STUDY OF MECHANICAL AND THERMAL PROPERTIES OF HDPE IN RESPONSE TO ACCELERATED THERMAL AGING

This report submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

by

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DECLARATION

I hereby, declared this report entitled "Study of mechanical and thermal properties of HDPE in response to accelerated thermal aging" is the results of my own research except as cited in the reference.

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APPROVAL

This report submitted to the family of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering The member of the supervisory committee are as follow:

…….

(Principal Supervisor)-Signature & Stamp

…….

(Co-Supervisor)-Signature & Stamp

ABSTRAK

Tujuan kajian ini adalah untuk mengkaji kesan penuaan termal dan kesan kepada sifat mekanikal dan terma HDPE. Kajian penuaan termal digunakan secara meluas untuk meningkatkan masa bahan ke usia. Penuaan termal yang dipercepatkan ialah kaedah untuk menentukan kesan jangka panjang tekanan yang dijangkakan dalam masa yang lebih singkat. Penentuan Q_{10} menggunakan persamaan Arrhenius akan diperinci. Penuaan haba yang dipercepatkan dari High Density Polyethylene (HDPE) telah dikaji dalam tekanan udara dan suhu atmosfera (30° C pada suhu bilik). Perubahan pemanjangan pada rehat, kekerasan bahan tua dan ketumpatan hasil daripada penurunan suhu termooxidatif telah diikuti. Hasil analisis haba dibandingkan dengan yang berkaitan dengan variasi pemanjangan pada rehat, kekerasan dan kepadatan sebagai akibat penuaan termal dipercepatkan. Suhu peralihan kaca, Tg akan dianalisis untuk melihat hubungan antara hasil ujian tegangan dan Tg.

ABSTRACT

The aim of this study is to study the effect of accelerated thermal aging towards the mechanical and thermal properties of HDPE. Accelerated thermal aging is the method to determine the long-term effects of expected levels of stress within a short period of time. The Q_{10} determination using Arrhenius Equation will be determine. The accelerated thermal aging of High Density Polyethylene (HDPE) was studied in air atmospheric pressure and temperature (30°C at room temperature). The changes in elongation at break, hardness of aged material and density as a result of accelerated thermooxidative degradation were followed. Thermal analysis results will be compare with those relating to the variations in the elongation at break, hardness and the density as a consequence of accelerated thermal aging. Glass transition temperature, T_g will be analyze in order to see the relationship between tensile test result and T_g.

DEDICATION

Big applause to my beloved father, Marzuki Bin Ismail, my mother Habibah Binti Baharum, for giving me a lot of support, motivation and encouragement.

Thank you so much & this is a small gift for you.

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Alhamdulillah, praise be to Allah the most gracious, the most merciful, with the highest praise to Allah that I manage to complete final year project successfully without difficulty.

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ASTM D638	-
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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The usage of thermal aging is widely use to speed up the aging process. Historically, those method of claiming deceptively accelerating the deterioration for paper through heat is known to be done since 1899 by W. Herzberg. Accelerated maturing might have been further refined throughout the 1920s, with tests utilizing daylight furthermore raised temperatures constantly utilized with rank the permalloy for different papers in the United States also Sweden. Done 1929, an every now and again utilized technique previously, which 72 hours toward 100 degrees celcius may be acknowledged proportional with 18–25 a long time from claiming characteristic maturing might have been made Toward r. H. Rasch. In the 1950s, specialists started an inquiry into those legitimacy for accelerated thermal aging tests which depended on dry warmth and a solitary temperature, calling attention to that relative humidity influences the substance forms which deliver paper degradation and that the responses which cause corruption to have diverse activation energies. Accelerated thermal aging is testing that utilization disturb states of heat should accelerate the typical thermal aging forms from claiming things. It will be used to help focus those long haul impacts about expected levels from claiming anxiety inside a shorter time, typically over a lab eventually controlled standard test techniques. It is used to gauge the advantageous lifespan of an item or its shelf life when genuine lifespan information may be inaccessibility.

1.2 Problem Statement

Measuring, evaluating or simulating aging of plastic materials can be important for a number of long-term plastic applications, such as in the construction industry. Plastic pipes and plastic insulation are expected to be stable and functional for a long time. On the other hand, it is important biodegradable medical polymers to break down at a desired rate. Polymer aging is directly connected to stability, and often can be predicted and programmed, if needed, for specific applications. Polymer aging naturally take a lot of time to happen. So accelerated thermal aging study is done in order to reduce the time of aging as thermal aging is a step to speed up aging process.

Thus, the effect of thermal aging to mechanical and thermal properties will probably differ from LDPE or other polymer. To obtain this information rapidly, materials of particular interest are subjected to accelerated aging, with observation of the time dependence of mechanical properties(elongation at break, compression, traction resistance, residual deformation under constant deflection. These result allow an evaluation of lifetime under the operating conditions. The thermal lifetime is predicted by the procedure recommended by IEC-216.

1.3 Objective

The objective of this research is :

1. To measure thermal property which is the glass transition temperature Tg at various aging time.
2. To measure the tensile strength at various aging time

1.4 Scope of study

The scope of this study is about the the accelerated thermal aging of HDPE at various temperature. The changes of elongation at break, tranction and density as a result accelerated thermooxidative degradation were followed. Study is focusing on HDPE material. HDPE is defined by a density of greater or equal to 0.941g/cm^3. HDPE has a low degree of branching. The mostly linear molecules pack together well, so intermolecular forces are stronger than in highly branched polymers. HDPE has high tensile strength. It is used in products and packaging such as milk jugs, detergent bottles, butter tubs, garbage containers, and water pipes. The study based on Arrhenius equation. Arrhenius equation is a simple but remarkably accurate formula for the temperature dependence of reaction rates.

CHAPTER 2

Literature Review

2.1 Accelerated Thermal Aging

The usage of thermal aging is widely use to speed up the aging process. Herzberg the one who discover this method told that the probability to boost the natural decay of paper by dry thermal treatment at the early twentieth century(citation). The knowledge of usage of polymeric material's behaviour is needed in response to the surrounding condition as example heat, light, humidity, nuclear radiation, etc and monitoring of the time weakness of mechanical properties (elongation at break, compression, traction resistance, residual deformation as stated by P. Budrugeac (1998). By performing aging process, properties like mechanical can be enhance moderately according to Cysne Barbosa, Ana P *et al.* (2017).

It is realized that the majority of polymeric material have a viscoelastic behaviour even under ordinary loading conditions. Their general mechanical properties change after some time because of aging either in rack or in vivo as referred to Othman Y Alothman *et al*. (2013). Accelerated aging tests have been widely utilized on engine and generator protection frameworks to mimic in a brief span period the weakening components happening amid ordinary operation of numerous years, to recognize protection framework outlines with longer life time and to help the capability of another framework as claimed by M Farahani *et al*.

(2010). A.A Edidin *et al.* (2000) found that accelerated maturing techniques have been created to duplicate the normal maturing process and to precondition add up to joint substitution parts preceding joint test system wear testing. While Ruijin Liao *et al.* (2009) in past study state that under a similar aging condition, both the degree of polymerization (DP) and the leveling-off level of polymerization (LODP) for normal ester aged paper were higher than the ones for mineral oil matured paper, and the small scale surface of common ester aged paper was obliterated less truly than that of the mineral oil aged paper.

Sun, D.C *et al*.(1994) claimed that the strategy requires an ideal beginning warming rate and an ideal maturing temperature to quicken oxidation responses. In view of oxidation-incited material property changes (crystallinity by DSC, ductile properties by ASTM D638 tensile test, and oxidation file by FTIR), connections between's quickened maturing time, rack maturing time, and implantation time can be acquired. Thermal aging of materials was uncovered to achieve the diminishing in shrinkage temperature, supreme estimation of enthalpy of denaturation in water and a few changes in non-isothermal parameters trademark for lack of hydration process in static air.

2.1 Arrhenius Equation

This section will explain about the background of Arrhenius Equation, the simple derivation of the equation and relationship against the accelerated thermal aging. Some of previous researched also will be showed.

2.2.1 Background

The Arrhenius mathematical statement is an equation to those temperature reliance about response rates. The comparison might have been suggested Toward Svante Arrhenius done 1889, In view of the worth of effort for dutch physicist Jacobus Henricus Van't Hoff who required noted done 1884 that Van't Hoff's mathematical statement for those temperature reliance for equilibrium constants prescribes such an equation for the rates from claiming both forward and reverse reaction. This mathematical statement need limitless and important requisition in determining pace of chemical reactions and for determining of energy of reaction. Arrhenius gives a physical support also translation to the equation.

Coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions can be used to model the temperature dissimilarity of dispersion. M. Celina *et al*. (2005) state that accelerated thermal aging exposure is strongly related to lifetime estimation studies on polymeric material. She also told that the study of polymeric aging had been used for decade relating to Arrhenius Equation. Arrhenius extrapolation assume that a chemical degradation process is controlled by a reaction rate k proportional to exp (-E_a/RT) where E_a is the activation energy, R is the gas constant (8.314J/mol K), T absolute temperature and A the pre-exponential factor. From the information above the equation of Arrhenius can be describe as

$$k = A \times \exp(\frac{-E_a}{RT}) \text{ or } \ln k = \ln A + \frac{-Ea}{RT}$$

2.2.2 The Equation

The Arrhenius is easy but remarkably accurate formula for the temperature dependence of reaction rate. Mathematically it can be described as

$$K = Ae^{-Ea/RT}$$

Equation 2.0

- K is the rate constant
- T is the absolute temperature (in kelvins)
- A is the pre-exponential factor, a constant for each chemical reaction. According to collision theory, a is the frequency of collisions in the correct orientation
- E_a is the activation energy for the reaction (in the same units as RT)
- R is the universal gas constant

Significantly, the formula of Arrhenius Equation give the dependence of rate of constant K of a chemical reaction on the absolute temperature T (Kelvin), where A is the pre-exponential factor, Ea is the activation energy , and R is the universal gas constant.

M. Celina *et al*. (2005) explained that chemical degradation process is assumed by Arrhenius extrapolation by reaction rate *K* is proportional to exp -(*Ea/RT)* . Previously in recent researched, a straight line will allowing simple extrapolation to lower the temperature will be the expected result as log-plot of reaction rates (K) or degradation times (1/K) versus inverse temperature (1/T). The temperature impact on the thickness took after an Arrhenius-type relationship and every single nectar assortment displayed Newtonian behaviour. On the

off chance that the Arrhenius condition constants (μ0 and Ea) for a specific nectar are known, the Arrhenius model can be utilized to figure the consistency of these nectars at particular temperatures, refuting the requirement for dreary thickness assurance as stated by Brenda Mossel *et al*. (2000). Mario Schwaab and Jose Carlos Pinto (2007) claimed that the Arrhenius condition is a standout among the most surely understood conditions in the compound field and is generally used to portray the temperature reliance of dynamic constants. This condition contains two parameters, the recurrence factor and the actuation vitality, which are generally assessed from trial information. Matt Petrowsky and Roger Frech(2009) found that the temperature reliance of the conductivity as an Arrhenius articulation and demonstrate that the tentatively watched non-Arrhenius conduct is because of the temperature reliance of the dielectric consistent contained in the exponential prefactor. Scaling the tentatively measured conductivities to conductivities at a picked reference temperature prompts an "adjusted" Arrhenius condition that gives an astounding portrayal of temperature-subordinate conductivities.

2.2.3 Relationship Arrhenius Equation with Accelerated Aging Time

The relationship between Arrhenius Equation and Accelerated Aging Time is strongly discuss in previous research and study. The relationship can be start by combining two first order of Arrhenius Equation which is equation 1.2 and 1.3.

$$K = Ae^{-Ea/RT}$$

Equation 2.1

$$K_1 = Ae^{-Ea/RT_1}$$

Equation 2.2

$$K_2 = Ae^{-Ea/RT_2}$$

Equation 2.3

To continue reviewing the relationship, natural log both side to both side of equation so that it will become :

$$\ln(k_1) = \ln(Ae^{\frac{-Ea}{RT_1}})$$

Equation 2.4

$$\ln(k_2) = \ln(Ae^{\frac{-Ae}{RT_2}})$$

Equation 2.5

Next use the log product rule to produce:

$$\ln k_1 = \ln(A) + \ln(\frac{-Ea}{RT_1})$$

Equation 2.6

$$\ln k_2 = \ln(A) + \ln(\frac{-Ea}{RT_2})$$

Equation 2.7

Since $\ln(e^x) = x$,

$$\ln(k_1) = \ln(A) - \frac{Ea}{RT_1}$$

Equation 2.8

$$\ln(k_2) = \ln(A) - \frac{Ea}{RT_2}$$

Equation 2.9

Make of previous equation equal $\ln(A)$ so the equation will be like:

$$\ln(A) = \ln(k_1) + \frac{Ea}{RT_1} \quad \text{and} \quad \ln(A) = \ln(k_2) + \frac{Ea}{RT_2}$$

Equation 2.10

Equalize the equation to become $\ln(k_1) + \frac{Ea}{RT_1} = \ln(k_2) + \frac{Ea}{RT_2}$

Equation 2.11

Then, rearrange the equation $\ln(k_2) - \ln(k_1) = \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$

Equation 2.12

Use the natural log quotient rule, $\ln(\frac{k_2}{k_1}) = \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$

Equation 2.12

Separate $\frac{Ea}{R}$ factor, so that $\ln(\frac{k_2}{k_1}) = \frac{Ea}{R}(\frac{1}{T_1} - \frac{1}{T_2})$

Equation 2.13

As the example to prove the relationship of *Ea* and $\frac{K_2}{K_1}$,

$k_2 = 2 \qquad T_1 = 290°K \qquad R = 8.134 \frac{J}{molK}$

$k_1 = 1 \qquad T_2 = 300°K$

$\frac{k_2}{k_1} = 2 \qquad T_2 - T_1 = 10°K$

$\ln(2) = \frac{Ea}{8.134}(\frac{1}{295} - \frac{1}{305})$ as the conclusion,

$Ea = 51.85 \approx 50 \frac{kJ}{mol}$

- $\frac{k_2}{k_1}$ rate doubles only if Ea$\approx 50 \frac{kJ}{mol}$
- If $T_1 = 295°K$ and $T_2 = 305°K$ remain constant

$\frac{k_2}{k_1}$ will increase as *Ea* increase.

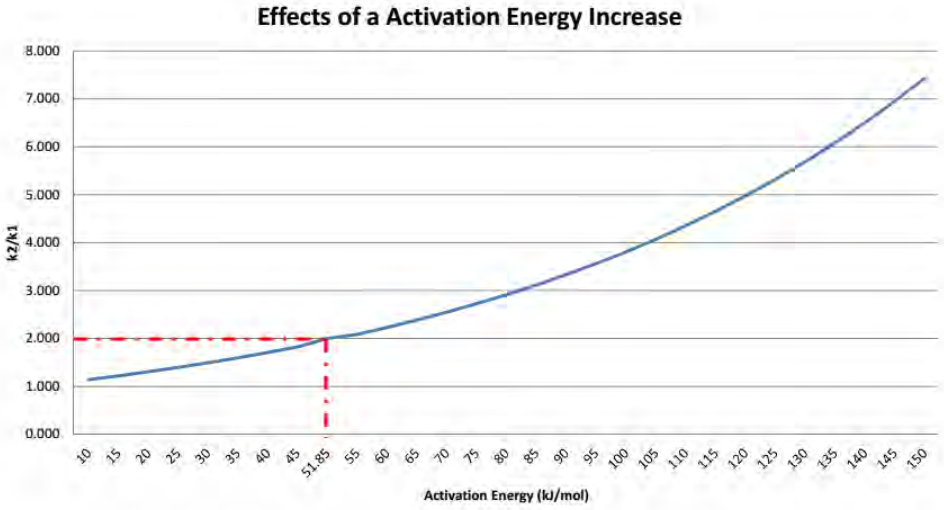

Figure 2.1: Example of graph of Activation Energy against $\frac{k2}{k1}$

This graph show the relationship of $\frac{k2}{k2}$and activation (Ea). Clearly shown that rate of reaction is increase when activation energy is increase which is they are directly proportional to each other.

Assume that the chemical reactions involved in the deterioration of materials follow the Arrhenius reaction rate function. A 10°c increase in temperature of a homogeneous process results in, approximately two times change in the rate of a chemical reaction (Q_{10}) as follow the ASTM F1980 where ASTM F1980 provides documentation for developing accelerated aging protocols to promptly determine the effects, if any at all, due to the passage of time on the sterile integrity of the sterile barrier system (SBS), as defined in ANSI/AAMI/ISO 11607-1:2006, and the physical properties of their component packaging materials.

As stated from ASTM F1980, a 10°c rise in temperature of a homogeneous process results in, roughly two times change in the rate of chemical reaction (Q_{10}) where (Q_{10}) is the a measure of the temperature affectability of an enzymatic response rate or on the other hand a physiological procedure because of an expansion by 10°C. Discontinuities are demonstrating physiological annoyances. Most Q10-values are double a multiplying of atoms with a vitality higher than the activation energy that is required for an enzymatic response to happen. Back to