

# A Method of Foretelling the Polymeric materials Lifetime: A Short Review

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**Abstract:** *The effective implementations for materials of polymeric structure require fixing the shelf life for them. The broad usages of this kind of materials (e.g., medicaments, engineering goods, food packaging,...., etc.) Impose upon scientists well understanding of the effects produced by various work circumstances factors (heat, light and UV radiation, oxygen, ozone, chemical substances, water vapor). Over a long term of the affecting, these factors acquire an essential role in polymeric aging. Considering of the produced alteration in the polymeric physical and chemical properties shows subjecting of these features of mathematical models. The ultimate durability of the stabilized polymer can be speculated. Moreover, using the technique of aging acceleration for polymer gives great results in this field. This paper recall shortly a review of a number of methods of account the impacting factors on degradation of polymers. As well as, it presents some examples of the postulated lifetime of rubber. The methods of describing degradation of polymers are present as well, through using the artificial accelerated aging, and extrapolation way from the induced thermal deterioration: the Arrhenius model.*

**Keywords:** lifetime; degradation; accelerated aging; polymer; kinetic models; thermal analysis.

## Introduction

The urban life almost has no aspect free by using the polymeric materials, which replaced the traditional materials in the various areas. Over the several past decades, invention of plastic supports the human life, economically and socially. This polymer's importance can be imagined through the average number of its production in 1950's is about 1.5 million tons, and then to be increased to 400 million tons in 2018. There are many characteristic features of this product, such as high mechanical properties, easy possibility, lightweight and affordable [1].

Polymeric materials applications count on their functional properties. The most common fields to use groups of plastic in them are: constructions, medicine, agriculture, household, food, chemical, automotive [2-10]. The employment of plastic as a cover material acquires a special prominence. Among all the different plastic types, polyethylene is produced by around 40 million tons, as plastic films [11].

The quality of every material is determined by so-called the shelf life. It is rated as of high quality, as long as it keeps its chemical and physical properties for a long time. The worst probable threaten for polymer is the aging. That loses polymeric materials their aesthetic and mechanical properties, to be eventually useless [12-15]. Polymer sensibility to the oxidation and degradation process is the reason beyond this effect. The direct exposure of the plastic parts of tools and devices to the weathering factors (like heat, moist, UV-visible light) leads them to the degradation at the end [16].

The continual effect of degradation of plastic material is extremely slow but for a long term, might lead to catastrophic damage depending on the nature of the usage of those materials. However, the early precise prognosis of decline of polymeric material performance represents a precaution to avoid the worst. Especially, for the elastomeric parts which are used in aircraft, nuclear reactor, defense equipment, and medical tools [11,15,17,18].

This paper shows the most important factors of environment cause deteriorations polymeric material and sophisticated methods used for analysis this phenomenon. The beginning is setting out several ways of polymeric degradation, giving a description of the factors, mechanisms different alterations produced by these procedures. The key point of this work is to make people know the importance of polymeric materials lifetime extrapolation going through analyzing their kinetics of some changing properties by the degradation. This matter entails an extensive knowledge of the degradation mechanism of the considered material. Consequently, it is necessary to review simple examples of some decomposition cases.

## 2. Reasons of Polymer Degradation

The molecular weight of polymer decreases through three basic kinds of processes lead to polymer chain scission: destruction, depolymerization, and degradation [19-21]. Destruction of polymer creates dissimilar compounds of lower molecular weight. Depolymerization is a result of the thermal influence returns the polymer chains to the original monomers [22]. Polymer degradation

means that the polymer chains being separated as fragments; the latter is simpler than those chains. These processes represent the most probable defects of a polymer material lifetime [23–26].

## 2.1 Fruit of Degradation

All the potential structural transformations which yield changes of chemical and physical properties of polymeric materials are listed under the topic of degradation. The effect of the environmental factors (e.g., heat, oxygen, ozone, light, radiation, UV radiation, water vapor, chemical substances, high energy radiation, dynamic stresses) advances progressively over the long term. Eventually, the result is a trace of accumulated changes. Losing of polymeric characteristics is shown as a discoloration (e.g. Yellowing), brightness (tarnishing), and/or texture [30,31]. In operation life, synchronization of more than one environmental factor effect give complex traces caused by the overlapping deeds [29].

In general, the involved chemical reactions within the polymer degradation are chain cutting, cross linking, thermal oxidation, and destruction. These products represent irreversible changes in polymer structure; products of degradation process are shown in Figure 1, [32].

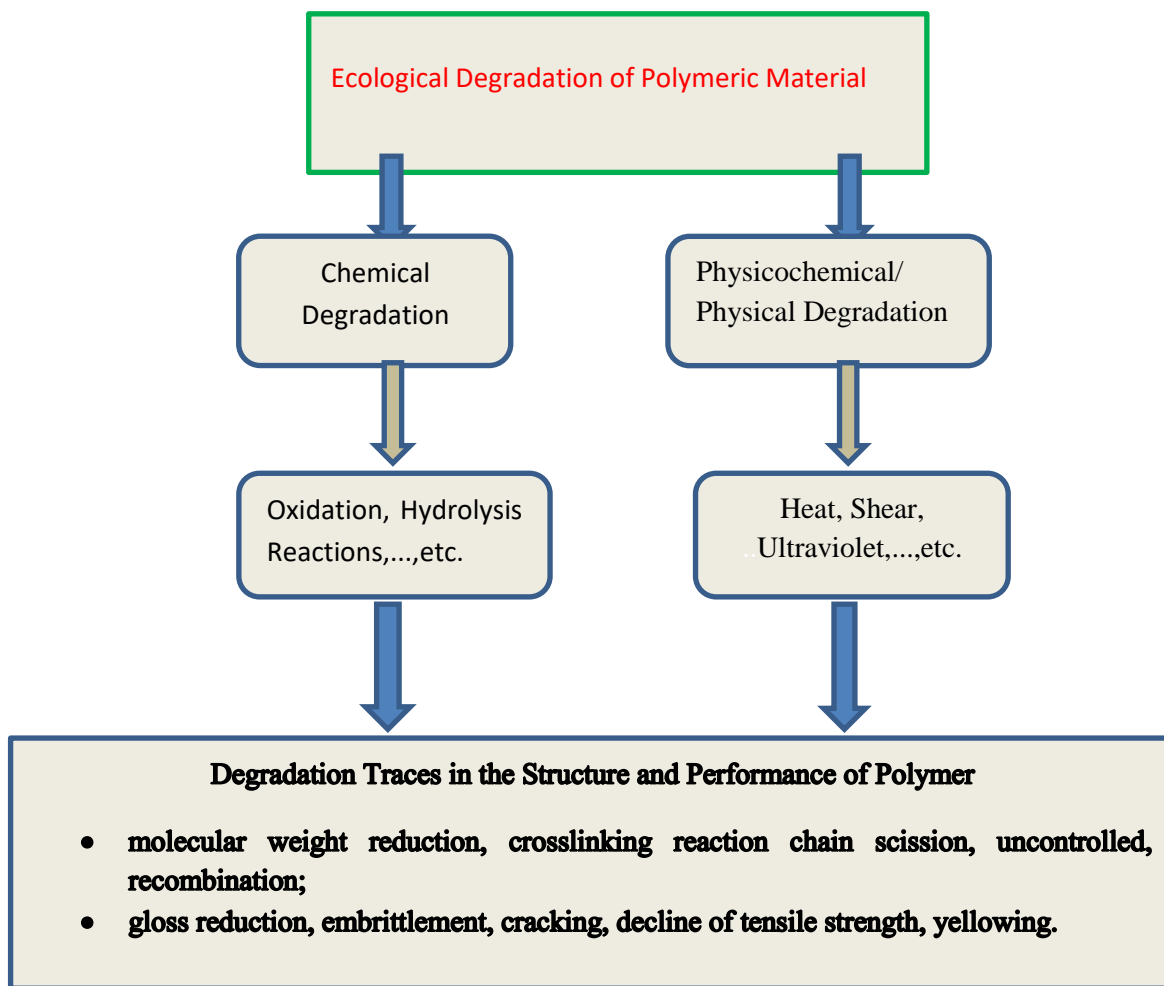


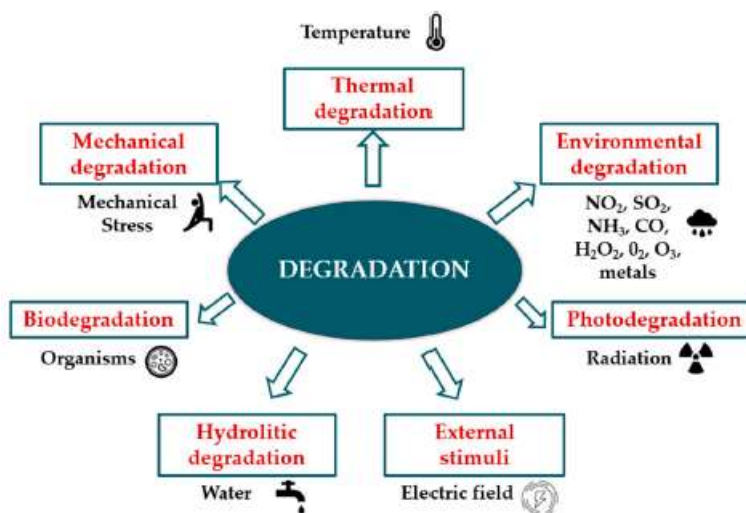
Figure1. Changes in polymer properties result from the factors of chemical degradation like oxidation, and hydrolysis; and photochemical degradation like shear, heat, and UV light.

As an overview of the conceivable natural degradation processes, all that kinds can be mimicked experimentally [29]. The used methods are subjected to international standards which enables the scientists to recognize affecting factors on polymeric material. The changes of degradation can be classified into two sorts: a first one is of a positive effect on the some of the polymeric material properties like that of increasing crosslinking which leads to higher mechanical feature and under the effect of a specific temperature.

The second one starts when the continuing of degradation becomes a reason of decline the performance of that material, such as decreasing the molecular weight or the over crosslinking that makes it a different effect of degradation backfire [33].

## 2.2. Kinds of Degradation

The polymeric degradation can be classified into different kinds, such hydrolytic, photo, thermal, mechanical, and bio [24]. Polymers are apt to deterioration by different levels. The initiators of degradation and corresponding types of degradation are summarized in Figure 2.



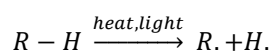
**Figure 2.** Chemical, physical and biological agents causing various types of degradation.

The most important factors of elastomer degradation are: oxygen, ozone, and elevated temperature. This kind of degradation is called thermo-oxidative aging [15]. The stated types of degradation are connected strongly. In most often natural cases of degradation are caused by more than one factor [34].

The concurrent impact of the deed for each of light, oxygen, and weather factors occur alongside with the action of the duration and resistance of the tested polymer (involving changing in molecular weight, and occurring of defects in polymer) in addition to kind of impurities in the product, shape, and thickness of the outcome [31]. Recent researches of polymer degradation proved that class of crystalline plays an axial role in supporting its resistance against the influencing factors in comparison with that of amorphous plastics. Moreover, branching of polymer enhances the shelf life more than those of linear structure [35]. Decay of the polymer show in obvious, relies directly on the molecular weight [36]. There are some certain chemical groups have an important impact in plastic degradation which is: ester, amide, and urea, through accelerating disintegration of polymers for their facility the hydrolyzing process [37].

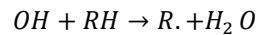
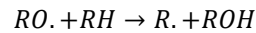
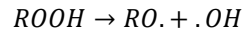
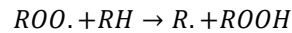
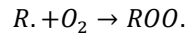
## 2.3. Mechanism of Thermal Degradation in General

There are several kinds of unique molecular mechanism matching the different kinds of polymer degradation. However, it is possible to occur more than one mechanism in degradation of material [34]. At all time, this process begins with cracking of a bond belongs to the polymer chain or other initiator molecules of degradation. The breaking of the chemical bond produces other subsidiary reactions causes more breakage, leads to substitution or recombination [38]. The initiation point of polymer decomposition represents the first stage of releasing the free radicals, in addition to disconnection of hydrogen atoms as a result of radiation, heat, light, or by an initiator existence [39], Equation (1):

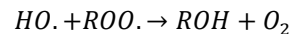
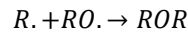
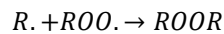
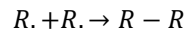


The next step is named propagation by which a series happening of reactions with molecules of oxygen to produce radicals of peroxides. The latter product grabs atom of hydrogen from another chain of polymer to compose a critical radical of peroxide. The next step is named propagation by which a series happening of reactions with molecules of oxygen to produce radicals of peroxides. The latter product grabs atom of hydrogen from another chain of polymer to compose critical radicals of peroxide radical, either

radical of hydroxides or new free peroxide. The high capability of an initiating radical to strip the atom of hydrogen from other polymer chains gives a facility in accelerating the chemical process by generating two new free radicals. The fastest free radicals, there would be more subject to termination by recombination and disproportionation. The reaction steps during the stage of propagation are summarized as follows [40,41]:



Eventually, occurring of the termination process as a result of a reaction between two compounds, each of them has won an unpaired electron, the come out is a feeble product. As an example of such reaction is that reaction happens between two radicals of peroxide, alkyl or even two different radicals in a system [41]:



The degradable polymers as polyolefin (polypropylene-PP, polyethylene PE), are considered here. There are two essential styles of degradation which are photodegradation, and thermal. They are regarded within the most kinds of deterioration to be experienced by the polymeric industrial practices [42]. The reason of beginning the initiation stage is the existence of the UV chromophores which involved in the blended polymer. The saturation of polyolefin makes them have no more the capability to absorb UV radiation in a direct way. Mostly, the absorption is caused by the double bond structures which can be found in the chromophores of pigments or retardants of flame, residues of catalyst or in every organic molecule has a double bond structure. The degradation process can result from absorption of UV radiation, high energy in this spectrum range of the electromagnetic radiation, bonds of material suffer breakage. This change of material structure leads to successive steps of degradations through releasing the free radicals as a byproduct for bonds breaking. There is no a unique behavior of degradation of all polymers, for example, polypropylene undergoes a series of scissions. While of polyethylene the yield of degradation is a structure of cross-linking [43]. The degradation of polyolefins by UV radiations produces bonds about 300 nm of PE and 370 nm for PP [42]. For more clarification, polyolefin loses its properties by the influence of UV light, as the strength of high density polyethylene (HDPE) plate of width 1.5 mm reduces to 80% after UV light exposure for 2000 h [43].

The kind of polymer, which is so-called Elastomer, suffers several alterations by the exposure time of the degradation factors of oxygen, heat, UV radiation. Nowadays, assessment of elastomers under the effect of a chemical environment or high temperature is achieved through using of some standards like ISO 188:2011 and ISO 1817:2015. Sharing of both heat and oxygen in aging of rubber reduces its mechanical properties, mostly the tensile strength. The process of measuring the changing values of tensile strength is not too easy to be determined for the reactions conflicting which are occurring at the same time [44,45]. Tobolsky et al. [46] Proposed a Tow-Network Theory to elucidate the mechanical conduct for the effected elastomer by different temperatures lead to cross-linked structure. There is a paradox in the attitude of elastomer at high temperatures, on one hand; it suffers softening as a result of degradation of molecular chains followed by cross-linking. On the other hand, there is an observable additional crosslinking produces a hardening in the material. The type of use antidegradants, fillers, and vulcanization order determine the dominated reactions, whether hardening or softening reactions under a certain conditions of aging [44,45].

Perhaps, one of the best examples of crosslinking presence is that in polybutadiene (BR) and its copolymers. The most polymeric chain susceptible to scission is that which has a side group with ability of donating electron and attached to a carbon atom neighboring to double bond. Here, we are referring to all unsaturated elastomers with electron donating groups [47,48].

The future handbill is devoted to presenting more detailed depiction for the generic mechanism of thermal degradation. A key role is occupied by the process of a radical chain. That is accomplished through processes of mechanochemical, thermoxidation, or photochemical impact which are occurring under the effect of radiation. These undesired processes can be avoided or inhibited by enhancing the stability, boosting the material's resistance of aging.

Among the different ways used to raise the degradation resistance of polymer in both kinds of chemical or physical methods, adding distinct additives like stabilizer, UV absorber, and antioxidants is regarded the most common used modifier [28,41,49].

### 3. Shelf life of Polymers

The long life of polymer is a quite important factor for each of the manufacturers and the consumer. However, the subject of the capability to manage the polymer waste seems highly interesting; we recall that not all polymers are recyclable. Therefore, the degradation processes are always underlined [50]. The service life of the polymeric materials is considered a vital feature. The polymer resistance against the aging boosts the confidence of the producers to give a long warranty. After the shelf life the properties of products gets down to the half at the work environment of heat, moist, UV light, ...,etc. [51,52]. The storage life is related to the storage conditions, in addition to the type of the stored elastomer. However, the manufactured tool from that elastomer and its conditions of usage are vital factors to prolong the lifetime [15]. Rubber is characterized by its long lifetime in condition of stored in protective store avoids it the natural aging factors, considered as suitable storing places like heat of 25 C, dark storage far off the aggressive chemical matters. The polymeric lifetime may extend from 3 to 25 years within the typical conditions [15]. Polymeric lives of stored different made items of rubber are listed in the following table 1 [53].

Table 1. Shelf life of products made out of different types of rubber [51].

Rubber	Abbreviation	Recommended Storage Life Without Inspection (Years)	Storage Life Extension After Visual Inspection (Years)
Natural Rubber	NR	5	2
Butadiene-styrene	SBR	5	2
Nitrile	N	7	3
Nitrile-butadiene	HNBR	7	3
Acrylic	ACM	7	3
Chloroprene	C	7	3
Ethylene-Propylene	E	10	5
Viton™/FKM	V	10	5
Kalrez™/FFKM	KLZ	10	5
Silicone	S	10	5

Constructing a clear vision about the capacity of polymer bearing the natural degradation requires applying an accelerated artificial weathering aging on considered polymer through achieving a simulation of natural degradation factors. The closer the simulation is to the conditions of use, the more effective the results. The precise prediction of the lifetime of polymer may offer a safe for people, when the tested polymer is used in a critical tool or equipment [18,30].

### 4. Accelerated Polymer Weathering

One of the greatest indicators to assess the shelf life of polymeric materials is artificial aging, by offering a comparison of the quantity or quality of polymers according to the stratified methodology [57-59]. Evaluation of plastics' goodness in nature requires not less than three and five years under the operating conditions of the considered soft and hard polymer, respectively. Hence, the simulated aging experimentally provides well means to satisfy the ultimate goal in a short time. The precise analysis of polymer degradation gives a good extrapolation for the polymeric resistance [28]. Given the importance of predicting the lifetime of polymer in its operation fields, such as defense types of equipment, safety components of nuclear reactors, and aircraft parts, enhancing and developing the accelerated aging of polymers are well underlined by inventing ways to approach the actual circumstances [17]. Quality of plastics is not significant just from an economic perspective but also from an environmental one. Due to the difficulty of several polymer degradation, this matter poses one of the most challenges for humanity to keep nature safe. Consequently, the necessity imposes to prepare polymer for long-term usage [50]. Searching in the field of polymer weathering highly needs to the similarity between the artificial and the natural condition, in which the polymer is used. In addition, to exposing it to different required temperatures for the process of aging, the chemical reaction rate is usually related to the temperature. The correlation

between rising polymeric sample temperature and changing its properties leads to deduce a relationship that binds the degradation reaction rate with the increasing temperature [15,51]. The degree of material degradation is extrapolatable after a certain period of time under a specific temperature [60]. Time of polymeric material degradation is shortened by subjecting the effective factors intensively, such as temperature, moisture, light, oxygen concentration, etc. Regardless of the selection of the type and intensity of the influencing agents, the speed of the changing of specimens is interesting as well. Accelerated aging results can tell the assessment of the polymeric resistance to aging.

## 5. Invented ways to the polymer Lifetime Predicting

### 5.1 Thermo gravimetric Analysis for Thermal Degradation Kinetics

Thermal analysis had had a great role in discussing the degradation mechanism of polymeric materials. The information is clear through the several notable published papers which are in specialist in this field [64-69]. In the last decade, Seifi et al. [70] Searched in the field of techniques of thermal analysis for the polymeric materials, specifically in the years (2010-2020). The goal was creation polymers of high thermo-degradation resistant. At the present, protection of the environment is the matter of importance to be managed through figuring out polymers of a specific lifetime [11,50,67,69,71]. Among many different methods to assign the altered state of the tested specimen according to the change of temperature are thermo gravimetric (TG), and differential scanning calorimetry (DSC), which are considered the most famous measuring ways of samples under different conditions [64]. The thermal analysis methods are useful in tracking and discussing the phase variations of polymer, in addition to the chemical reactions resulting from substance temperature changes. It is found significances by those methods to the parameters of kinetic and thermodynamic reactions [74,75]. However, it is likely to deduce the related relationship which links the degradation reaction rate with temperature via exposing the polymer to upraised temperatures. It is feasible to reckon, at a known temperature, the degradation degree of polymeric material later than a limited duration, or the requested time for completion of a particular degradation degree [76]. Several authors embrace variant models of the kinetics, as well as their corresponding functions of conversion [77,78]. Using thermal analysis modes and their techniques has manifested specifically helpful [79,80]. A remarkable aspect of the degradation activity pattern is referred to by activation energy ( $E_a$ ), Arrhenius pre-exponential factor ( $A$ ), and order of reaction ( $n$ ) [69,81-83]. The latter parameters have a special significance in both practical and theoretical aspects. These factors are supportable through the well realizing the mechanism of the degradation of polymer by the arisen chemical reactions. For processing sample at a constant temperature, since the parameter  $K$  is a function of temperature, therefore in this case it becomes a constant. As stated in the Arrhenius equation [64,84] the dependence of the fundamental kinetic of the degradation proceeding is depicted by the following differential equation (2) [78,85]:

$$\frac{d\alpha}{dt} = K(T) \cdot f(\alpha) \quad (2)$$

Whereas:

$K(T)$  refers to the temperature-dependent reaction rate constant

$F(\alpha)$  indicates the paradigm of the chemical reaction.

### 5.2 Arrhenius Style

The measuring of the degradation stage of a material can be assessed by relying on the retreating of its properties [15,23,86]. Temperature is an essential player in determining the deterioration rate; the latter varies in according to the temperature [86]. Raising the temperature is the main reason for accelerating the reaction rate, consequently, raising the value of the reaction rate constant ( $K$ ) [87,88]. The related links between the temperature and the reaction rate constant ( $K$ ) are given in equation (3) as follows [78,89,90]:

$$K = K(T) = A e^{\frac{-E_a}{RT}} \quad (3)$$

Whereas:

$A$  is the factor of the frequency.

$E_a$  refers to the activation energy.

$R$  is the general constant of the gases.



T refers to the absolute temperature.

The usual representation of the above equation is given in a logarithmic formula [15,91], see the following equation (4):

$$\ln k(T) = -\frac{E_a}{RT} + \ln A \quad (4)$$

The reaction rate is obtainable from every change of the potential property of a polymer related to the temperature according to an exposure time at each particular temperature [92]. For successive reaction rates  $K_i$  at varying temperatures  $T_i$ , a specified property ( $X_a$ ) is reachable after different reaction times  $t_i$  (Figure 3) [15,93], Equation (5):

$$F(X_a) = K_i (T_i) t_i \quad (5)$$

Where  $F(X_a)$  indicates the function of the reaction state.

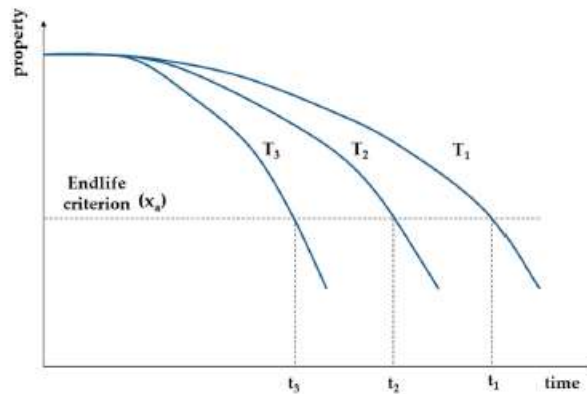


Figure 3. Variation of feature with time at three variant temperatures  $T_1 < T_2 < T_3$  [59].

It is possible to get a logarithmic relationship [15,94], Equation (6) by merging the two equations (4) and (5), as shown below:

$$\ln t_i = \frac{E_a}{RT} + B \quad (6)$$

Whereas, B is a constant.

The relationship is depicted as  $\ln(t)$  proportions with an inverse value of temperature. This representation is called the Arrhenius equation graph [95],  $\ln(t)$  proportional directly with  $T^{-1}$ . This method presents an extrapolation for a specified polymeric material at a given temperature. That is accomplished by calculating the following Equation:

$$e^{\ln t_i} = t_i \quad (7)$$

To cancel the reliance on time in Equation (2), which is linked with the temperature (T) and diversion rate ( $\alpha$ ), when heating progressive throughout equal time intervals, in this case, the differential equation is divided by the heating rate [85], Equation (8):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} f(\alpha) \quad (8)$$

The heating rate is indicated by  $\beta = dT/dt$ .

By applying the velocity equation which depends on the time, in addition to the linear transformation, evaluating the parameters of kinetic: activation energy ( $E_a$ ), and echo factor (A) [85], Equation (9):

$$\ln \left( \frac{\frac{d\alpha}{dT}}{f(\alpha)} \right) = \ln \left( \frac{A}{\beta} \right) - \frac{E_a}{RT} \quad (9)$$

Observation the procedure of aging with one exposure time is inadequate. The requirement imposes to specify the direction of the curves for properties of material at different experimental circumstances. The eventual target of this assessment is to find the extrapolation of the polymer lifetime. Arrhenius plot, Figure 4, shows the extrapolated time as a function of inverse temperature of the material.

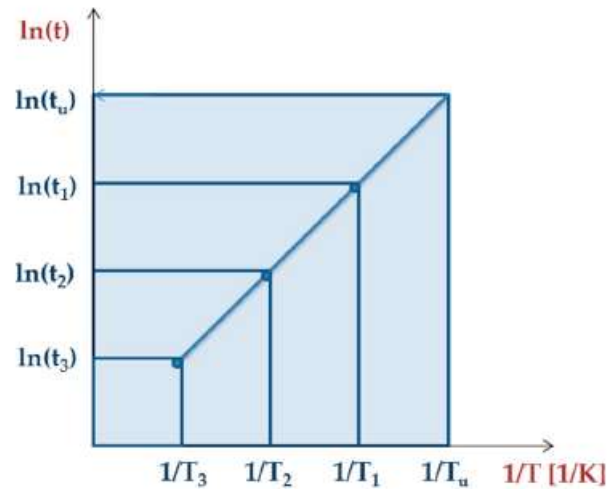


Figure 4. Arrhenius diagram shows a changing of time extrapolating versus the inverse temperature [59].

$\ln(t_e)$  proportionate to  $E_a/RT$ , the activation energy is represented by  $E_a$ .  $R$  is the gas constant. An aging time  $t_{han}$  can be extrapolated in accordance with  $t_n$  (temperature of using) [59]. Arrhenius' method postulates the degradation mechanism at elevated temperature is alike to that under the operating conditions of the material. However, that is not fruitful for all cases because some queer behavior happens for several materials, especially at low temperatures. Therefore, it is not possible to apply such dealing to taking an idea about the polymeric material's lifetime [88].

When were Lewandowski et al. (2016) [15] working on characterizing elastomers by using Time-Temperature Superposition, and Arrhenius' methods, they figured out that the obtained comets were unprocessed. However, this disappointed result might happen just for degradation of elastomers at the complicated conditions. The circumstances under which polymer materials are exposed to physical and chemical interference. Furthermore, the condition of degradation which leads to, alteration of the degradation mechanism is relying on temperature.

In addition, Xiong et al. (2013) [96] exploited this way in order to predict the lifetime of the Nitrite-Butadiene Rubber (NBR) sheet if composite in aviation kerosene by utilizing a fitted nonlinear curve of ATR-FTIR spectra. The measurements were 11, 113 days at 20°C, and 6467 days at 40°C. For the authors, the Arrhenius equation gave valuable results. The composite panels of NBR are still safely applicable in storing the flight kerosene if they succeeded in this use at room temperature for eight years.

Madej-Kiełbik et al. (2019) [97] used the methodology based on analyzing the protective materials of motorcyclists depending on Arrhenius' equation. The constituents of the characterized material were a copolymer of ethylene-vinyl acetate (EVA) and polyurethane. The kinetics changes of the physical or chemical properties polymeric material are helpful to assign the eventual life normal ( $x_a$ ) of that material, at intervals of temperature of 10°C. Conclusively, the calculation of the real material aging time has being possible.

In (2019) Koga et al. [98] search in the field of PVC deterioration and analyzing the causes and results of that chemical reaction. The temperature of that reaction was an essential factor to be considered. The tests of the investigation were Fourier transform infrared spectroscopy (FTIR), small punch testing (SP), and tensile testing. According to the outcomes tests activation energy and the estimated time have been calculated by using Arrhenius method. It turned out the results of the small punch test gave the best result of accuracy. In addition, the latter test predicts the life time of the early minimum destructive effect.

Wang et al. (2019) [99] submitted a model that predicts the lifetime which is related to the aging of the polyethylene (PE) natural gas pipeline. The most important considered condition was the various exerted pressure on the pipeline by the aging of the oxidation under the effect of heat which is so-called Thermal Oxidation Aging (TOA). The relation of Arrhenius was expounded and dealt with as a linear correlation between the oxidation induction time (OIT) as a logarithmic scale at variant temperatures of tests and the



inverse of temperature ( $1/T$ ). The prognosis of the lifetime is over the range 0-0.4 MPa at 20°C. The result shows a surplus required lifetime of 50 years. The authors demonstrated that the method is proper for the pipes of PE and for whatever plastic pipes under the same conditions.

Arrhenius method is helpful for several polymeric materials (e.g., EVA, PE, PVC, NBR, EPDM). The obtained consequences by Arrhenius are helpful but not for the limited degradation by diffusion. This methodology is applicable for predicting polymer lifetime within a temperature domain in a condition of a particular degradation mechanism. Arrhenius Model is the most preferable for the authors to foretell the polymer lifetime for its ability to save time, high reliability, and account for the alteration of aging performance at any time.

## 6. Conclusions

Several factors take part to produce the polymeric material degeneration. These factors could be chemical such as the operation conditions, physical as temperature and radiation, and mechanical factors like stress. Hence, the expected degradation mechanism is to be of massive complication. The most public factors are covered in this paper. Kinetic analyses based on prognoses, because of their practical importance the kinetic style of the polymers can be assessed at potential temperatures out the used values at the laboratory. Arrhenius paradigm presumes the degradation mechanism at temperatures higher than that of the natural using circumstances is resemble at all. Unfortunately, this postulation is not right for all the cases.

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