

Review

LIFE-TIME PREDICTION FOR POLYMER MATERIALS

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Abstract. Polymer testing including natural, accelerated testing or creep and fatigue testing, etc. is very important to evaluate changes in properties, structure, morphology and durability of polymer materials. This is also the basis for experts to predict the life-time or service working life or safe working life of polymer materials. Thereby, it can contribute to the selection of appropriate technologies and machines to fabricate polymer materials to meet requirements and use in different environments and conditions, especially, in harsh conditions. This review presents an overview of life-time prediction for polymer materials through natural tests or accelerated ageing tests and methods of extrapolating data from induced thermal degradation. The life-time or service working life of a polymer material is the continuous service period of the material from the time it is affected by usage conditions or environment until its decomposition or degradation according to some failure criterion. The accuracy of predicting the life-time of a polymer material depends on a forecasting equation that fully reflects climatic factors, weather, environment, usage conditions, etc. affecting the material as well as the selected failure criterion.

Keywords: polymer materials, life-time prediction, degradation, Arrhenius equation.

Classification numbers: 2.9.3, 2.9.4.

1. INTRODUCTION

Nowadays, the usage demand for polymer materials is constantly increasing in the fields of engineering, industry, agriculture, healthcare, defense, security and civil use in our country and around the world. The main advantages of these materials are that they are light, more durable than traditional materials, easy to shape at will, easy to decorate, soundproof and good heat insulation, etc. However, during the process of use, due to the influence of natural factors and conditions of use, polymer materials are prone to change in properties, structure, morphology and durability, causing catastrophic failure for users and manufacturers. Over the past thirty years, environmental problems related to the disposal of polymers that have completed their lifecycle have begun to

arise, and the need to foresee their end of life has become increasingly urgent. In many cases, polymer materials have been used under severe, long-term or critical application conditions, so a better understanding of the failure mechanism of polymer materials to be able to predict their life-time. Therefore, the research of characteristics, properties, composition, structure, morphology, durability of polymer materials by various methods such as spectroscopy, molecular weight analysis, elemental analysis, X-ray diffraction, electron microscopy, thermal analysis, mechanical property analysis, electrical property analysis, electrochemical property analysis, environmental resistance, chemical and solvent resistance, etc. is essential to evaluate the ability of their safe use. From there, it is possible to predict quickly the working life of polymer materials for practical applications, particularly while their use in harsh environments.

The most accurate and reliable method of predicting the life-time of polymer materials is by continuous testing in natural environments, in outdoors or under actual conditions of use. This method is widely applied when the life-time of polymer materials is short, for example when they are used under extreme conditions. For rapid prediction of the life-time of polymer materials, the determination of the effectiveness of additives introduced into the polymer by the accelerated test or artificial test is often used. This test simulates the effects of natural conditions or climatic or weather conditions where the material used in combination with acceleration to allow the material to decompose/deteriorate faster without changing the nature of the material degradation mechanism. Some popular life-time prediction methods using accelerated ageing tests are thermal ageing based on Arrhenius model, radiation ageing

based on power law extrapolation and combined thermal and radiation ageing based on superposition of time dependent data or superposition of dose to equivalent damage (DED) data. The time-temperature superposition principle (TTSP), Williams-Landel-Ferry (WLF) model as well as Friedman, Flynn-Wall-Ozawa (FWO), Sergey Vyazovkin (SV), Sbirrazzuoli (Vya/CE), Trache-Abdelaziz-Siwani (TAS) isoconversional methods have been widely used to predict the life-time of polymer materials.

In fact, both natural testing and accelerated testing are used together to predict the life-time of polymer materials. This can combine the advantages of both natural and accelerated tests such as quick determination of life-time of polymer materials and coverage of all environmental and usage impact factors. Moreover, it can determine the correlation coefficient between the natural test and the accelerated test.

This paper presents an overview of the life-time prediction for polymer materials. First, weathering test methods for polymer materials, where testing methods and standard test procedure are considered. Then, we pay attention to degradation of polymers with influencing factors, types and general degradation mechanism of polymers under different conditions. The last section focuses on different methods for predicting the life-time of polymer materials.

2. WEATHERING TEST METHODS FOR POLYMER MATERIALS

2.1. Natural exposure

The natural test of polymer materials is to expose them (sheets, films, etc.) to natural contact at outdoor exposure sites or under conditions of use to assess changes in characteristics, properties of polymers, thereby determining the durability, especially the weather stability of polymer materials, and predicting the life-time of polymer materials. The exposure period required should be at least as long as the life-expectance of the product. Standard weathering test procedures for polymers in direct and under glass exposures (ASTM G7, ASTM D1435, ASTM

G24), in black box (ASTM D4141, GM 9163P), AIM box (ASTM G201, GM 7455M, GM 9538P, GM 3619M, GM 7454M, GMW 3417, Ford DVM 0020), Q-TRAC Natural Sunlight Concentrator (ASTM D4141, ASTM G90, ASTM D4364, SA J1961) have been presented in “Q-Lab weathering research service” [1]. Some requirements for natural exposure are as follows:

- (i) Test site: The test site for polymer materials is the one with climatic/weather characteristics as close to the conditions of use as possible. The ground of the test station and the yard has a short grass layer to regulate the air and reduce the influence of dust, sand and other agents. The natural test site should be located relatively independent from residential areas, industrial zones, and production facilities to limit the effects of high-rise buildings, public works, and contaminant factors to the natural test site. This helps to avoid the error of microclimate factors, especially solar radiation, humidity and temperature at the natural test site.
- (ii) Test shelves: The test shelf is usually made of metal (stainless steel, aluminum, etc.). The samples are tested in different sizes on the shelf but they can still stretch naturally during the test process with changing weather factors that can cause evaporation of additives from the surface of the test specimen. The lowest position of the test shelves should be at least 45 cm above the ground so that the specimen not affected during the test. The angle of inclination of the test shelf relative to the ground varies according to the purpose of assessing the change in properties, characteristics, structural morphology and weather stability of polymer materials.
- (iii) Sample jig: Polymer samples often have variable dimensions, so when placing the polymer sample on the test shelf, a jig used to fix the test sample on the shelf.

Besides, brackets, shields, test time, etc. are also required in the testing process.

2.2. Artificial exposure

Currently, there are different types of accelerated or artificial tests for polymer materials. These tests reflect the influence of one or several climatic and weather factors as well as a combination of the effects of climate and weather factors on the characteristics, properties and morphology of polymer materials. The advantage of artificial weathering is that it is easier to accelerate the testing of polymer materials under standard conditions.

2.2.1. Thermal stability test

The test of thermal stability of polymer materials is a common method used to evaluate the effects of temperature, including the effect of high temperature on the deterioration of mechanical properties, thermal properties, electrical properties as well as changes in structural morphology of polymer materials [3 - 9]. From this, the active energy for thermal decomposition of polymer materials can be determined and their life-time can be predicted according to a selected failure criterion, for example, a reduction of 20 % or 50 % in tensile strength or elongation at break from the initial value obtained before testing of polymer materials. In this test, samples are thermally aged at a constant (isothermal) temperature in an inert gas or natural air according to a certain standard, for instance, DIN 53508-00. First, the sample suspended or mounted in a test device was heated to a certain fixed temperature (60 °C, 80 °C, 100 °C, 120 °C, 150 °C, 180 °C, 200 °C, etc.) with different extended times (72 hours, 144 hours, 168 hours, 240 hours, etc.). Based on test duration or cycles, samples

were drawn and stored under standard conditions (temperature of 20 ± 2 °C and relative humidity of 65 ± 5 %) before determining their properties and morphology.

The standard procedure for testing thermal stability of polymer materials used the Arrhenius equation according to the ISO 2578. This standard can make long-term prediction from multi-point polymer ageing data only based on the Arrhenius equation or any other procedure. The ASTM D1203 and ISO 176 present effectiveness of plasticizers in polymer materials [2, 3].

2.2.2. Artificial light source test

Carbon-arcs, fluorescent tubes, xenon-arcs are the light sources used in an accelerated weathering apparatus, which ideally simulate solar radiation. For artificial testing of polymer material, a fluorescent tube or a xenon-arc lamp test chamber with a wavelength of 315 - 420 nm is often used [10 - 16]. The test using a solar carbon-arc lamp performed with short wavelength ultraviolet radiation (375 - 400 nm) is a rather harsh test. In the xenon-arc lamp test chamber, the xenon-arc lamp continuously generates sunlight radiation (including ultraviolet rays with long wavelengths and visible light as well as very strong radiation at near infrared region wavelengths), which is close to the temperature from midday sunlight. When a radiation filter is used, the intended ultraviolet wavelengths obtained for accelerated testing of polymer films. Currently, carbon-arc lamp testing for polymer materials conforms to ISO 4892: part 5, ASTM D1499-99; xenon-arc lamp testing to ASTM D2565-99 and ISO 4892: part 2 [2]. Standard test procedures for the use of fluorescent tube are in ASTM D4329-99 and ISO 4892: part 3. In addition, some other standards for testing artificial light source for plastics are ASTM G155, ISO 11341, JASO M346, AATCC TM16, TM 169, etc.

2.2.3. Ozone cracking test

The ozone cracking test is very commonly used to evaluate the effect of ozone on the deterioration of mechanical, thermal, electrical properties, and structural morphological changes of polymer and rubber materials, especially unsaturated polymers, natural rubber, and synthetic rubber [15, 17]. This test is conducted according to the ASTM D4575-99, ASTM D1171-99, ASTM D1149-99, ISO-1431-1: 2012 (E) standards. Polymer and rubber testing is performed in an ozone chamber with different sample expansion, ozone concentration, and duration of action. The impact of ozone on polymeric and rubber samples is determined according to the crack appearance time, crack size and density on the sample surface.

2.2.4. Salt-accelerated test

Salt-accelerated test is a test that simulates the impact of a salt solution (a corrosive factor) on the deterioration of mechanical, thermal, electrical properties, and structural morphology of polymer materials, especially the deterioration of the surface and protective properties of polymeric paints and coatings, etc. [1, 18]. Polymer samples are in spraying with saline solution with different spray time according to ASTM D6675, ASTM D1654, etc.

2.2.5. Fungi and bacteria action test

The effects of fungi and bacteria on polymer materials are determined through visual examination or measurement of changes in mass or physical properties of polymer materials [19].

The general principle of fungal impact testing is to conduct artificial acceleration when placing the test sample (with spray of fungal spores on both sides of the sample and on the nutrient medium) under the most favorable conditions for fungal growth. Spores of the following fungi are commonly used to spray both samples and nutrient media: *Aspergillus amstelodami*, *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus versicolor*, *Chaetomium ND 201*, *Cladosporium herbarum*, *Gonytrichum*, *Paecilomyces varioti*, *Penicillium waksmani*, *Penicillium wortmani*, *Penicillium citrium*, *Tricoderma virede*, *Scopulariopsis brevicaulis*, and *Curvularia lunata*. The standard procedure of fungal impact testing for polymer materials is in the ISO R-846-78.

In addition, accelerated tests that often combine the impact of two or more factors (also known as complex tests) are increasingly used because they contribute to the evaluation of deterioration in properties, durability and structural morphology changes of polymer materials, prediction of their life-time as well as determining the effectiveness of additives introduced into polymer materials. Some typical acceleration tests that reflect the combined effects of two or more factors are UV-thermo-humidity complex test, heat and oxygen impact test, heat and moisture condensation test, UV and salt-accelerated test, etc. [20 - 28].

3. DEGRADATION OF POLYMER MATERIALS

3.1. Effect of some factors on degradation of polymer materials

The degradation process of polymer materials is the partial decomposition of polymers into low molecular weight products as well as fragments with large but smaller molecular weights than neat polymers. This is the most common process during the life-time of a polymeric material. Structural changes during degradation process of polymer materials can lead to physical or/and chemical transformations that take place in polymer materials under the influence of degradation factors. These factors are thermal - static heat ageing; sub-zero exposure or thermal cycling; humidity (hot/wet) exposures; weathering (rain, sand erosion, sunlight, etc.); salt water immersion or spray; freeze/thaw and dry/wet cyclic conditions; combined loaded and environmental exposures; ozone, oxygen and chemical substances; UV and light radiation; high energy radiation; electrical stress; and micro-organisms [1, 27].

3.2. Degradation types of polymer materials

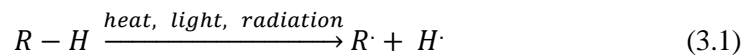
The degradation of polymer materials is the result of such reactions as chain cutting, scission, crosslinking, thermal oxidation and even destruction. There are two main degradation types of polymer materials, namely chemical degradation and physical/physicochemical degradation. The chemical degradation of polymer materials is caused by oxidation, hydrolysis reactions, etc. while the physical/physicochemical degradation due to heat, shear, UV light, etc. Therefore, the degradation types of polymer materials include thermal degradation (caused by temperature), photo-degradation (caused by light radiation), bio-degradation (caused by organisms), hydrolytic degradation (caused by water), external stimulus degradation (caused by electrical stress), environmental degradation (caused by NO₂, SO₂, NH₃, CO, H₂O₂, O₂, O₃, metals, etc.) and mechanical degradation (caused by mechanical stress) [1, 27].

3.3. General degradation mechanism of polymer materials

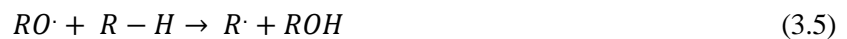
Polymer materials can be degraded according to different mechanisms depending on the impact sources, for example, thermal or thermal oxidation degradation, weathering or more specifically photo-oxidation, chemical degradation, environmental stress cracking, ionizing radiation, biological degradation, creep, and fatigue. In general, each type of polymer degradation follows a degradation mechanism, which in turn causes different changes in polymer materials. Thermal ageing and weathering can cause chemical and physical changes while chemical degradation refers to the failure of polymer materials

hydrolyzed by chemical attack.

The degradation mechanism of polymer materials begins with an initiation stage, in which free radicals formed by energy from any source such as light, radiation, heat, etc.



Next, propagation occurs through a series of reactions as follows:



The final stage is termination, whereby free radicals react with each other:



4. METHODS FOR PREDICTING LIFE-TIME OF POLYMER MATERIALS

4.1. Definition of life-time of polymer materials

The life-time (or secure working life/shelf life/service life) of a polymer material is the continuous service period of the polymer material starting from when the polymer material is affected by conditions/environment of use until it is decomposed or deteriorated according to a certain failure criterion.

The life-time of polymer materials is closely related to their weather durability. It is a stable working time in natural environments, outdoors (with the impact of climatic factors and weather) or accelerated conditions that simulate the effects of climatic factors and weather, without obvious deterioration in properties, durability and morphology of polymer materials.

4.2. Scientific basis for predicting life-time of polymer materials

The scientific basis for predicting the life-time of polymer materials is that failure, degradation or deterioration of the properties, characteristics, durability, and structural morphology of polymers must fully reflect climatic factors, weather, environment, conditions of use, etc. affecting polymer materials. In addition, the failure criteria, the deterioration of characteristics and

properties of the selected sample may or may not be the most typical. The accuracy of the polymer materials' life-time prediction depends on the test method, the nature and origin of the polymers. During the impact of climatic factors and weather on polymers for a certain period of time, one or more characteristics or properties of the polymer materials are deteriorated, leading to a decrease in durability, usability, recycling ability and reprocessing ability of polymers.

In fact, some degradation processes of polymer materials occur in a very short time, while others can take decades to reach equilibrium, meaning that the decline does not happen anymore. During the test process, there is a continuous decline in the properties of the polymer material, showing a tendency decreasing to a certain value called the dynamic equilibrium state. In practice, for most materials, there are both types of above declines with various degrees. In addition, the terms such as long-term decrease (irreversible) and temporary decrease (reversible) are used. A polymeric material considered to suffer long-term degradation (irreversible) when it has undergone prolonged deterioration caused by the effects of climatic and weathering factors, bringing the degradation to a critical level. In the meantime, a polymer is considered to have degraded temporarily (reversible) when the degradation disappears as soon as the climatic factors/weather drop below the critical threshold or stops due to the impact of one or more climatic factors/weather or some other reasons. For temporary decrease process, the test can be performed under simulated laboratory conditions without acceleration, while for long-term deterioration, the material should be tested under accelerated conditions to obtain laboratory results more quickly.

During natural testing, the polymer materials will exhibit similar weather resistance in regions with the same climatic conditions. Thus, it is possible to set up typical climate test stations in regions with the most reference typical climate, in which the properties and durability of polymer materials, especially the weather resistance, are determined. Their life-time can also be predicted in other similar climates around the world according to the failure standards for polymer materials.

In general, degradation and ageing of polymer materials alter their mechanical-, physical-, thermal-, and electrical properties, leading to a reduction in their usability, shelf life, etc. In particular, changes in mechanical properties of polymers (elongation at break, tensile strength, impact strength, flexural strength, elastic modulus, flexible modulus, etc.) are often quite sensitive due to the effect of one or several factors causing polymer degradation [27, 29]. Some popular models exhibiting a correlation that reflects the deterioration in mechanical properties of polymer materials over time in either natural or artificial tests are as follows:

- Linear: $y = a + bx$ (4.1)

- Parabolic: $y = a + bx + cx^2$ (4.2)

- Exponential: $y = ax^b$ (4.3)

- Cube: $y = a + bx + cx^2 + dx^3$ (4.4)

The most appropriate model is the one with the reliability coefficient or linear regression coefficient r^2 (calculated by a computer-based statistical analysis system) which can be achieved as high as 1 [28].

Until now, the Arrhenius equation is still considered and used for establishing the equation that predicts the life-time of polymer materials:

$$\tau = Ae^{\frac{-E_a}{RT}} \quad (4.5)$$

where, τ : life-time, year; E_a : activation energy of polymer degradation reaction, kJ/mol; T: test temperature, °K; R: ideal gas constant (8.314 J/mol °K); A: the exponential pre-factor, characterizing the probability of a polymer degradation reaction.

Transforming Eq. 4.5 to a logarithmic form:

$$\log \tau = \log A - \frac{E_a}{2.303RT} \quad (4.6)$$

$$\text{or } \ln \tau = \ln A - \frac{E_a}{RT} \quad (4.7)$$

where, A and E_a can be determined by using: (i) experimental data; (ii) the least squares method; (iii) differential methods; (iv) multiple heating rate calculation methods.

A plot of $\log \tau$ or $\ln \tau$ against $1/T$ should yield a straight line with a slope of E_a/R , which can be extrapolated with the caution.

In general, the Arrhenius equation is the first choice to evaluate the influence of temperature on a property of polymer materials but no general rule can be given for the measurement of reaction rate to be used. A failure criterion indicates the remaining percentage of this property from its initial value and is chosen to assess the life-time of polymer materials.

When a form of the change in parameter with testing time is proposed, the power law is often applied first:

$$f(X) = X^n \quad (4.8)$$

Combining Eq. 4.8 with Avrami equation 4.9 gives Eq. 4.10:

$$X = X_0 e^{-At^n e^{\frac{En}{RT}}} \quad (4.9)$$

$$\ln K = \ln K_0 + B \frac{T_0 - T}{10} \quad (4.10)$$

where K_0 is the reaction rate at a reference temperature T_0 , K the reaction rate of the process, T absolute temperature, A and B are constants, n is the reaction order, t testing time, E the reaction energy, and R is the gas constant.

When the properties of polymer materials are changed with time in the degradation process, the rate of the change of those properties with the level of one or more degrading agents can be recorginized. A series of semi-empirical relationships (linear and logarithmic) for the degradation of polymeric properties have been proposed. They usually take the form:

$$P(t, T) = P(\infty, T) + [P(0, T) - P(\infty, T)]e^{-k(T)t^n} \quad (4.11)$$

where k is the reaction rate or degradation rate, P the polymeric property, T the ageing temperature (in K), t the ageing time, and n an experimentally determined constant.

The strength of polymer materials decreases exponentially with testing time to an asymptotic value (usually zero). The limitation of this approach lies in the assumption that only one time-dependent process is occurring, although in practice, several processes can occur simultaneously. Therefore, an extended approach to determine the combined effect of temperature, stress and moisture with the failure time t_f is given:

$$\log t_f = C - \log T + \frac{E_a}{2.303 RT} - b \frac{S}{T} \quad (4.12)$$

where T is absolute temperature, C and b constants, E_a the activation energy, R gas constant, and S the uniaxial stress.

Changes in the properties of polymer materials under the impact of ionising radiation can be predicted using a time-temperature-dose rate superposition principle. The model is based on the Arrhenius expression and the dependence of degradation vs time obtained at different temperatures can be given by a shift factor a_T :

$$a_T = e^{\frac{E_\alpha(T_0^{-1}-T^{-1})}{R}} \quad (4.13)$$

where T_0 and T represent the reference and service temperatures.

Converting Eq. 4.13 to logarithmic form:

$$\log a_T = \frac{E_\alpha}{2.303 R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (4.14)$$

Equation (4.13) is an equation reflecting the time-temperature superposition principle (TTSP), one of the bases of the experimental acceleration methodology for polymer materials. The reference temperature in this case is often the lowest value of the ageing temperature. This method can give a high accuracy of predicting the life-time of polymer materials and activation energy. From the graph reflecting the dependence of $\ln a_T$, $\log a_T$ - on the operating temperatures, life-time (t_e) of a polymer material at operating temperature can be extrapolated:

$$t_e = \frac{a_{T_0}}{a_{T_e}} \cdot t_0 \quad (4.15)$$

where, a_{T_0} and a_{T_e} are the shift factor for the reference temperature and the extrapolated shift factor for operating temperature, respectively; t_0 is the life-time of the polymer material at the reference temperature.

The Williams-Landel-Ferry (WLF) model is also applied to predict the life-time of polymer materials based on any physical property through the temperature induced physical/chemical changes as a function of processing and storage conditions. This model uses a TTSP without any additional assumptions regarding the dependence of the properties of polymer materials on time at any temperature:

$$\log a_T = \frac{C_1(T-T_0)}{C_2+(T-T_0)} \quad (4.16)$$

where C_1 and C_2 represent the experimental constants, which depend on temperature and the nature of the material and can be calculated as follows:

$$C_1 = -\frac{1}{2.303} \frac{E_\alpha}{RT_0} \quad (4.17)$$

$$C_2 = T_0 \quad (4.18)$$

The iso-conversional methods including Friedman, Flynn-Wall-Ozawa, Sergey Vyazovkin, Sbirrazzuoli, Trache-Abdelaziz-Siwani, Kissinger-Akahira-Sunose methods have also been widely used to predict the life-time of polymer materials. These powerful tools are important for determining the activation energy of a reaction or degradation process as a function of conversion degree α .

Friedman equation:

$$\ln \frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E_\alpha}{RT} \quad (4.19)$$

Flynn-Wall-Ozawa equation:

$$\ln \beta = \ln \frac{AE_\alpha}{Rg(\alpha)} - 5.331 - 1.052 \frac{E_\alpha}{RT_p} \quad (4.20)$$

where, β is the heating rate and T_p is the temperature peak.

Sbirrazzuoli equation:

$$g(\alpha) = \frac{AE_\alpha}{R\beta} \left[\frac{e^{-x}}{x} - \int_x^\infty \left(\frac{e^{-x}}{x} \right) dx \right] = \frac{AE_\alpha}{R\beta} p(x) \quad (4.21)$$

where, $x = E_\alpha/RT$ is the minimized activation energy at temperature T. E_α in this equation is assumed to be constant.

Kissinger–Akahira–Sunose equation:

$$\ln \frac{\beta}{T_p^2} = -\frac{E_\alpha}{RT_p} + C \quad (4.22)$$

Sergey Vyazovkin equation:

$$E_\alpha = -R \frac{d \ln \left(\frac{\beta}{T_p^2} \right)}{dT_p^{-1}} \quad (4.23)$$

Trache-Abdelaziz-Siwani equation:

$$g(\alpha) = \int_0^{\infty} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-\frac{E_\alpha}{RT}} dT \quad (4.24)$$

where $g(\alpha)$ is the integral form of the reaction model.

4.3. Some popular methods for predicting life-time of polymer materials

4.3.1. Methods for predicting life-time of polymer materials based on deterioration of mechanical properties

During test process, the properties of polymer materials usually decrease, especially, mechanical properties such as tensile strength, elongation at break, impact strength, flexible strength, young modulus, etc. The change in elongation at break of a polymer material after testing (remaining 30, 50 or 80 %) compared to that of the sample before testing is one of the typical failure criteria to predict the life-time of the polymer. The half-life time (HLT) of polymer materials is an important function for predicting their life-time.

Choudhury *et al.* have predicted the life-time of hydrogenated nitrile butadiene rubber (HNBR)/organo-modified clay nanocomposites based on a 50 % change in tensile strength after thermal ageing at 70 °C, 100 °C and 135 °C according to ISO 11346 standards [4]. In this study, the Arrhenius equation was used to predict the life-time of the nanocomposites. The authors indicated that the life-time of HNBR at 40 °C was improved up to 45 years in the presence of 8 wt.% of organo-modified clay as compared to the HNBR life-time of 15 years. This is explained by the presence of the organo-modified clay, which has high thermal stability and is regularly dispersed in the HNBR matrix at nanometer size, and thus acts as a barrier to prevent the penetration of oxygen and heat into the HNBR matrix, resulting in reduced oxidative decomposition and rupture reactions of HNBR.

In another report, the life-time of polyvinylchloride (PVC) was forecasted by thermal ageing methods at different temperatures (105 °C, 120 °C and 135 °C) based on a reduction of 50 % in elongation at break of PVC samples [7]. Two PVC samples chosen for investigation were the PVC-I containing thermal stabilizers such as cadmium stearate, barium stearate, 2,4-toluylene diisocyanate trimer; a plasticizer -dioctylphthalate; an antioxidant - bisphenol A; and the PVC-II containing thermal stabilizers such as cadmium stearate, barium stearate, dilauryl dilaurate tin, and a plasticizer - dioctylphthalate. Table 4.1 presents the time for decreasing 50 % of elongation at break of the two PVC samples after thermal ageing.

Table 4.1. Time for reduction of 50 % of elongation at break of PVC samples ($t_{50\%}$) after thermal ageing at different temperatures [7].

Sample	$t_{50\%}$ (hours)		
	105 °C	120 °C	135 °C
PVC-I	1224	660	240
PVC-II	1152	684	252

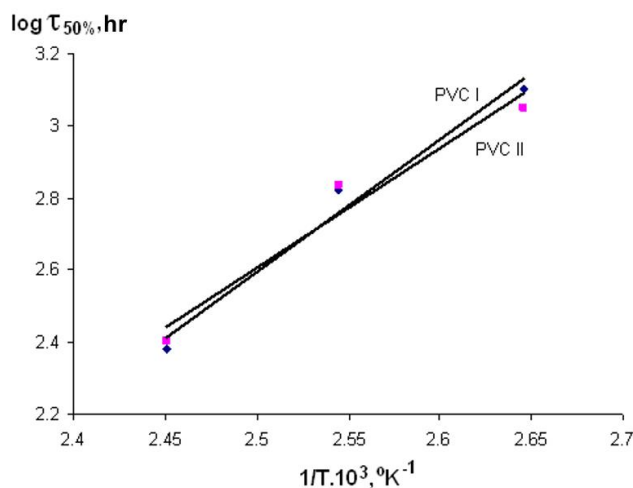


Figure 4.1. Dependence of $\log t_{50\%}$ of PVC samples on heating temperature [7].

The life-time of PVC samples at 40 °C was predicted based on the Arrhenius equation with activation energy (E_a) exaggerated from the graph in Figure 4.1. The E_a and life-time of the PVC-I at 40 °C was 69 kJ/mol and 14.37 years, while the E_a and life-time of the PVC-II at 40 °C was 65 kJ/mol and 10.17 years, respectively.

Malic *et al.* also predicted the life-time of polypropylene (PP) films stabilized with a hindered amine light stabilizer (HALS) based on a 50 % reduction in the tensile strength of the samples after being irradiated with a xenon-arc lamp [3]. The life-time of the PP films increased with increasing HALS content in the samples.

Kahlen *et al.* predicted the life-time of polycarbonate (PC) films according to different models (ISO 2578 (1993), model of Gillen *et al.* and model of Hoang and Lowe) [5]. The PC films were in acceleration test at hot air temperatures (at 120 °C, 130 °C and 140 °C) and hot water (at 70 °C, 80 °C and 90 °C). The change in tensile strength of PC films after testing was used for the prediction of their life-time according to two failure criterions (a reduction of 80 % and of 50% in tensile strength). The authors recognized that the life-time of PC films was different when predicted by different models. For example, in the case of testing at 90 °C in air, the life-time of PC films based on a 50 % (80 %) reduction in tensile strength was 54 (17) years, 204 (164) years and 96 (66) years when predicting according to Hoang and Lowe model, Gillen *et al.* model and ISO 2578, respectively.

Kaci *et al.* carried out an investigation of low density polyethylene (LDPE) films under natural conditions at Bejaia (Algeria) and reported that the half-life time of LDPE with and without HALS was 650 days and 140 days, respectively [30].

Hamid *et al.* reported that the correlation coefficient between a natural test in Africa Saudi and an artificial test in an Atlas Ci65 weathering test instrument (ASTM D 2565) was 2.8 times (5,000 hours of artificial test corresponding to 14,000 hours of natural test) [28].

The results from a natural test in Dong Hoi (Quang Binh, Viet Nam) showed that the half-life time of high density polyethylene (HDPE)/organo-modified CaCO_3 composite sheet was 25.6 months [31]. The correlation coefficient between the natural test in Dong Hoi and an artificial test in a UV-CON 327 weathering test instrument using each cycle of 8 hours of UV irradiation at 60 °C and 4 hours of humidity condensation at 50 °C (ASTM D 4329-99) was determined. This value was 41.3 times according to the failure criterion of a 50 % reduction in tensile strength (Figure 4.2) [31] and 38.27 times for the failure criterion of a 50 % reduction in elongation at break (Figure 4.3) [16].

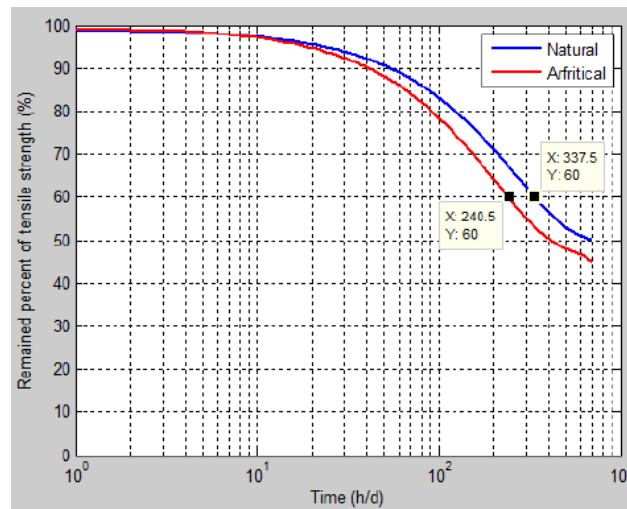


Figure 4.2. Graph reflecting correlation coefficient between natural exposure and artificial test based on remained percentage of tensile strength of HDPE/organo-modified CaCO_3 composite [31].

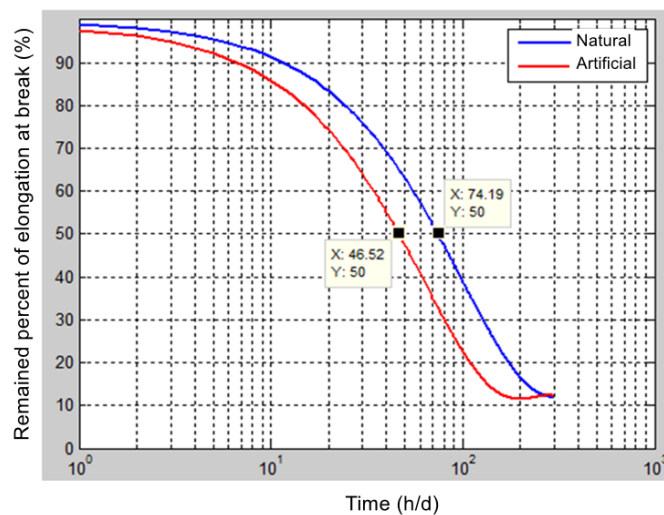


Figure 4.3. Graph reflecting correlation coefficient between natural exposure and artificial test based on remained percentage of elongation at break of the HDPE/organo-modified CaCO_3 composite [16].

Wallner *et al.* predicted the life-time of PP which was naturally tested in Beijing (China), Graz (Austria), Pretoria (South Africa), Athens (Greece), Fortaleza (Brazil) according to Arrhenius model and Gugumus model based on experimental failure data at high temperature (95 °C) [32]. The constant endurance time of PP predicted according to Arrhenius and Gugumus models was 47 years and 32 years for the sample tested in Beijing. Similarly, 46 years and 21 years for the sample tested in Graz, 45 years and 14 years in Pretoria, 41 years and 15 years in Athens, 31 years and 8 years in Fortaleza.

Deroiné *et al.* based on the relationship of stress at break and molecular weight vs. immersion time in distilled water at 25 °C, 30 °C, 40 °C and 50 °C after 360 days of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and the Arrhenius equation to calculate the activation energy of degradation reaction and to predict the life-time of PHBV [33]. The activation energy for the degradation of PHBV immersed in distilled water is 93 kJ/mol. The authors also predicted the life-time of PHBV based on the evolution of the failure strain.

Abdulsalam S. Alghamdi and Rayan K. Desuqi forecasted the life-time of cross-linked polyethylene (XLPE) insulated cables working at high temperatures (95 °C and 105 °C) by an accelerated thermal ageing test (according to the BS 7870-2 standard) and using the Arrhenius equation. Based on the failure criterion of a 50 % reduction in elongation at break, the shelf life of XLPE cables was predicted to be around 40 years to 60 years when used at 90 °C, and about 7 years to 30 years when used at temperatures between 95 °C and 105 °C [34].

4.3.2. Methods for predicting life-time of polymer materials based on deterioration of thermal properties

The life-time of polymer materials can be predicted by thermal analysis methods based on the deterioration of properties combined with changes in weight or heat of the sample. Thermal gravimetric analysis (TGA) is a useful technique to calculate the kinetic parameters of the degradation process of polymer materials.

Table 4.2. Activation energy of degradation reaction of EN/DDS film at different degradation levels [35].

Degradation level (%)	Activation energy (kJ/mol)
0.5	161
1	153
2.5	155
5	200
10	205
15	205
20	234
25	234
30	208

Tran Vinh Dieu *et al.* predicted the life-time of epoxy-novolac (EN) blend film cured with 4,4'-diaminodiphenyl sulfone (DDS) using TGA method with heating rate of 1 °C/min, 2 °C/min,

5 °C/min, 10 °C/min. The authors calculated the activation energy of the degradation reaction of EN/DDS films at different degradation levels (Table 4.2) [35].

Dao Van Luong and Ton That Minh Tan predicted the life-time of unsaturated polyester (UPE) using TGA method [36]. The predicted life-time of UPE is in good agreement with the experimental data. For example, at a weight loss of 1 %, the life-time of UPE predicted by TGA method was 100.5 days, pretty close to the real use time of UPE (105.0 days).

Peter Raymond Hondred used isoconversional methods based on Friedman and Flynn-Wall-Ozawa (FWO) equations and TGA method to calculate the activation energy of the thermal degradation process of polytetrafluoroethylene (PTFE), poly(ethylene-alt-tetrafluoroethylene) (ETFE) and poly[(5,7-dihydro-1,3,5,7-tetraoxobenz[1,2-c:4,5-c']dipyrrole-2,6(1H,3H)-diyl)-1,4-phenyleneoxy-1,4-phenylene] (Kapton) [37]. The activation energy of the thermal degradation process of PTFE was 70 - 130 kJ/mol, depending on the weight loss of the sample. The activation energies of the thermal degradation process of ETFE and Kapton were 140 kJ/mol to 210 kJ/mol and 20 kJ/mol to 190 kJ/mol, respectively. The predicted time to failure of the Kapton samples at 12 and 14.7 kV voltages (10 % and 20 % weight loss, respectively) at 350 °C was 1,200 hours and 729 hours, respectively.

I. Rusu and A. Cailean applied isoconversional methods based on FWO and Sergey Vyazovkin (SV) equations as well as TGA method to predict the life-time of PVC-I containing lead sulfate and PVC-II containing lead sulfate and magnesium carbonate. The authors found that PVC-I and PVC-II both achieved a 48-hour life-time when used at 110 °C and 140 °C, and both reached a 1-year lifespan when used at 55 °C and 97 °C, respectively [38].

Agmar Jose de Jesus *et al.* also applied the FWO isoconversional method combined with TGA/DTG data to calculate the activation energy of the thermal degradation process of poly(vinylidene fluoride) (PVDF) and predict the life-time of PVDF (about 50 years) [39].

The oxidation induction time (OIT) is a reliable parameter to evaluate the thermo-oxidation stability of polymer materials and is usually determined by differential scanning calorimetry (DSC) method according to PN-EN 728:1999 or ISO 11357-6:2002. Based on the OIT data obtained, one can calculate the activation energy of thermo-oxidation process and predict the life-time of polymer materials according to the Arrhenius equation [38].

$$k(T) = A \cdot e^{-\frac{E_a}{RT}} \quad (4.25)$$

$$t_{f(P)} = \frac{f(P)}{A} e^{\frac{E_a}{RT}} \quad (4.26)$$

where, $k(T)$ is the rate constant of the decomposition process, E_a the activation energy, T the absolute temperature, R the gas constant, A the constant, and $t_{f(p)}$ is the failure time of the polymer.

The OIT value corresponds to the time of initiation of polymer chain degradation, i.e. to the failure time and thermal stability of the polymer materials, which means that the OIT corresponds to the P value of the failure time function in Eq. 4.26.

$$t_{f(OIT)} = C_{ox} e^{\frac{E_a}{RT}} \quad (4.27)$$

where, C_{ox} is the constant corresponding to A in Eq. 4.26.

The failure time of linear low density polyethylene (LLDPE) samples modified with chemical agent (grafting), physical agent ($Al(OH)_3$) and unmodified was predicted owing to the graph depicting the dependence of $\ln t_{f(OIT)}$ on $1/T$, where the OIT was determined at different temperature ranges (190 - 220 °C, 180 - 210 °C and 210 - 240 °C). Table 4.3 indicates the E_a of

thermo-oxidation process, correlation coefficient (r^2) and failure time of LLDPE samples, which increases from chemical modified LLDPE, up to unmodified LLDPE, then up to physical modified LLDPE [40].

Table 4.3. E_a of thermo-oxidation process, correlation coefficient (r^2) and failure time of LLDPE samples [40].

Parameter	Unmodified LLDPE	Chemical modified LLDPE	Physical modified LLDPE
E_a (kJ/mol)	149	150	180
r^2	0.817	0.924	0.992
$t_{f(OIT)}$ at 210 °C (min)	9	4	75
$t_{f(OIT)}$ at 100 °C (min)	1.0	0.5	80

Tarri' o-Saavedra *et al.* predicted the life-time of poly(DL-lactide) (PDL02A) and copolymer L-lactide/DL-lactide 70/30 (PLDL7028) biopolymers using kinetic models based on logistic functions combined with S-shaped model and TGA/DSC methods according to ASTM E 1641, E 1877 and E 698 [41]. However, these standards only provide activation energy for one process and the first order kinetic model, so iso-conversional methods with dependence of activation energy on α conversion was applied to calculate the life-time of biopolymers. The authors found that the apparent energy barrier, critical temperature and activation energy of PDL02A samples were 17.71 kJ/mol, 119.3 °C and 5837.63 kJ/mol for, and of PLDL7028 samples were 44.02 kJ/mol, 80.4 °C and 6659.34 kJ/mol, respectively. From that, the life-time of PDL02A (at 210 °C) and PLDL7028 (at 230 °C) with 5 % loss of sample weight was 6.78 minutes and 51.05 minutes, respectively. According to ASTM E 1641, these corresponding values were 1.39 minutes and 0.82 minutes, respectively, while the real use time of these samples was 33.71 minutes and 107.53 minutes (determined by TGA method). This indicates that the use of logistic functions is more suitable and closer to the experimental data when predicting the life-time of polymer materials.

Fouzia *et al.* used iterative-FWO, Trache-Abdelaziz-Siwani (TAS), and Sbirrazzuoli (Vyazovkin/compensation effect-Vya/CE) isoconversional methods to predict the life-time of polypropylene/poly(lactic acid)/stearate iron (PP/PLA/IS) composites based on TGA data [42]. From the result of a 21-day artificial test, it can be predicted the life-time of PP/PLA blend and PP/PLA/IS composite at 25 °C was 85.7 years and 0.47 years, respectively. The extreme life-time reduction of the PP/PLA/IS composite may be due to the iron ions that initiated the accelerated thermal degradation process of the PP/PLA blend.

4.3.3. Methods for predicting life-time of polymer materials based on deterioration of chemical and physical properties

Changes in physical and chemical properties during testing can be used to predict the life-time of polymer materials. Malic *et al.* based on the loss of HALS in LDPE and PP films to predict the photo - stabilization time of these films [3]. The failure criterion applied to evaluate the photo - stabilization time of these films was an increase in the absorption intensity of the carbonyl group in the infrared region by up to 0.3 (T-03). The authors determined that the photo - stabilization time or protect time (T-03) of PP and LDPE was 30-40 hours and 270-310 hours, respectively. Besides, owing to Billingham and Calvert's theoretical model of stabilizer weight loss, the authors also found that the photo - stabilization time at a HALS weight loss of 0.2 (80 % reduction in HALS weight) for LDPE/HALS and PP/HALS films was 2,530 hours and 1,130 hours, respectively.

From the parameters calculated from the infrared (IR) spectra, Dao Van Luong gave the life-time of nitrile butadiene rubber (NBR)/silica composite based on the failure criterion of 30 % reduction in any properties of the composite (t_{30}) [36]. At the ageing temperature of 70 °C, 90 °C, 100 °C, and 120 °C, the t_{30} of the composite was determined as 87.181 days, 29.929 days, 10.146 days, and 2.782 days, respectively. From the graph reflecting the dependence of $\log t_{30}$ on $1/T$, the author found that the life-time of NBR/silica composite at 20 °C, 25 °C, 30 °C, 35 °C, and 40 °C was 1,1113 days, 6,467 days, 3,831 days, 2,309 days, and 1,414 days, respectively.

Zhao *et al.* found that the correlation coefficient between the natural test (in Shanghai, China) and the artificial test (xenon-arc lamp chamber - ASTM G26) based on the change of the carbonyl index in the IR spectra of the samples was 10.73 times, i.e. 10.73 hours of the natural test corresponding to 1 hour of the artificial test [43].

Minh *et al.* found that the time required for HDPE/organo-modified CaCO_3 composite to achieve a 50 % reduction in HDPE molecular weight was 384.3 days for the natural test in Dong Hoi (Quang Binh, Viet Nam) and 258.3 hours of for the artificial test (UV-humidity-heat complex) (Figure 4.4) [44].

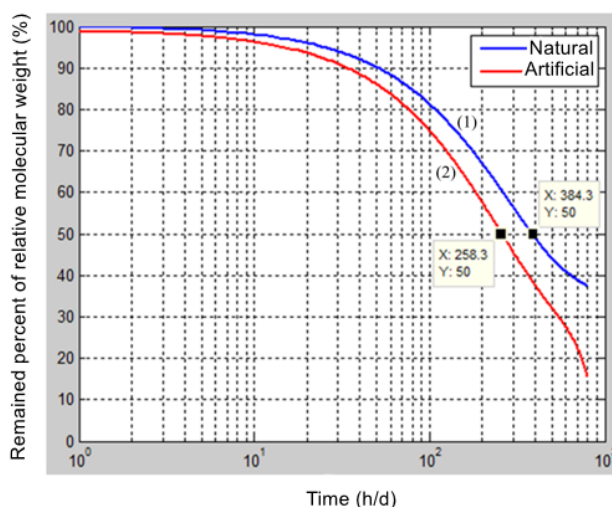


Figure 4.4. Graph reflecting correlation coefficient between natural exposure and artificial test based on remained percentage of relative molecular weight of HDPE in the HDPE/organo-modified CaCO_3 composite [44].

4.3.4. Methods for predicting life-time of polymer materials based on deterioration of fatigue and creep properties

In recent years, polymer materials with high modulus and durability have been developed to meet the demand for advanced lightweight materials and applied load (static and fatigue) materials working in hostile environments. Therefore, it is necessary to develop test procedures to evaluate the shelf life/working life of these materials in hostile environments. Since the life-time of polymer materials is usually measured in years, it needs to be predicted through accelerated testing. The effect of long-term loads on the deformation and failure behavior of polymer materials is important for predicting their failure time.

Creep behavior is the increase in strain or deformation of a material at the time when the material tested at a constant load over an extended testing period. The dependence of creep inside polymer material on the testing time is as follows: In the first stage, primary creep starts at a rapid rate and slows down over time; creep in the second stage occurs at a relatively uniform rate; and in the third stage, creep takes place at an accelerated rate and terminates due to material failure at the time of rupture [3].

Fatigue is often expressed in terms of maximum applied fatigue stress S and fatigue life (number of cycles to failure N_f). This property is suitable to predict the fatigue performance of composite laminates (including statistical, fracture mechanics, empirical models) [3].

Fukushima *et al.* presented a method to accurately determine the time-temperature shift factor in the dynamic viscoelastic test (to give storage modulus) and creep test (to give creep compliance) to predict the failure time of polymer composite based on epoxy resin (deglycidyl ether of bis-phenol A (jER828), methyl nadic anhydride and 2-ethyl-4-methyl-imidazole) according to time-temperature superposition principle (TTSP) [45]. Bin *et al.* predicted the life-time of glass fiber reinforced polymerized cyclic butylene terephthalate composites (GF/pCBT and nano-GF/pCBT) under hydrothermal conditions (at temperature of 50 °C, 60 °C, 70 °C, and 90 °C, and relative humidity of 60 % and 90 %) [46].

For these composites, the strength degeneration ratio (SDR) is calculated as:

$$SDR = SDR_m f_m + SDR_f (1 - f_m) - \Delta \ln f \quad (4.28)$$

where SDR_m and SDR_f are the strength degeneration ratios of matrix and fiber, respectively, f_m is the weight ratio of matrix in the composite, $\Delta \ln f$ is ageing effect caused by the fiber/matrix interface in the composite.

The model used to predict the life-time of the composites is as follows:

$$\log t = A + \frac{B}{T} - C \log P_{H_2O} \quad (4.29)$$

The TTSP is an effective tool to predict the life-time of polyurethane (PU) derived from glycol ester (poly(ethylene adipate) glycol), 4,4 -dibenzoyldiisocyanate and the extension parts - diethylene glycol (DEG) and trimethylol propane (TMP). The PU composites containing different TMP contents changed from 0 to 1.8 %, 2.6 % and 3.4 % in weight were assigned as PU-DEG, PU-DEG-1.8 TMP, PU-DEG-2.6 TMP and PU-DEG-3.4 TMP, respectively [47].

Based on the modulus curves, the authors calculated the shift factor and activation energy of the PU composites using Williams-Landell-Ferry (WLF) model. Some parameters based on the DMA behavior of PU composites indicate in Table 4.4 [47].

Paul *et al.* evaluated the failure time of nylon-6 using TTSP and dynamic mechanical analysis (DMA) technique based on the test data according to ASTM D2990. The authors predicted the failure time of nylon-6 to be about 6 weeks [48].

Rui Miranda Guedes assumed that the unidirectional strain response of a linear viscoelastic material, under arbitrarily stress, σ_t can be expressed by the power law [49]:

$$\varepsilon(t) = D_0\sigma(t) + D_1 \int_0^t \left(\frac{t-\tau}{\tau_0}\right)^n \frac{\partial\sigma(\tau)}{\partial\tau} d\tau \quad (4.30)$$

where D_0, D_1, n are material constants, τ_0 is time unity.

Table 4.4. Some parameters related to DMA behavior of PU composites [47].

Sample	T_0 (°C)	C_1	C_2 (°C)	$f_0/B \cdot 10^3$	$\alpha_f/B \cdot 10^3$	E_a (kJ/mol)	R^2
PU-DEG	-28 (T_g)	63.6	348.9	6.8	19.48	215.6	0.997
	0	31.2	200.8	13.9	68.7	221.6	0.999
	15	34.4	278.8	12.6	45.2	196.4	0.998
PU-TMP	-22 (T_g)	16.2	78.3	26.7	341.0	249.8	0.990
	0	8.3	68.5	52.3	763.0	173.1	0.996
	15	6.4	78.6	68.3	869.0	128.5	0.995
PU-DEG-1.8TMP	-15 (T_g)	73.6	399.6	5.9	14.7	235.0	0.991
	0	28.0	164.7	15.5	94.0	242.9	0.999
	15	23.3	171.8	18.5	108.0	199.8	0.999
PU-DEG-2.6TMP	-10 (T_g)	44.4	248.9	9.78	39.3	236.0	0.994
	0	29.2	177.9	14.9	83.7	234.5	0.996
	15	20.6	146.0	21.0	144.0	224.6	0.999
PU-DEG-3.4TMP	-0 (T_g)	38.9	215.9	11.2	51.8	240.0	0.997
	0	29.8	177.3	14.6	82.3	239.3	0.998
	15	26.5	178.3	16.4	92.0	231.0	0.999

T_g : glass temperature obtained from loss modulus peak at frequency of 1 Hz, T_0, C_1, C_2 are parameters in WLF equation, f_0 : free fraction volume at reference temperature, α_f : coefficient of thermal expansion, B is constant, E_a is activation energy.

The prediction of failure time of a material with viscoelastic properties under fatigue (creep) testing when a load σ_0 applied under instantaneous condition with loading σ_R is calculated according to the following criterions:

Reiner-Weissenberg (R-W) criterion:

$$\left(\frac{t_f}{\tau_0}\right) = \left(\frac{1}{2-2n}\right)^{\frac{1}{n}} \left(\frac{D_0}{D_1}\right)^{\frac{1}{n}} \left(\frac{1}{F_a^2} - 1\right)^{\frac{1}{n}} \quad (4.31)$$

Maximum Work Stress (MWS) criterion:

$$\left(\frac{t_f}{\tau_0}\right) = \left(\frac{1 D_0}{2 D_1}\right)^{\frac{1}{n}} \left(\frac{1}{F_a^2} - 1\right)^{\frac{1}{n}} \quad (4.32)$$

Maximum Strain (MS) criterion:

$$\left(\frac{t_f}{\tau_0}\right) = \left(\frac{D_0}{D_1}\right)^{\frac{1}{n}} \left(\frac{1}{F_a^2} - 1\right)^{\frac{1}{n}} \quad (4.33)$$

where $F_a = \sigma_0/\sigma_R$ (4.34) is normalized applied stress.

Based on the creep properties of glass-fiber/urethane composites as well as the TTSP and R-W, MWS, MS criteria, the authors found that the experimental data are complied with the R-W and MS failure criteria.

Bora *et al.* gave a model for predicting the life-time based on the impact-fatigue properties of carbon fiber reinforced poly (ether imide) composites [50]. The parameters such as the impact number until fracture and the impact energy used to establish the impact-fatigue life curve expressed as follows:

$$y = 1.2226.10^{12} [e^{(x/-0.02737)}] + 90.66097 \quad (4.35)$$

where y is impact energy and x is impact number.

The “strain-life time” method has been used to predict the life-time of carbon fiber reinforced poly (lactide-co-glycolide) composites [51], which can work under the same usage conditions as in a simulated human body environment below 1,000 cycles of loading.

4.3.5. Some other methods for predicting life-time of polymer materials

Wenhua *et al.* combined the data of DMA, DSC and mechanical properties analysis with the Arrhenius equation to provide a prediction of the life-time of poly (methylmethacrylate) (PMMA) under tensile stress and liquid scintillation conditions at 20 °C for about 25 years [52].

Nguyen Thien Vuong determined the correlation coefficient between the accelerated test (samples were exposed in a UVCON UC-327-2 weathering test instrument according to ASTM D 4587-91) and the natural test (samples were exposed to the open air in Ha Long (Quang Ninh, Viet Nam)) to be 1.33, based on the change in surface gloss property of acrylic coatings [53].

Based on the calculation of surface defects of polymer films under water condensation or salt spraying conditions according to the ISO 4628-2, ISO 4628-5, ISO 6260, ISO 7253, the life-time of the films can be predicted at different levels. It was determined that the low life-time of polymer films was from 2 years to 5 years, their adequate life-time was from 5 years to 15 years, and their high life-time was higher than 15 years [54].

The failure time of some polymers can be determined as a function of relative humidity (RH):

$$\frac{1}{t_{fail}} = A e^{\frac{-E_a}{RT}} [RH]^2 \quad (4.36)$$

The activation energies, E_a , of polycarbonate, poly(ethylene terephthalate) and resorcinol polyacrylate obtained from the bending test data after a hydrolysis process at a temperature of 65-95 °C and a relative humidity of 23-95 % were 92 kJ/mol, 129 kJ/mol and 102 kJ/mol, respectively [55].

Gac *et al.* predicted the life-time of polyurethane (PU) coated on steel pipe under salt water conditions (I: 105 days, 85 °C, and II: 279 days, 125 °C) based on the ratio between remaining urethane bonds [U] and initial urethane bonds [U₀] in the material [56]:

$$\alpha = \frac{[U_0] - [U]}{[U_0]} \quad (4.37)$$

In case of PU is not hydrolyzed, $\alpha = 0$, while if PU is completely hydrolyzed, $\alpha = 1$. The PU coating can work for a period of 20 year.

Gillen *et al.* based on the change in induction time of ethylene propylene diene monomer (EPDM), TTSP and Arrhenius equation to determine the activation energy of EPDM degradation as 116 kJ/mol. From that, the life-time of EPDM at 25 °C was predicted to be 55,000 years [9].

Bellenger *et al.* also determined the activation energy (E_a) of hydrolysis process of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) based on the adsorption rates of different types of water. It was found that the E_a was 70 kJ/mol, 43.7 kJ/mol and 56.5 kJ/mol for salt water, deionized water and distilled water, respectively [57].

From the data of total UV radiation (TUVR) energy combined with the natural test, the life-time of homopolypropylene, polypropylene random-copolymer, and polypropylene impact-copolymer were predicted to be about 1,160 hours, 796 hours and 755 hours, respectively [10].

The life-time (t) of polypropylene (PP) can be calculated according to the ozone concentration (\overline{O}_3) during the ozone ageing test or the oxidation rate (OR) under irradiation conditions [58]:

$$\frac{1}{t} = a + b (\overline{O}_3) \quad (4.38)$$

$$OR = \sum_{\lambda_1, \lambda_2} I_a(\lambda)^\alpha \exp\left(\frac{-E_a}{RT}\right) \quad (4.39)$$

where a , b are the parameters depending on stability of materials and temperature; λ_1 and λ_2 are the limited wavelength of radiation causing the polymer oxidation; I_a is the intensity of light absorbed at wavelength λ ; E_a is activation energy; T is absolute temperature.

Meng Huang and Yuanxiang Zhou set up the space charge dynamics based model to predict the life-time of insulating polymers, for example, LDPE [59] as follows:

$$L_h = \frac{1}{K_T + K_D} \ln \frac{C}{C - C_h^*} \quad (4.40)$$

$$C = \frac{K_T}{K_T + K_D} \quad (4.41)$$

$$C_h^* = \frac{p_c}{U_p K_D N} \quad (4.42)$$

where, L_h is the life-time of material, N the trap density, K_T the trapping coefficient ($K_T = 8.66 \cdot 10^{-5} \text{ s}^{-1}$), K_D the detrapping coefficient ($K_D = 1.32 \cdot 10^{-5} \text{ s}^{-1}$), p_c the critical released energy density rate, and U_p the electromechanical energy.

In addition, the life-time of polymer materials can be evaluated based on Lambert W function:

$$L_l = C_l^* \left(\frac{1}{K_T} + \frac{1}{K_D} \right) + M \frac{1}{K_T + K_D} \quad (4.43)$$

$$C_l^* = \frac{w_c}{U_p N} \quad (4.44)$$

$$M = 1 - \exp\left[-\frac{C_l^* + C(1-C)}{C(1-C)}\right] \quad (4.45)$$

where, L_l is the life-time of material, w_c is the cumulated released energy density.

When comparing the calculated lifetime of static and dynamic breakdowns (Eq. 4.40 and Eq. 4.43) with the experimental data, the authors indicated that the life-time of LDPE decreased with increasing electric field, and the difference between the static and dynamic breakdown models was very small and the life-time prediction obtained from these models was in good agreement with the experimental data.

From the data on plasticizer content, volume mass, water adsorption coefficient and water vapor permeability of poly(vinylchloride) (PVC) after natural testing, the life-time of PVC was predicted to be about 30 years [59].

Ariannik *et al.* based on the degree of polymerization (DP) of cellulose to predict its life-time [60]. When DP of cellulose reached 200, the estimated life-time of cellulose in case I (load limit of 75 %) and case II (load limit of 100 %) was 80.4 years and 42.5 years, respectively.

5. CONCLUDING REMARKS

In order to predict the life-time or service working life of polymer materials, there are some methods to test and evaluate the change in characteristics, properties, morphology, durability, etc. of these materials. Common weathering tests for polymer materials are natural exposure test and artificial exposure test, in which the latter includes thermal ageing test, light source test, ozone cracking test, salt-accelerated test, fungal and bacterial activity test.

The degradation mechanism of polymer materials is very complicated due to the profound influence of one or more factors such as chemical factors, physical factors, mechanical factors, biological factors, weather, and climate, etc.

From the degradation data of polymer materials, it is possible to predict the life-time of polymer materials when applying the Arrhenius equation and power law model. However, these models are not applicable to all cases of degradation data of polymer materials. Therefore, a time-temperature superposition principle is used to improve the accuracy of predicting the life-time of polymer materials and the activation energy of the degradation process. Williams-Landel-Ferry and Friedman methods are also used to predict the life-time of polymer materials in the case of temperature-independent changes of properties or diffusion-limited degradation processes.

The iso-conversional methods are reliable kinetic methods for processing thermal analytical data obtained after testing polymer materials. They allow the activation energy to be determined without assuming any specific form of the reaction model. The activation energy is mainly used to predict the life-time of polymer materials in the case of physical and chemical processes occurring within the material.

Scientists are still developing new methods or improving existing ones to predict the life-time of polymer materials due to their great interests and various applications in almost all areas of engineering and our life.

CRedit authorship contribution statement. Nguyen Thuy Chinh: conceptualization, methodology, data analysis, investigation, and writing; Thai Hoang: conceptualization, formal analysis, review and 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.

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