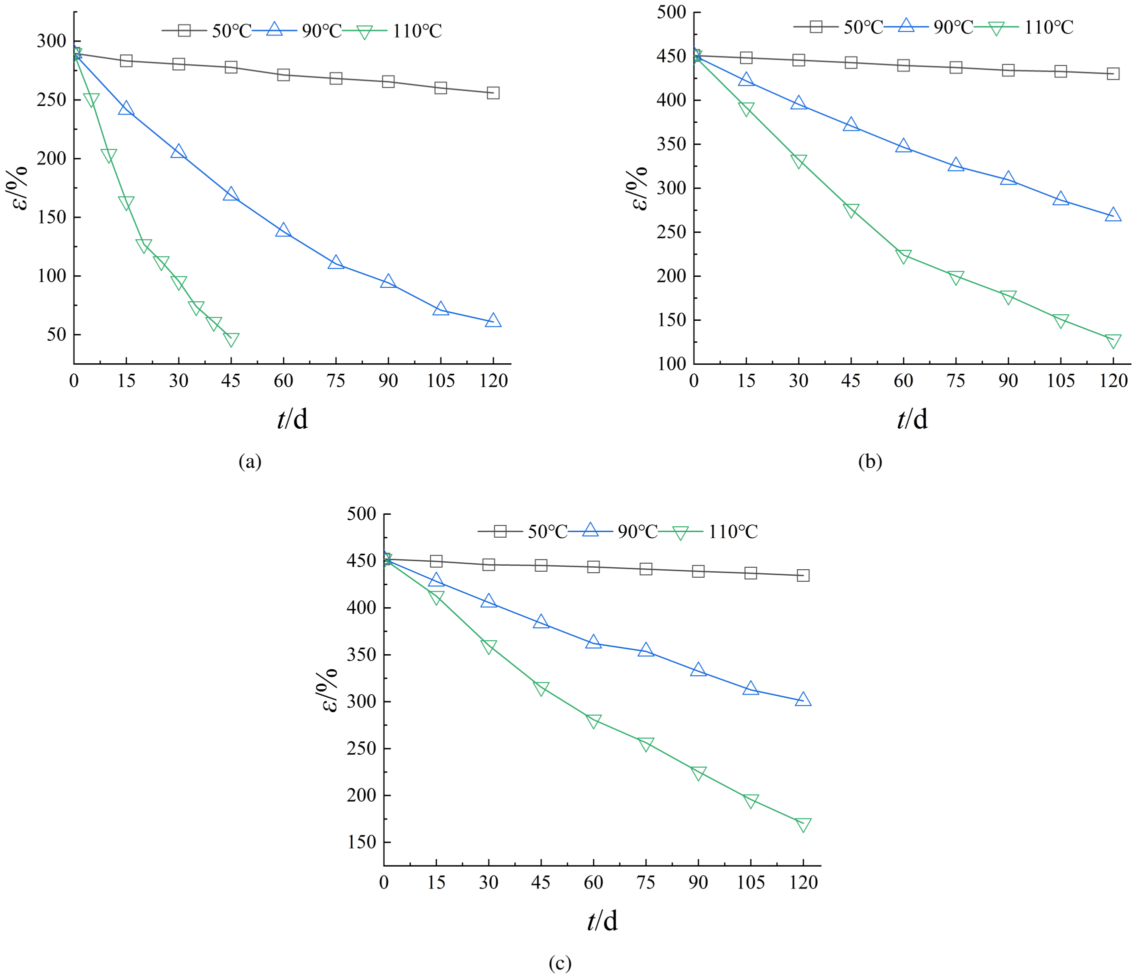


Figure 5. Elongation of PVC-P geomembranes (a) Elongation of PVC-HX geomembranes, (b) Elongation of PVC2.0-JT geomembranes, (c) Elongation of PVC2.5-JT geomembranes

3.4 Analysis of Physico-Mechanical Property Changes

Study by Ekelund et al. [17], employing infrared spectroscopy and differential scanning calorimetry (DSC), concluded that the loss of plasticizers is pivotal in the aging process of PVC materials. In PVC-P geomembranes, the loss of plasticizers results in volume shrinkage, increased density, color alterations, enhanced brittleness, and a reduction in elongation [18–20]. The thermogravimetric analysis suggests that the test temperatures employed did not lead to the destruction of the PVC polymer chains; thus, aging in the three PVC-P geomembrane types was predominantly attributed to the loss of plasticizers. Accordingly, the variations in physical characteristics, tensile strength, and elongation observed in the three types of PVC-P geomembranes, pre- and post-test, are linked to plasticizer loss.

When considering equal test temperatures and durations, the magnitude of change in tensile strength and elongation for each geomembrane type correlates with the rate of plasticizer loss. Table 3 presents the calculated plasticizer loss rates at 110℃ for the three geomembrane types. The PVC-HX geomembranes experienced significant early-stage loss of internal plasticizers during thermal air aging tests, leading to increased hardness and a substantial rise in tensile strength. This was followed by a decrease in tensile strength as the ongoing loss of internal plasticizers resulted in greater brittleness. Conversely, PVC2.0-JT and PVC2.5-JT geomembranes exhibited a smaller extent of plasticizer loss during the test period, leading to a consistent decrease in tensile strength, albeit at a lesser magnitude. The observed decline in elongation for the three geomembrane types suggests a gradual loss of plasticizers over time, with the rate of loss accelerating at increased temperatures. This indicates a positive correlation between elongation decay and plasticizer loss.

Table 3. Plasticizer loss rate of PVC-P geomembranes at 110°C

Test Time (t)	PVC-HX	PVC2.0-JT	PVC2.5-JT
	$P_L(\%)$	$P_L(\%)$	$P_L(\%)$
0	0.00	0.00	0.00
5	32.60	5.13	4.09
10	42.95	8.53	9.11
15	54.78	13.11	12.17
20	59.72	17.69	14.87
25	66.21	20.86	17.13
30	72.39	23.08	18.85
35	74.68	25.10	20.02
40	80.22	27.53	20.57
45	82.62	28.86	21.16
50	84.09	30.10	21.54
55	85.97	31.24	22.08
60	88.14	32.05	22.54
65	90.21	32.53	22.99
70	91.03	33.11	23.46
75	91.99	33.60	24.06
80	92.56	34.03	24.41
85	93.13	34.57	24.81
90	93.64	35.06	25.19
95	94.08	35.78	25.53
100	94.23	36.47	25.87
105	94.42	37.10	26.14
110	94.61	37.94	26.33
115	94.82	38.47	26.51
120	95.03	39.12	26.70

4 Development of Thermal Air Aging Model and Lifespan Prediction

4.1 Establishment of Failure Criterion

In polymer science, it is widely acknowledged that the life limit of polymeric materials is reached when their performance deteriorates to half of the properties of the original material, a time span termed as the "half-life" period [21]. Although PVC-P geomembranes maintain some resistance to deformation even when their elongation is reduced by half, this state might pose latent risks to the normal functioning of hydraulic engineering anti-seepage structures. Therefore, in this study, the criterion for failure is established as the point where the elongation decays to half of the original material's rate.

4.2 Construction of the Thermal Air Aging Model

Within anti-seepage structures, the significance of PVC-P geomembranes extends beyond mere seepage prevention to include the capacity to adapt to uneven foundational settlements. Hence, elongation is deemed a more critical factor than tensile strength. Observations have indicated that the rate of reduction in elongation surpasses that of tensile strength degradation during thermal air aging tests. This study, therefore, proposes a thermal air aging model centered around elongation. The decay pattern of elongation in the three PVC-P geomembrane types during testing aligns closely with a first-order degradation kinetics equation, resulting in the following exponential decay model:

$$\varepsilon = \varepsilon_0 e^{-kt} \tag{1}$$

where, ε represents the elongation (%) of PVC-P geomembrane at aging duration t; ε_0 denotes the initial elongation (%) of the PVC-P geomembrane; k is the aging rate of the PVC-P geomembrane, linked solely to temperature; t is the aging duration (d); and e is the base of the natural logarithm (/).

4.3 Application of the Arrhenius Equation

The observed changes in mechanical indices such as tensile strength and elongation during the thermal air aging tests of the PVC-P geomembranes demonstrate an increase in the aging rate with rising test temperatures. Arrhenius's extensive research underscored the dependence of reaction rate constants on temperature, ultimately leading to the formulation of the well-known Arrhenius theorem [22]. The exponential form of the Arrhenius equation is expressed as follows:

$$k = Ae^{-\frac{E_a}{RT}} \tag{2}$$

where, k is the aging rate (/), associated exclusively with temperature; A denotes the Arrhenius constant (/); E_a is the activation energy $\left(\mathrm{J} \cdot \mathrm{mol}^{-1}\right)$; T represents the thermodynamic temperature (K); R is the molar gas constant $\left(\mathrm{J} \cdot (\mathrm{mol} \cdot \mathrm{K})^{-1}\right)$; and e is the base of the natural logarithm.

4.4 Determination of Aging Rates of Three PVC-P Geomembranes

Initial analysis involved fitting the elongation decay curves, derived from tensile testing of the three PVC-P geomembrane types, using Eq. (1). This fitting process is illustrated in Figure 6 and detailed in Table 4. The high correlation coefficients, nearing 1, reflect the efficacy of the fitting. The calculated k values indicate the aging rates for the PVC-P geomembranes across the thermal air aging tests conducted at temperatures ranging from 50℃ to 110℃. Further analysis, utilizing Eq. (2), elucidated the relationship between the PVC-P geomembranes' aging rates and the testing temperatures. Transforming Eq. (2) logarithmically led to Eq. (3).

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \tag{3}$$

In this context, thermodynamic temperatures T for the 50-110℃ range (323.15-383.15K) were considered. The reciprocal of T served as the x-axis, and the natural logarithm of the reaction rate constant k at these temperatures as the y-axis, culminating in a lnk versus $1/T$ plot, which was linearly fitted. The fitting's slope $(-E_a/R)$ and intercept (ln$A$) were determined. Table 5 presents the linear fitting results for lnk against $1/T$ for the three geomembrane types, with correlation coefficients for all three test temperatures exceeding 0.99, affirming the applicability of the Arrhenius equation. Substituting the fitted parameters into Eq. (1) yielded the thermal air aging models for each PVC-P geomembrane type, as defined in Eqs. (4)-(6). The aging rate of PVC-HX geomembrane was found to be higher than the other two types, attributed to its lower plasticizer content, suggesting less resistance to aging. The marginally higher aging rate of PVC2.0-JT, compared to PVC2.5-JT, implies that the aging rate k is influenced by both material composition and geomembrane thickness.

The aging model for the PVC-HX geomembrane is encapsulated in Eq. (4).

$$\varepsilon = \varepsilon_0 e^{-(e^{16.14-7437.17/T})t} \tag{4}$$

For the PVC2.0-JT geomembrane, its aging model is described by Eq. (5).

$$\varepsilon = \varepsilon_0 e^{-\left(e^{13.33-6840.64/T}\right)t} \tag{5}$$

The aging model for the PVC2.5-JT geomembrane is presented in Eq. (6).

$$\varepsilon = \varepsilon_0 e^{-\left(e^{12.58-6662.81/T}\right)t} \tag{6}$$

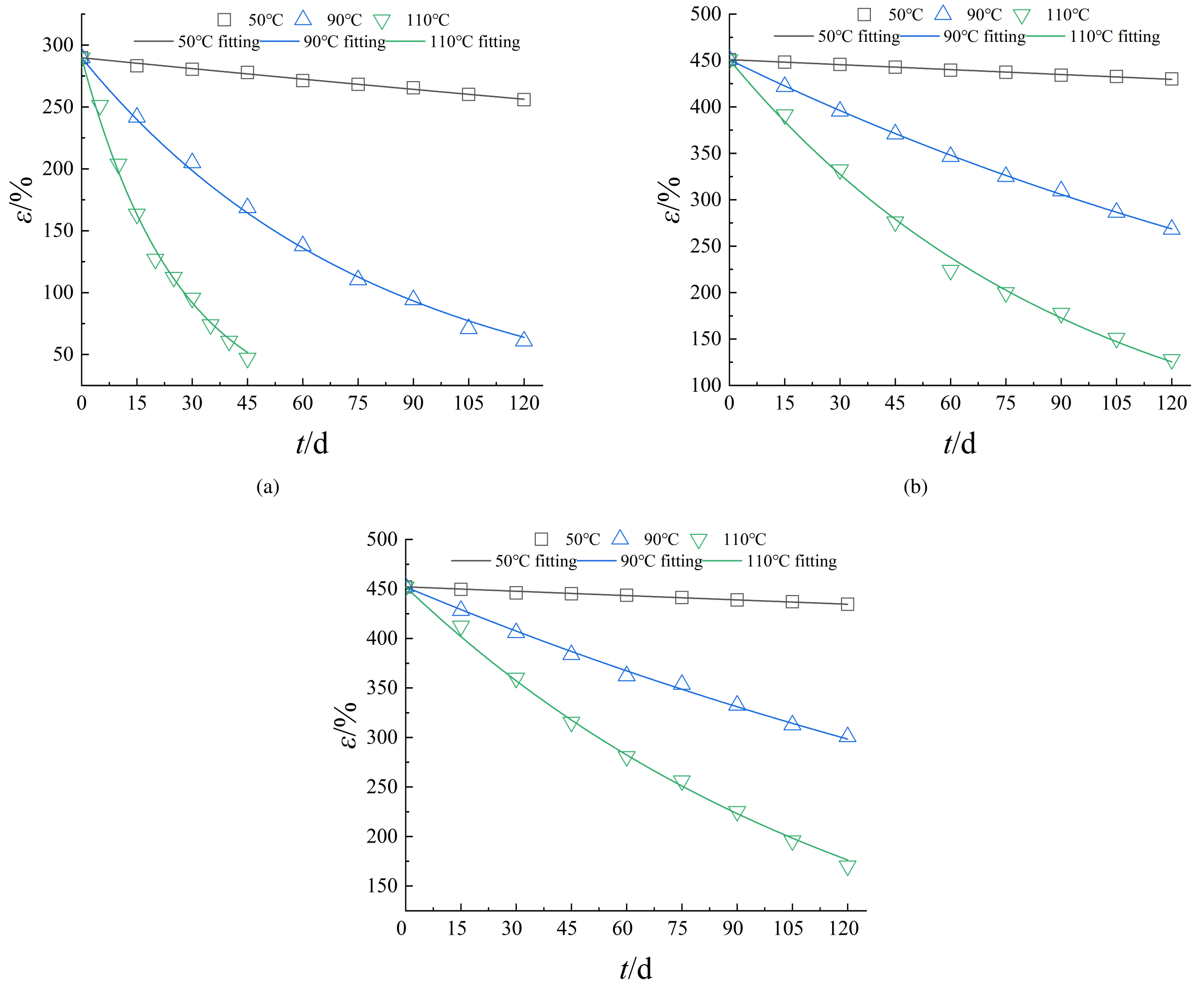


Figure 6. Fitting results for elongation of PVC-P geomembranes (a) Fitting of PVC-HX geomembranes, (b) Fitting of PVC2.0-JT geomembranes, (c) Fitting of PVC2.5-JT geomembranes

Table 4. Fitting results for elongation of PVC-P geomembranes

Test Temperature (°C)	**PVC-HX**		**PVC2.0-JT**		**PVC2.5-JT**	
	$k\ (10^{-4})$	Correlation Coefficient	$k\ (10^{-4})$	Correlation Coefficient	$k\ (10^{-4})$	Correlation Coefficient
50.0	10.2	0.991	4.0	0.996	3.3	0.988
90.0	125.9	0.997	43.2	0.995	34.6	0.996
110.0	382.6	0.995	106.6	0.996	78.4	0.997

Table 5. Fitting results of lnk and $1/T$ of PVC-P geomembranes

Geomembranes	**Intercept**	**Slope**	**Correlation Coefficient**
PVC-HX	16.14	-7437.17	0.997
PVC2.0-JT	13.33	-6840.64	0.995
PVC2.5-JT	12.58	-6662.81	0.996

4.5 Lifespan Prediction Utilizing the Thermal Air Aging Model

The lifespan of PVC-P geomembranes in anti-seepage structures was estimated by incorporating the annual average environmental temperature (expressed as thermodynamic temperature in K) and a value of ε equating to half of the original elongation ($\varepsilon = 0.5\varepsilon_0$) into Eqs. (4)-(6). For instance, considering the PVC-HX geomembrane at an operational temperature of 5℃, this data was input into Eq. (4), resulting in Eq. (7). Solving this equation determined the time t to aging failure as 76.06 years. Table 6 presents the lifespan predictions for PVC-P geomembranes deployed in anti-seepage structures at environmental temperatures ranging from 5℃ to 25℃.

$$0.5\varepsilon_0 = \varepsilon_0 e^{-\left(e^{16.14-7437.17/278.15}\right)t} \tag{7}$$

Table 6. Predicted lifespan of PVC-P geomembranes

Annual Average Temperature (℃)	Predicted Lifespan (Year)		
	PVC-HX	PVC2.0-JT	PVC2.5-JT
5.0	76.06	147.96	165.27
10.0	47.44	95.84	108.27
15.0	30.07	63.02	71.97
20.0	19.36	42.04	48.52
25.0	12.65	28.42	33.14

5 Analysis and Discussion

5.1 Plasticizer Loss Rate

The plasticizer loss rate during the thermal air aging tests was deduced employing Eq. (8). As illustrated in Figure 2 and presented in Table 2, the aging test temperatures did not induce decomposition of the PVC resin. The decline in the geomembranes' mechanical properties is exclusively ascribed to the depletion of internal plasticizers. Among the components of the three geomembrane types, the plasticizer, besides the PVC resin, constitutes the largest proportion, with other additives being present in minimal quantities and less susceptible to evaporation. Consequently, the weight loss in standard strip samples over the course of the test period, influenced by time and temperature, is approximated as plasticizer loss. The initial quantity of plasticizers in the geomembranes is calculated based on their concentration and the initial mass of the strip samples.

$$P_L(t) = \frac{M_{p0} - M_p(t)}{M_{p0}} \times 100\% \tag{8}$$

where, $P_L(t)$ represents the plasticizer loss rate (%) at time t; M_{p0} denotes the initial mass (g) of the plasticizer; $M_p(t)$ signifies the mass (g) of the plasticizer at time t.

The plasticizer loss rates at the point of failure for PVC-HX, PVC2.0-JT, and PVC2.5-JT geomembranes were 58.2%, 32.5%, and 24.8%, respectively, under a testing temperature of 110°C.

5.2 Correlation Between Plasticizer Loss and Mechanical Property Degradation

Figure 7 illustrates the relationship between plasticizer loss rate and the variation in elongation during the thermal aging tests for the three PVC-P geomembrane variants. Both the increase in plasticizer loss rate and the reduction in elongation initially occur rapidly, subsequently slowing over time, with the rate of change intensifying at elevated temperatures. This substantiates that the decline in elongation results from plasticizer depletion, identifying it as the predominant factor in the degradation of the PVC-P geomembranes' mechanical properties. The thermal aging process predominantly entails plasticizer loss within the 50-110℃ range. The loss rate of plasticizers in PVC-HX geomembranes surpasses that of the other types, achieving a 95% loss after 120 days at 110℃. The observed pattern of plasticizer loss mirrors the thermal air aging dynamics of PVC-P geomembranes: higher temperatures accelerate the aging process, with an initially more pronounced aging rate that diminishes as testing continues.

5.3 Factors Contributing to Plasticizer Loss

In PVC-P geomembranes, plasticizer loss predominantly occurs via diffusion. Upon heating, plasticizers migrate to the geomembrane's surface and subsequently diffuse into the surrounding atmosphere. The observed reduction in plasticizer loss rate over time is primarily influenced by two factors: Firstly, the continuous depletion of plasticizers results in a lowered internal concentration, consequently diminishing the rate of diffusion to the surface. Secondly, the aging process enhances the surface's compactness, which acts to partially obstruct the outward migration of plasticizers.

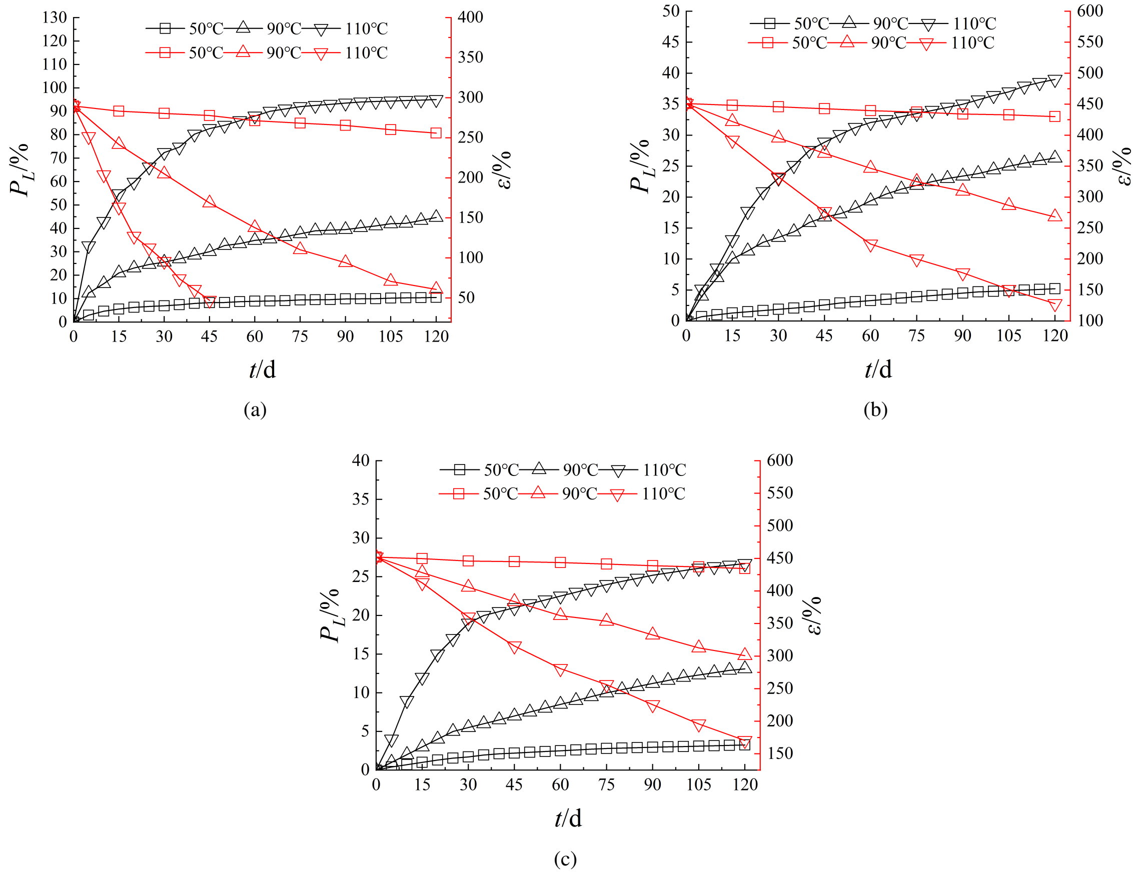


Figure 7. Comparative analysis of plasticizer loss rate and elongation in PVC-P geomembranes (a) PVC-HX geomembranes, (b) PVC2.0-JT geomembranes, (c) PVC2.5-JT geomembranes

The first factor aligns with the principles of Fick's laws and diffusion theory: under analogous conditions, migration is facilitated by higher concentrations. Conversely, as the loss of plasticizers progresses, the concentration gradient between the geomembrane's interior and its surface lessens, leading to a decreased migration rate. The second factor finds support in the observed correlation between plasticizer loss and the increased density of the geomembrane. The gradual loss of plasticizers elevates the density and lowers the porosity of the membrane, making the escape of plasticizers more challenging.

5.4 Impact of Plasticizers on the Lifecycle of Geomembranes

Comparing PVC-HX and PVC2.0-JT geomembranes, which are similar in thickness, it is noted that the lower plasticizer content in PVC-HX correlates with its shorter lifespan compared to PVC2.0-JT. Between PVC2.0-JT and PVC2.5-JT, which have nearly identical plasticizer content, the thinner PVC2.0-JT demonstrates a slightly reduced lifespan and a higher rate of plasticizer loss compared to the thicker PVC2.5-JT. As plasticizers in geomembranes disperse gradually from their interior towards the surface, the marginally thicker PVC2.5-JT exhibits a lower rate of plasticizer loss than PVC2.0-JT. Hence, while ambient temperature is an external factor influencing lifespan, the critical determinants are the plasticizer content and its stability within the geomembrane. Enhancing the plasticizer content and optimizing its integration with PVC polymer chains can effectively prolong the operational life of the geomembranes.

6 Conclusions and Prospects

6.1 Conclusions

In the pursuit of understanding the durability of PVC-P geomembranes within anti-seepage structures in hydraulic engineering, this study embarked on accelerated thermal air aging tests on three distinct PVC-P geomembrane variants. The investigation yielded insights into the elongation decay pattern, facilitated the development of a thermal aging model, and established criteria for predicting service life. Key conclusions drawn are as follows:

a. PVC-P geomembranes used in anti-seepage structures exhibit a tendency towards mechanical property degradation over time and with varying environmental temperatures. This degradation is predominantly ascribed to the extensive loss of plasticizers, as evidenced by thermogravimetric analysis and the geomembranes' mass loss rate.

b. The decay pattern of the break elongation of PVC-P geomembranes across different temperatures and over time aligns with the Arrhenius equation, with the model fittings exhibiting correlation coefficients nearing unity. The thermal air aging model and established failure criteria devised in this study precisely predict the service lifetimes of the three PVC-P geomembrane types under specific operational temperatures.

c. The rate of plasticizer loss demonstrates a non-linear relationship with time, showing positive correlation with temperature and an inverse relationship with operational duration. Augmenting the plasticizer quantity in PVC-P geomembranes or increasing their thickness can effectively mitigate plasticizer loss, thereby prolonging the lifespan of anti-seepage structures.

6.2 Prospects

Despite the achievements in lifecycle prediction from this study, certain aspects warrant further exploration. Future research directions may encompass:

a. Recognizing the discrepancies between accelerated thermal air aging tests and the actual operational environment of PVC-P anti-seepage membranes, subsequent studies should consider conducting field tests for a more accurate prediction of service life, including assessments of geomembranes that have been in use for extended periods in engineering projects.

b. Establishing a model that correlates the internal diffusion coefficient of plasticizers with test temperatures, coupled with precise measurements of plasticizer loss rates via Gas chromatography mass spectrometry (GC-MS) methods and integrating these findings with Fick's laws of diffusion, can significantly enhance the reliability and accuracy of the predictive outcomes.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflict of interest.

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