# A STUDY ON TENSILE PROPERTIES OF ACRYLNITRILE BUTADIENE STYRENE (ABS) SUBJECTED TO THERMAL DEGRADATION



# UNIVERSITI TEKNIKAL MALAYSIA MELAKA

# A STUDY ON TENSILE PROPERTIES OF ACRYLNITRILE BUTADIENE STYRENE (ABS) SUBJECTED TO THERMAL DEGRADATION

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A report submitted in fulfilment of the requirements for the degree of Bachelor of Mechanical Engineering (Structures & Materials)



# UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2017

# **DECLARATION**

I declare that this project report entitled "A Study on Tensile Properties of Acrylonitrile Butadiene Styrene (ABS) Subjected to Thermal Degradation" is the result of my own work except as cited in the references



### APPROVAL

I hereby declare that I have read this project report and in my opinion this report is sufficient in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering (Structures & Materials).



# **DEDICATION**

I dedicated this Final Year Report to Faculty of Mechanical Engineering, my supervisor, Dr. Mizah Binti Ramli, my beloved parents and friends.



### ABSTRACT

Nowadays, ABS polymers are widely used in order to upgrade of new and more versatile of polymer time by time. ABS is one of the thermoplastic polymer types which have some properties such as it can be reheated to soften and reshape after reheating process occurs. It also does not undergo significant chemical change. The ABS polymer has weaker bonding among molecules when reheating that allowing reshaping occurs. Some of application of ABS relates with varying temperature. However, the performances of ABS polymer can change based on different temperatures applied on it. So, this project was conducted to investigate the strength and tensile properties of ABS samples at thermal degradation with varying temperatures and duration of heat treatment applied. Besides, morphological study were conducted in order to investigate the behavior and changes surface of samples when thermal degradation process applied on it with different time duration and room temperature. There are few procedures, equipment and machine used for achieving these project objectives such as hot press machine, laser machine, tensile machine and scanning electron microscope. After completing the testing, it can be concluded that the longer time duration for heat treatment on thermal degradation process, the higher brittleness of the ABS material. The morphological surface of ABS material shows the different time duration of heat treatment on samples, it results difference changes of surface behaviour of ABS samples.

### ABSTRAK

Pada masa kini, Polimer ABS telahpun digunakan secara meluas dan ditambahbaikkan produk terbaru yang lebih versatile dari semasa ke semasa. Polimer ABS terdiri daripada thermoplastik polimer yang mempunyai ciri-ciri tertentu seperti dapat dibentuk kembali selepas proses pre-pemasanan untuk dileburkan dan dibentuk semula. Selepas proses pemanasan, Polimer ini juga tidak mengalami perubahan kimia yang ketara serta mempunyai rintangan suhu yang tinggi. Polimer ABS mempunyai ikatan yang lemah antara molekul-molekul apabila dipanaskan dimana ia membenarkan pembentukkan semula berlaku, Namun, prestasi kekuatan ABS polimer boleh berubah berdasarkan keadaan suhu yang digunakan keatasnya. Oleh itu, projek ini dikendalikan bertujuan untuk mengkaji ciri- ciri kekuatan penarikkan sampel ABS pada keadaan pemburukkan thermal keatas sampel tersebut. Selain itu, kajian morpologikal juga dijalankan bagi menyiasat sifat dan perubahan sampel-sampel tersebut apabila dikenakan suhu dan masa yang berbeza semasa proses pemburukan termal. Terdapat beberapa prosedur dan alatan serta mesin yang digunakan bagi menjayakan projek ini seperti mesin 'hot press', mesin laser, mesin tensil dan elektron mikroskop. Selepas mengkaji keadaan kekuatan bahan dan kajian morpologikal pada permukaan sampel-sampel, hal ini dapat dirumuskan bahawa semakin lama masa yang diambil untuk ujian pemanasan, tahap kerapuhan pada bahan ABS menjadi semakin tinggi. Kajian morpologikal juga menunjukkan perubahan pada struktur dan sifat keatas sampel ABS apabila ia dikenakan tindakan suhu dan masa yang berbeza.

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# LIST OF ABBREVATIONS

ABS	=	Acrylonitrile Butadiene Styrene
PVC	=	Poly Vinyl Chloride
PE	=	Poly Ethylene
PP	=	Poly Propylene
EN ISO	=	International Organization for Standardization
HB	-TY In	Horizontal Burn
UL	TEKAN	Underwriters Laboratories
FR	The	Flame Retardant
ESC	= 200	Environmental Stress Cracking
SEM	ملاك	اوینوم سینی نی Scanning Electron Microscope
UTM	UNIVE	Universal Testing Machine
LOI	=	Limiting Oxygen Index

# LIST OF SYMBOL

т	=	Mass
ρ	=	Density
v	=	Volume of Material
3	=	Engineering Strain
σ	=	Engineering Stress
Р	=	Applied Load
Ao	=	Original Area of Cross-section Sample
Lo	=	Original gauge length
Е	=	Modulus of Elasticity
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### **CHAPTER 1**

### **INTRODUCTION**

#### 1.0 Background

#### 1.1 Polymer

The word of polymer was known since 1866 by Berthelot in an article of the Chemical Society of France, noted that "sty Rolene (styrene) was heated at 200°C during a couple hours then transforms itself into a resinous polymer" (Nouveau, 1900). Then in year 1920, Herman Staudinger proposed concept of polymers which is been used until today and for his work he got Nobel Prize in 1953 in science of macromolecules (Nouveau, 1900). The introduction of new and more versatile of polymer was upgraded time by time.

There are two types of polymer that are thermosetting polymer and thermoplastic polymer. The main different of these both type of polymer is thermosetting polymer cannot be reheated to soften, shape and mould meanwhile thermoplastic polymer can be reshape after reheating process and they also do not undergo significant chemical change. Process of shaping and reheating of the thermoplastic polymer can be repeated (Wiley, 2011). Example of thermoplastic polymer is poly Ethylene, Polyamide, Polystyrene, poly Vinyl Chloride (PVC) and Acrylonitrile Butadiene Styrene (ABS) polymer.

#### 1.1.2 Thermoplastic Polymer

Thermoplastic polymer is the materials that are made of polymers that are connected by van der Waals forces to produces linear or branch structures (Wiley, 2011). This kind of polymer tends to be constituted of long chain monomers and possess a common property. They soften when heated and are frequently used to form shapes. This is because the bonding among molecules is weak and become weaker when reheating to allowing reshaping occurs.

Thermoplastic polymers are dissolving in certain solvent and swell in presence of certain solvents. Thermoplastic also highly creep materials (Toyolac, 2012). ABS polymers have these criteria because ABS polymers are in thermoplastics categories. The strength of ABS polymer can be measured by conducting tensile test according to international standard EN ISO 527 Plastics (CEN, 1996). There are some applications of ABS polymers like casing for telephone, luggage, Lego, computer housings, pipes, and car bumpers. Figure 1.1 below shows the casing of electronic device that was made by using ABS polymer materials



Figure 1.1 Casing of Telephone by Using ABS Polymer.

(Source: Campo, 2007)

Even though ABS plastics are widely used for mechanical purposes, they also have excellent electrical properties that are over a wide range of frequencies. These properties are little affected by temperature and atmospheric humidity which is acceptable operating range of temperatures. The final properties will be influenced to some level by the conditions under which the material is processed to the final product. For example, moulding at a high temperature can enhance the gloss surface and heat resistance of the product meanwhile the highest impact resistance and strength are obtained by moulding at decrement in temperature (Kulich, Gaggar, Lowry, & Stepien, 2007). ABS polymers also have disadvantages like poor weatherability because it is not weather resistant and opacity (Kulich et al., 2007). ABS polymers also have poor solvent resistance and will produce high smoke when it is burned. Table 1.1 below shows the standard properties of ABS polymers.

Table 1.1: Mechanical Properties of Acrylonitrile Butadiene Styrene (ABS) Polymer

Common Name	Density (g/cc)	Flexural Strength (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Heat Resistance (°C)	Melting Temperature (°C)	Wall Thicknes s (3mm)
ABS	75.84	1.04	25 - 50	3 - 75	110	175 - 200	3
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(Source: Test Standard Labs LLC, 2014)

# **1.2 Problem Statement**

Nowadays, ABS polymers are widely used in many applications. Among other type of polymer, ABS is commonly used as a principal material for devices and housing appliances. The certain application of ABS is relates with the varying temperatures. Therefore, it can affect the performances of ABS application due to the temperature effect on ABS. The past research shows that ABS plastics was sensitive to boiling treatment and the strength rate of ABS decreased significantly with increasing boiling time (Chong et al.,2014). Apart from that, Fraunholcz (2004) found that ABS polymer at elevated temperature facilitate molecular arrangement and change the surface of boiling treated may be attribute to molecular arrangement. However, it is possible to optimize treatment and reprocessing conditions in order to produce better ABS performance specifications. Based on that, a new method, heat treatment on thermal degradation will be conducted on different temperature with several duration conditions in order to analyze the tensile properties of ABS polymers at different temperature and time as compared to the room temperature properties. Thus, the surface of ABS also will also tested in electron microscope in order to investigate morphological surface on each conditions.

# 1.3 Objectives

The objectives of this study are:

1. To investigate the tensile properties of ABS material at differences temperature and time duration.

2. To characterize the morphological surface of ABS material at differences of temperature and time duration.

# 1.4 Scope of Project

The focus of this project is to conduct literature review on ABS polymer material and other thermoplastic polymers on its tensile properties under varying temperature. After that do the sample preparation such as prepare raw material and mold it into pieces then setting the experimental apparatus. The sample will be fabricates according to the ISO 527 plastic standard. Then, experimental testing will be conduct by using Humidity Oven at varying temperature and using INSTRON machine for tensile testing. All the experiment results and data will be analyzed and relates with the morphological surface study at fracture surface of the specimen in order to understand the behavior and characteristics of ABS under varying temperature. Finally, do report writing.



# **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Introduction

This chapter review the history of ABS plastics, application, challenges, properties of ABS, processes and mechanisms of ABS by discussing the literature published in recent years. Advance technology in industry nowadays has produce complex and sophisticated components and device in order to match world demands. Along with this development, researcher has explored the advancement of ABS polymer materials potential to completing the lack of technology components in term of preventive maintenance involved temperature.

ABS is a thermoplastic polymer that has butadiene part that will distributed over the acrylonitrile-styrene matrix. This material has high toughness, excellent dimensional stability, easy to process, chemical and wears resistance. ABS also can enhance the strength and structural integrity as well as to improve durability and thermal resistance resulting in plastic properties of the material.

#### 2.2 Acrylonitrile Butadiene Styrene (ABS)

### 2.2.1 Definition of ABS

The name of ABS is derived from combinations of three main monomers which are Acrylonitrile, Butadiene and Styrene. The bonding of this monomer is shown as figure 2.1 below.



Figure 2.1: Chemical bonding structure of ABS monomers; Acrylonitrile,



These three monomers are typically added together in specific proportions: 15-35% of Acrylonittile, 5-30% of Butadiene and 40-60% of Styrene (Steinwall, 2003). A small change even in one of the monomers can create drastic changes in the mechanical and physical properties of ABS (Campo, 2007). Each of these monomers has their own function such as Acrylonitrile can improve the enhancements of chemical and thermal in the structure. It also is used as a precursor in the manufacture of synthetic polymers, especially acrylic fibers, nylon and synthetic rubber (Steinwall, 2003). Meanwhile, Butadiene is used in the manufacture of synthetic rubber, latex paints and nylon because it can enhance impact strength and toughness of the plastic. Butadiene also has high wear resistance meanwhile Styrene is used to make glossy surface on plastics. All in all, ABS materials have high impact strengths up to 4 to 5 times as compared to polystyrenes. The atomic components of these three chemical compounds are exclusively carbon, nitrogen and hydrogen which is carbon being the predominant atomic species (atomic weight/molecular weight). The only source of nitrogen in the plastic is acrylonitrile, which contains approximately 26% nitrogen. The weight percentage of hydrogen is relatively small (joseph, 1986).

Moreover, ABS can be recycled by using a process called "froth flotation". Froth flotation is a process that separates high purity plastics from waste streams containing a mixture of plastics (Argonne, 2008). This is the only process that can recover over a 99% purity level from recycled ABS (Argonne, 2008).

# 2.2.2 Application of ABS

Rapid development of technology and industrial engineering has created various kinds of new devices and components that use ABS materials to satisfy the working mechanism in high performance. ABS is everywhere, from refrigerator's part to instrument panels of cars and even to electronic devices. The future worldwide growth of ABS predicted to increase until 4 to 5% by industry observers annually (Icis, 2008). It seems as if there will be no shortage of demand for the ABS industry any time soon (Icis, 2008). Among the applications of ABS discussed are household items, automotive applications, construction industry and electronic tools as shown in Table 2.1 below.

Main Topic	Application	Description	Source
Household	refrigerators	ABS used in crisper pans, breaker strips, shelves, shelf supports, evaporator parts trays and kick plates.	(Campo, 2007)
	Kitchen Applicants	Blenders, electric can openers, coffee makers, and vacuum cleaners	
	Air Conditioning Units	Covers of Air Cond	
111	Toys	Lego bricks	(Brisimitzakis, 1994)
Automotive Applications	Car's components	Bumpers, seating, dashboard, exterior trim, light's covers	(Katarina, 2010)
Constructions	کل ملیسی IVERSITI TEKN	Waste, vent pipes, pipe fittings and poor filter housings.	(Campo, 2007)
Electronic tools		Telephone housings, portable phones, electric drills, and keyboard keys	

Table 2.1: Application of ABS Polymer

### 2.3 Challenge of ABS

#### 2.3.1 Flammability

Most plastic are carbon-based materials and will burn and give off gases and smoke when subjected to flame. Plastics are excellent fuels but are generally classed as ordinary combustible and fall into the same category as wood, leather and many other common materials. All of these materials will degrade at very high temperatures into volatile and gaseous combustion products.

Basically, ABS has a low Limiting Oxygen Index (LOI) with a range of 17 to 18 % (Pál and Macskásy, 1991). ABS materials without flame retardant are easily burned with a luminous yellow flame, smoking strongly and continue to burn after removal of the ignition source. The high impact ABS will have a smell of burnt rubber (Troitzsch, 1980). ABS grades that meet various standards for flammability performance are available. The non-flame retardant (FR) generalpurpose grades are generally classified as 94HB according to Underwriters' Laboratories Test Method UL94, and also meet Motor Vehicle Safety Standard 302. These grades are used in applications having a reduced fire risk. For applications requiring higher degrees of flame retardancy, ABS grades have been developed based on alloys with PVC or through an additive approach using halogen in combination with antimony oxide. Included among the FR grades are materials that meet the Underwriters' UL94 VO requirements beginning at a minimum thickness of 1.47 mm (Bach and Knorr, 1989).

# 2.4 Tensile Testing

The tensile test is used to study the strength of a material when it is subjected to a tensile load which is tends to pull apart the two ends of an objects (V.Rajendran, 2011). The tensile test is carried out in a Universal Testing Machine (UTM). In this project, the UTM that was used is INSTRON Machine Model- 8872. The material under test is usually round, square or rectangular. It is sufficient to obtain the parameters of materials because UTM has provision to hold the samples with pin end, threaded end and shouldered end.

Standard used for this project is ISO 527 to determine tensile properties of ABS samples. The test specimen should be in dumbbell shaped based on (CEN, 1996). This testing is carried out on the basis of ISO 527 standard test method for tensile testing of ABS material.

#### 2.4.1 Strain Rate Effects

For many materials, the stress – strain curves are sensitive to strain rate,  $\varepsilon$ . The lowest range of strain rates corresponds to creep and stress – relaxation tests. The tensile test are usually conducted in the range  $10^{-4}s^{-1} < \varepsilon < 10^{-2} s^{-1}$  (Chawla, 2009). The highest range of strain rates correspond to the passage of a shock wave through the material. Figure below shows the stress strain curve of polymers.



Figure 2.2: Stress - Strain Curves for Polymers Material

(Source: Turner and Burr, 1993)

From the strain-stress curve, the following mechanical properties are obtained for the specimen under test.

# 1. Engineering Stress

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It is obtained by taking the ratio applied load (P) to the original area of cross-section of the sample (Ao). The formula of Engineering stress can be obtained by eq. 2.1 below;

Engineering Stress, 
$$\sigma = \frac{P}{Ao}$$
 (2.1)

2. Engineering Strain

Engineering strain is the ratio between elongation and the original gauge length (Lo) as shown as equation 2.2 below.

Engineering strain, 
$$\varepsilon = \frac{L-Lo}{Lo}$$
 (2.2)

3. Yield strength

The stress at which the slip becomes noticeable and significant is known as yield strength. It also defined as the stress required to producing a small value of plastic deformation.

#### 4. Modulus of Elasticity

The modulus of elasticity or young modulus is the slope of the stress-strain curve in the elastic region. The modulus is a measure of stiffness of the material. A stiff material with a high modulus of elasticity maintains its size and shape even under an elastic load. The formula as shown as eq. 2.3 below;

Modulus of Elasticity, 
$$E = \frac{\sigma}{\varepsilon}$$
 (2.3)

Where the symbol of  $\sigma$  is for mechanical stress and  $\varepsilon$  is the mechanical strain.

### 5. Tensile Strength or Ultimate Tensile Strength

The ultimate tensile strength is the ratio of the maximum load applied to the original area of cross section of the material. The tensile strength is the stress at which necking begun in ductile materials. The tensile strength is not relatively important as compared to yield strength but it is used to estimate the other properties that are very important to measure. The tensile strength is an easily measurable quantity and it is also available in handbooks.

### 6. Percentage Elongation

The percentage elongation is the ratio of increase in length to the original length of the sample. The formula 2.4 below shows the ways to calculate percentage elongation.

Percentage elongation = 
$$\frac{\text{increase in length}}{\text{original length}} X 100$$
  
=  $\frac{Lf - Lo}{Lo} X 100\%$  (2.4)

Where Lf and Lo are respectively original length and gauge length after fracture occurs.



#### **CHAPTER 3**

#### METHODOLOGY

### 3.1 Introduction

This chapter will give a chronology on how the material of ABS plate is made up starting from the beginning of the process until the testing process. There are five crucial parts that need to be completed for this project. The actions that need to be carried out to achieve the objectives in this project are lists below.

### 1. Sample Preparation and Fabrication

ABS is used as material for specimen preparation. In this step, specimen will be prepared. ABS has been chosen as raw material and the fabrication process will be conducted by using Hot Press Machine. After that, the specimen will be cut according to specific dimension. Moreover, the next step is testing reliability of sample by gone through cyclic temperature. Finally, the process goes through tensile test.

# 2. Environmental Testing

After completing sample fabrication, the sample will be tested on heat treatment by inserting sample into oven to compare the behaviour and strength of the specimen that in elevated temperature with sample in room temperature.

# 3. Tensile Testing

Tensile testing will be conducted after completing the sample. All the samples will be conducted by using tensile testing in order to compare the Modulus Strength, Young Modulus, Stress-Strain behaviour of all samples at room temperature and cyclic temperature.

### 4. Morphological Analysis

In this step, the morphological surface study will be done to verify the failures that occur within the specimen. The sample will be examined by using Scanning Electron Microscope (SEM) for analyse the structure and surface behaviour of an ABS.

# 5. Report Writing

All the data will be gathered and analysed. The explanation and discussion of along the project will be stated in the report.

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A flowchart is also prepared as a guideline for the execution of this project. The methodology of this study were summarize in the flow chart as shown in Figure 3.1 below.



Figure 3.1 the Flow Chart of the Methodology along this final year project

### **3.2** Sample Preparation and Fabrication

# 3.2.1 Material

There are two types of ABS raw material that can be used in this project which is in powders and pellets sizes. The ABS materials that are used are in pellets sizes. The sizes of these pellets are in range 2 to 3 mm each. Figure 3.2 below shows the raw materials of ABS before and after fabrication process.



Table 3.1 below shows the mechanical properties of ABS material based on manufacturer Chi Mei Corporation. There are a little bit different of amount and parameters of ABS properties in this manufacturer. The main factor of this case is the different step of manufacturing process and environment of this company that affect the mechanical properties of the material.
Туре	Mass density (g/cc)	Melt flow index (°C)	Tensile Yield Strength Kg/cm <sup>2</sup>	Tensile elongation (%)	UL Flammability
PA-757	1.05	200	470	25	1.5mm HB

Table 3.1: Mechanical Properties of ABS Material According to Chi Mei Corporation.

(Source: C.Corp, 2013)

## 3.3 Molding Process

#### 3.3.1 Motorize Hydraulic Molding Test Press

The ABS pellets was fabricate into acrylic sheet by using Motorize Hydraulic Molding Test Press Model-GT-7014-A as shown in Figure 3.3 below.



Figure 3.3 Motorise Hydraulic Molding Test Press Model-GT-7014-A

This machine is very convenient for preparing test specimens. This machine also known as hot press machine that have capacity up to 50 ton and can held the temperature until  $300 \, {}^{0}$ C. This model can heat or cools the material by clamp mold between the electric heating and cooling plates of

the machine and compress the mold with specific pressure and time. The maximum dimension of mold can be used in this machine is with 100 cm length, 150 cm width and 70 cm thickness.

#### 1. Sample Fabrication Process

There are four steps must be followed in order to conducting Hot Press Machine which is setting temperature and pressure, preheat or soaking time, pressing time and cooling time. The first step to conducting this machine is by on the machine and switching the On/Off button as labelled on the Figure 3.3 above. The machine can be run after key in the desired Temperature (T) and Pressure (P) on the machine. The Hot Press Machine will be automatically heated and take a few times to reach the desired temperature. After that, ABS raw material will be weigh with desired amount and then spread it into the mold. After the temperature reached, the mold with raw material inside it will be put on to 'electric heating plates' for heating process. For preheat time, 'compress' button will be push and press the 'stop' button after the upper mold surface almost reach the upper plates of hot press machine. The function of preheat or soaking time is to make sure the mold of material and the hot press machine reach temperature equilibrium. That mean, the temperature of mold and machine's plate are in same degrees to ensure the material melt completely. After preheat the mold, press the compress button until it completely clamp with upper plate and set pressing time at 'timer' button. In this process, the material in the mold will be melt and turn into liquid condition then the material will fill the mold shape. The function of compress button is to lift up the plates and it can be controlled by pushing

stop button. The return button is used to pull down the plates if over compress occurs. After done the pressing process, the mold will be put on the 'electric cooling plates' to undergo cooling process. For activate the cooling machine, switch on the pump and press the 'cooling' button. After few minute, open the mold and carefully remove the material.

#### 2. Parameters

The mold that has been used to get 3 mm thickness of sheet is with dimension of 300 mm length, 300 mm width and 3 mm of thickness as shown in figure below. The sample that can be produced is in dimension with 250 mm of length and 250 mm of width and 3 mm of thickness. The parameter of the mold and ABS sheet can be seen in figure 3.4 below.



Figure 3.4: The Dimension of (a) Mold Casing (b) ABS Sheet Produced

By using formula (3.1) and (3.2) below, the amount of raw material needed is 195g.

Volume = length x width x thickness 
$$(3.1)$$

Density, 
$$\rho = \frac{\text{mass}}{\text{volume}}$$
 (3.2)

The table 3.2 below shows the parameters that have been used while fabricate ABS pellets into ABS sheet.



Table 3.2 Parameters Used In Fabrication of ABS Materials

3.3.2 CUTTING PROCESSNIKAL MALAYSIA MELAKA



Figure 3.5: The Shape and Dimension of Sample

The Figure 3.5 above show the shape and dimension of the samples that need to be cut before tensile test were conducted. The shape of sample that has been used is in dumbbell shape. After fabricate the samples and get around 4 pieces of acrylic ABS sheet, the sample needed to be cut into dumbbell shape with specific dimension based on ISO 527 standard as shown in figure 3.5 above.

There are many ways to cut the sample into dumbbell shape. The best way is by using Laser Machine as shown in Figure 3.6 below. This machine can cut the samples by setting amount of samples needed in one sheet of acrylic ABS and key in dimension using on Solidwork drawing into the CorelDrawX5 software. The format of Solidwork is must be in dwg or dxf format. The software cannot detect the drawing if it not saved into this format. Besides that, this machine use laser as a medium of cutter. The maximum thickness that can be cut by using this machine is 5 mm. The time taken to cut one pieces of sample is 1 minute. In one piece of ABS sheet, the sample can be obtained maximum 9 or 10 pieces.



Figure 3.6: Trotec Laser Machine Model Speedy300flexx

#### 3.4 ENVIRONMENTAL TESTING

After fabricate ABS raw material into plates, three of the sample was set under room temperature in order to investigate the strength of material by using different temperature. These samples will be examined directly by using tensile testing. The room temperature is considered 24°C because the samples were kept in tensile room. 24°C is the temperature of the tensile room. The samples was labelled as shown in table 3.3 below to avoid confusing during experiment were conducted.

N	Name of Sample	Amount of Sample	
Ser.	ABS-RT-1	1	
TEKA	ABS-RT-2	1	
Field	ABS-RT-3		
140	(in the second s		
للك	کل ملیسیا ہ	ومرسيتي تيكنيه	وي
UNIV	ERSITI TEKNIK	AL MALAYSIA MELA	KA

Table 3.3: Label of samples for Room Temperature

#### **3.4.1** Thermal Degradation



Figure 3.7: Humidity Oven Model MEMMERT 100-800

Figure 3.7 above shows the humidity oven that will be used in order to test the reliability of samples in few temperatures. This model size has 160 mm of width, 1190 mm of height and 710 mm of depth in this oven. This machine has temperature range between 20°C to 220°C and has two stainless steel grids. This oven also can hold maximum loading until 160 kg.

In this process, 18 samples were used to test heat treatment on ABS sample. These samples were tested on two condition of temperature which is in 50°C and 80°C because the best range of to test ABS sample is from -20°C to 80°C and the Humidity Oven Model MEMMERT 100 – 800 only can set temperature on  $+30^{\circ}$ C to  $+220^{\circ}$ C. From these two temperatures, each temperature was set on three type of time which is in 10 hours, 30 hours and 50 hours. Three of samples were tested on  $50^{\circ}$ C of temperature and placed in the oven for 10 hours. The sample then taken out and then the process repeated by using same temperature and difference time which is in 30 hours and 50 hours. After the tests done, the same method was repeated by using 80°C. This method used to investigate the strength of ABS sample based on difference temperature and time. Table below show the condition and amount of ABS sample tested in this Humidity Oven.

	Temperature		Time (hours)			
	(°C)	10	30	50		
	50	3	3	3		
	80	3	3	3		
3.5 Tensile	Testing			اونيومري IELAKA		

Table 3.4: Condition and Amount of ABS sample in Heat Treatment

E.

Figure 3.8: INSTRON Tensile Machine Model-8872

This testing machine has double-acting servo hydraulic actuator with load cell capacity up to 20 kN or 5620 lbf as shown in figure 3.8 above. This model also is compatible with a large range of grips, fixtures, chambers, video extensometers and protective shields. It uses extensometer to record the elongation or extension of the sample test by using Bluehill software. Tensile testing will be conducted after performing reliability test on climatic chamber. The specimen gripped faces of the universal testing machine but not placed in under stress. The specimen will be clamped properly to ensure that misalignment avoided. The test sample must be straight and the top grips are in the correct direction to hold the sample to prevent from slipping. Experimental testing tensile strength of ABS plastics must be realized according to international standard EN ISO 527. The extensometer was slide from its yellow hanger fixed to the test frame.

The Gage Length extensioneter attached on the specimen, which is use to record the elongation data automatically. The knobs will be continued to hold and the spring clips opened just enough to slide the extensioneter knife-edges to the specimen. The extensioneter oriented to the front or back of the test frame to avoid the contact with the grips of the testing machine. The knobs will be released and physical setup will be completed then tensile test conducted. The computer software named Instron Bluehill was set up to recorded all the data and graph along the tensile processes. The test will be run until fracture occurs. The extensioneter will be removed quickly after the 'beep' sound on the system. The sound acts as a signal to indicate that the test sample has reached the desired point and will break. The fractured sample will be removed from testing machine and the dimensions of failed sample region will be measured.

## 3.6 MORPHOLOGICAL TESTING

Figure 3.9 below shows the model JEOL JSM- 6010PLUS/LV of the Scanning Electron Microscope instrument.



Figure 3.9 The Scanning Electron Microscope (SEM) machine Model- JEOL JSM-6010PLUS/LV

SEM was used to observe the surface behavior of the sample by using electron **WERSTITEKNIKAL MALAYSIAMELAKA** microscope with the help of light to form an image. The fractures on the sample can be seen clearly by using SEM compare to by observe it with naked eye. The electron beam follows a vertical path through the microscope which is held within a vacuum (Bogner, Jouneau, Thollet, Basset, & Gauthier, 2007). After performing the tensile test, the samples will be examined. Ensure the water must be removed from sample in order to avoid it vaporize in the vacuum.

The sample was placed on double-sided sticky tape on a specimen stub. The specimen was mounted on a stub and accommodated in the specimen chamber. ABS is a non-metals and it is need to be made conductive by covering the sample with a thin layer of conductive material (Olivera, Muralidhara, Venkatesh, Gopalakrishna, & Vivek, 2016).

The fracture surface was coating with sputter coater with a layer of platinum on biotech machine to facilitate examination under the SEM.

The sputter coater uses an electric field and argon gas and the sample is placed in a small chamber that is at a vacuum (Olivera et al., 2016). Argon gas and an electric field cause an electron to be removed from the argon, making the atoms positively charged and then become attracted to a negatively charged platinum foil (Olivera et al., 2016). The argon ions knock platinum atoms from the surface of the platinum foil (Bogner et al., 2007). These gold atoms fall and settle onto the surface of the sample producing a thin platinum coating. SEM picture were taken at different magnifications and the data will be analyzed (Olivera et al., 2016).



## **CHAPTER 4**

# DATA AND RESULTS

## 4.1 Preliminary Result

# 4.1.1 Result of Tensile Testing on ABS samples at Room Temperature

The figure below show result of ABS specimen on tensile testing at room temperature. There are three sample tested on INSTRON 8872 Tensile Machine. Sample 2 gives the best result because of the location of failure is in the middle part



Figure 4.1: (a) Sample of ABS before testing, (b) sample of ABS after tensile testing

Statistical interpretation of test result estimation of the mean and confidence interval is defined by ISO 527 standard. The results obtained from tensile testing of samples at room temperature are shown in table 4.1 below.

Table 4.1: The Result Tensile Testing of Sample at Room Temperature

sample	Lc (mm)	A <sub>o</sub> (mm)	B <sub>o</sub> (mm)	S <sub>o</sub> (mm <sup>2</sup> )	F max (kN)	Fmax – dL (mm)	Break – dL (mm)	Max σ (Mpa)	Max ε (mm/ mm)
1	80	3	10	30	0.9983	1.4129	1.4129	33.2782	0.0565
2	80	3	10	30	1.0787	1.5921	1.5921	35.9566	0.0637
3	80	MALAYS	10	30	1.0426	1.5101	1.5101	34.7527	0.0604

The average tensile strength is calculated by using the equation (1):

$$\bar{\sigma} = \frac{1}{n} \sum_{i=1}^{n} \sigma_i$$
(1)
  
INVERSITI TEKNIKA =  $\frac{1}{3}$  (33.2782 + 35.9566 + 34.7527)

# = 34.6625 MPa

Confidence interval for the average file is calculated from the estimated mean and standard deviation. The estimate of the standard deviation  $\sigma$  is calculated set of squares of deviation from the arithmetic mean by the equation (2):

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(\sigma_i - \bar{\sigma})^2}$$
(2)

$$s = \sqrt{\frac{1}{3-1} \left( \left( 33.2782 - 34.6625 \right)^2 + \left( 35.9566 - 34.6625 \right)^2 + \left( 34.7527 - 34.6625 \right)^2 \right)}$$

 $S_{RT} = 1.3415$ 

Two – sided confidence interval for average file is for a confidence level of 60% is used because the size of sample is small; we need to use t distribution in equation (3). From table, df = n-1 = 3-1 = 2, so the value of  $T_{0.975} = 1.060$ .

$$\bar{\sigma} - \frac{t_{0.975}}{\sqrt{n}} \cdot s < m < \bar{\sigma} + \frac{t_{0.975}}{\sqrt{n}} \cdot s$$
(3)

$$\bar{\sigma} - \frac{t_{0.975}}{\sqrt{n}}$$
.  $s < m < \bar{\sigma} + \frac{t_{0.975}}{\sqrt{n}}$ .s

 $\frac{1.060}{\sqrt{3}}(1.3415) = 0.8201$ 

The actual value of ultimate tensile strength of test specimen of ABS plastic is  $\sigma = 34.6625 \pm 0.8201$  MPa with a probability of 60%.

From the calculation, it shows the value of standard deviation of sample at room temperature without heat treatment condition is 1.3415 mm. The average of tensile stress at maximum loaded for three samples are 34.6625MPa and in temperature at 24°C room condition.

Graph below show stress- strain curve after tensile testing. These graph shows that among all three samples, sample 2 have highest tensile stress and tensile strain at maximum load. The trends of elastic region is nearly similar among these three samples but at the plastic region, the samples 2 shown the highest ultimate tensile strength. From this graph, it can be explained that samples at room temperature experience ductility behaviour before rupture occurs based on the elongation of strain after ultimate tensile stress were achieved. The temperature is 24°C and it is considered as Room Temperature because of the temperature in tensile room is 24°C. This graph will be used for the next tensile testing experiment to compare the tensile stress of each sample with heat treatment condition.



Figure 4.2: Result of Stress – Strain of room temperature's samples.

4.1.2 Tensile test on Thermal degradation condition

Figures below show the fracture occurs after tensile testing was conducted.



(a)



(b)

# Figure 4.3: (a) 50°C for 10 hours and (b) 50°C for 50 hours of sample after tensile testing experiments



Figure 4.4: (a) 80°C for 10 hours and (b) 80°C for 50 hours of sample after tensile testing

After tensile testing was done, the data obtained can be seen as shown as table below. The tables below show the average value of data after tensile testing of ABS sample. Table 4.2 and 4.3 below shows the total average value of result after tensile test done in condition of heat treatment of 50°C and 80°C.

Temperature Condition (°C)	50			
Time for Heat Treatment in oven (h)	10 h	30 h	50 h	
Maximum load (kN)	1.0563	1.0885	1.1051	

Table 4.2: The data of tensile testing based on temperature condition of 50°C

Tensile Stress (MPa)	35.2103	36.2825	36.8355
Tensile Strain (MPa)	0.0598	0.0597	0.0609
Tensile Extension (mm)	1.4946	1.4927	1.5237
Time taken to failure occurs (s)	76.298	77.0273	77.8043

Standard deviation of sample under heat treatment of 50°C based on formula (3) is:

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (\sigma_i - \bar{\sigma})^2}$$
(3)

For 10, 30 and 50 hours of sample are;  $S_{50/10h} = 2.0326$   $S_{50/30h} = 0.8021$   $S_{50/50h} = 1.7760$ Solve a state of the sample are;  $S_{50/50h} = 1.7760$ 



Figure 4.5: Comparison of tensile strength of sample on 10 hours, 30 hours and 50

hours of heat treatment under 50°C of temperature.

Figure above shows the differential result of samples strength on thermal degradation at 50°C of temperature for 10 hours, 30 hours and 50 hours of time duration for heat treatment in the humidity oven. After the experiments have been conducted, the standard deviation at time of 30 hours has shown the lowest standard deviation which is 0.8021 compared to the others two conditions which are 10 hours and 50 hours. The lowest standard deviation shows that the results are more accurate than others two conditions even though the value of the strength is smaller than samples in condition 50 hours of time duration. From the graph, the strength of the ABS sample has maximum value of 36.8155MPa at 50 hours of heat treatment. At 10 hours of heat treatment, the ABS sample has the lowest value of strength which is 35.2103 MPa. It can be explained that the longer time duration of heat treatment on ABS samples, the better strength results can be achieved on the samples.





From graph above, sample 1 has highest tensile stress compare to others samples. From this case, it is experience brittle phenomena while sample 3 experience ductile phenomenon's which is that can be explained by observe at the elongation of tensile strain rate on the graph. There is some necking on sample 3 before rupture occurs. The others two samples undergoes fracture after achieved ultimate tensile strength and based on this cases, it can be said that these two samples have higher brittleness compare to samples 3.



Figure 4.7: Stress-Strain curve under 50°C for 30 hours

Form graph 4.7 above, sample 1 has the lowest tensile strain but it has highest tensile strength compared to others samples and from the trends of graph, it can be said that samples 1 is experience brittle phenomena. Meanwhile, sample 3 experience ductility phenomenon's which is that can be explained by looking at the tensile strain rate. The sample 3 has longer elongation after achieved ultimate tensile strength and it shown that the plastic region on this sample is longer compared to the others samples. The elongation of tensile strain between sample 1 and 2 is quite same even though the strength of sample 1 higher than sample 2.



Figure 4.8: Stress-Strain curve under 50°C for 50 hours

Form graph above, the results from sample 1 and 2 shows that the tensile strength has nearly the same value but sample 1 has the highest value of strain among the others two samples. These three samples shows ductility phenomenon based on the elongation and plastic region of all samples.

Temperature Condition (°C) NIKAL	MALAYSIA 80ELAKA			
Time for Heat Treatment in oven (h)	10 h	30 h	50 h	
Maximum load (kN)	1.0271	1.0075	1.0072	
Tensile Stress (MPa)	34.2347	33.5832	33.5743	
Tensile Strain (MPa)	0.0540	0.0517	0.0481	
Tensile Extension (mm)	1.3495	1.2934	1.2028	
Time taken to failure occurs (s)	72.6287	71.7037	69.2780	

Table 4.3: The data of tensile testing based on temperature condition of 80°C

Table 4.3 above shows the data of tensile testing based on 80°C of temperature condition. From this data, the value of standard deviation can be obtained. The standard deviations for 10, 30 and 50 hours of sample are;

$$S_{80/10h} = 1.5771$$
  
 $S_{80/30h} = 1.7441$   
 $S_{80/50h} = 1.9970$ 



Figure 4.9: Comparison of stress – strain rate sample in 10, 30 and 50 hours of heat treatment under 80°C of temperature.

From the graph above, it can be found that the strength values of 80 °C under 10 hours are highest among the others two time duration of heat treatment. This conditions has standard deviation of 1.5771 which is lowest compared to others condition which is this sample has most accurate value of strength. At this temperature, it can be said that the trends of strength between samples at three time duration of heat treatment are different compared to the trends at 50 °C because it can be seen that the longer time taken used for heat treatment of ABS sample in 80°C, the strength of material will decreased. From this case, it can be said that the increasing of temperature has changes the behavior and strength properties of the ABS samples. The strength of samples becomes weaker when they are put in longer duration of time in heat treatment.



Figure 4.10: Stress-Strain curve under 80°C for 10 hours

Based on graph above, it can be seen that samples from 10 hours shows ductility behaviours. Sample 1 has lowest strength and strain compared to others sample. Meanwhile, sample 2 shows the highest ultimate tensile strength even though rate of elastic region are nearly similar with all samples but after pass the elastic section, the strength of sample 2 become increasing drastically. But, sample 3 shows longer elongation compared to others samples and the strength also higher than sample 1.



Figure 4.11: Stress-Strain curve under 80°C for 30 hours

From figure 4.11 above, all the three specimens have slightly high differs value of strain but sample 1 has the longest strain rate after it reached ultimate tensile stress compared to others samples. Samples 1 also have highest ultimate tensile strength. Meanwhile, sample 3 resulted lowest strain rate and tensile strength. From this graph, it can be seen that the trends of elastic and plastic region are similar at the beginning but the strength of samples become different when they reached ultimate tensile strength and it can be said that time taken for sample 3 experience fracture is faster than others two samples.



Figure 4.12: Stress-Strain curve under 80°C for 50 hours

Based on graph 4.12 above, sample 1 and 2 has value of strain that is nearly same even though the strength of sample 1 has higher compared to sample 2. It can be observed that sample 2 experience ductility because after the sample reach ultimate tensile strength, the strength decrease slowly then rupture occurs meanwhile sample 1 have some brittleness when it experience rupture faster than sample 2. In addition, sample 3 has differs value of strength and strain from sample 1 and 2 because it has higher strength and strain. Even though all three sample has nearly similar elastic region but they have experience different value of strength and strain at plastic region.

## **CHAPTER 5**

## ANALYSIS AND DISCUSSION

### 5.1 Data Analysis



Figure 5.1: Comparison of stress-strain rate between room temperature and heat treatment's samples.

From graph of stress versus temperatures above, it shows that the trends of strength values between all samples with all thermal degradable condition are fluctuated and this means that there are no huge significant changes of results to compare with results from room temperatures samples. Meanwhile, the samples from heat treatment at 50°C under 50 hours have highest value of stress and strain compared to others temperatures condition. Moreover, the lowest strength that can be found from the graph is 33.5743 MPa at 80°C

under 50 hours. This can be explained because of the group of covalent bond of samples 50 hours are acts as bridge to the molecules, so it will increase the tensile strength. But, at the temperature of 80°C has decrease on strength because this is due to ABS material has reached the maximum temperature range.

By comparing the maximum tensile strength with the condition between samples at thermal degradation and room temperature, only 2.1730MPa differences between maximum strength of heat treatment temperature and room temperature. It can be seen only 5.9% of difference between both temperature. The range of strength of all samples in difference conditions are between 33MPa to 37MPa only. Therefore, the differential strength between all samples is considered have no significant changes because the differential difference is less than 5MPa and this are considered low changes.

## 5.2 Morphological Analysis

The figure below shows the morphological figure based on ABS sample at room temperature, 50°C with 10 hours and 50 hours, and 80°C with 10 hours and 50 hours. These morphological analyses were done on samples of ABS at 10 hours and 50 hours because the SEM machine allowed student to test the 5 sample only. Based on the result, the data for tensile testing shown the minimum and maximum value on these two conditions, so that why it is been choose to test the samples from these condition.

Figures 5.2 to 5.6 below show the differences of morphological surface of the samples in conditions between room temperature and heat treatment. The power of magnificent used is X500 and X3000. The location of micrographs are same but the magnificent used is different in order to investigate better distribution of surface behavior on samples.



Figure 5.2: The morphological surface of sample at room temperature (a) magnificent X500 and (b) X3000 magnificent

Figure 5.2 above shows the morphological surface of room temperature's sample at X500 and X3000 magnificent under SEM machine. Based on the surface, it can be seen that the structural of ABS sample are not compacted. There are large sizes of voids in the samples which mean the specific interaction covalent bonding of ABS materials is weaker while fabrication samples process. This can affect the performance of samples strength while tensile tested were conducted. There arrangement of structure also shown scattered pattern which mean that the voids affected the way of fracture on samples.

Meanwhile, Figure 5.3 and 5.4 below shows the surface behaviour of samples at 50°C of temperature condition with different time duration of thermal degradable.



Figure 5.3: Morphological surface with magnificent (a) X500 and (b) X3000 on ABS samples at 50 °C on 10 hours of time duration of thermal degradation.

Based on figure above, it can be explained that there are existence voids on the samples when the micrograph of magnificent at X500 were zoom to X3000 of magnificent. The surface structures above shows that the rupture on samples occurs at that point because of the voids in the samples. Moreover, the structural surfaces of the samples are more compacted compared to samples at room temperature. Based on magnificent X500, the trends of fracture are come from many different ways before rupture occurs.





(a)

Figure 5.4: Morphological surface with magnificent (a) X500 and (b) X3000 on ABS samples at 50 °C on 50 hours of time duration of thermal degradation.

The morphological surface of the samples at 50 °C on 50 hours of time duration of thermal degradation shows the percentage of voids on samples are lower compared than previous samples. From Figure (a), it shows that the flow of ABS bonding is gathered at one surface before rupture occurs. It can be said that the samples experience brittle phenomenon before fracture.

Figure 5.5 and 5.6 below shows the surface behaviour of samples at 80°C of temperature condition with different time duration of thermal degradable.



Figure 5.5: SEM micrographs of ABS sample at (a) X500 and (b) X3000 magnificent in condition at 80°C of temperature on 10 hours of heat treatment

Based on Figure 5.5 above, the morphological surfaces of samples also shows that there are voids in the samples but the structure is quite packed and the surface of fracture also shows the samples experience brittle phenomenon before fracture occurs.



(a)



(b)

Figure 5.6: SEM micrographs of ABS sample at (a) X500 and (b) X3000 magnificent in condition at 80°C of temperature on 50 hours of heat treatment

Based on figure 5.6 above, the trend of fracture shows that the samples experience ductile phenomenon because the bonding of covalent shows some elongation on surface interface before the samples totally fracture. The mixture of material also packed and from micrograph (a) above, it can be seen that there are low percentage of voids compared to others temperature condition and time duration. The duration of time for heat treatment can be the factors for the decreasing of voids in the samples.

#### **CHAPTER 6**

#### CONCLUSION AND RECOMMENDATION

#### 6.1 Conclusion

Specimen of ABS materials for room temperature and temperature condition under heat treatment were tested for their mechanical properties and the tensile strength of ABS was recorded and analysed. The experimental result shows that the ABS sample under thermal degradable condition at temperature of 50°C under 50 hours has highest tensile strength compared to others samples. Moreover, the results from all samples shows the differential changes are less than 5MPa and it is can be concluded that there are no significant changes of samples based on condition because of the low changes of strength differences. By comparing the maximum tensile strength with the condition between samples at thermal degradation and room temperature, only 2.1730MPa differences between maximum strength of heat treatment temperature and room temperature. It can be seen only 5.9% of difference between both temperature. Moreover, the morphological surface of ABS material shows the difference of micrograph structure based on all conditions of sample. From this morphological graph, the samples from room temperature has ductility phenomenon compared to others samples conditions. It can be concluded that the longer time duration of heat treatment for thermal degradation, the higher brittleness of the ABS material.

## 6.2 **RECOMMENDATION**

Research of testing ABS polymer is still in a developmental stage and to improve polymer composites conductivity is the great challenge. Therefore, there have some possible recommendations needed to be done in the future and here is the possibility that made the data obtained not perfect.

#### 6.2.1 Method to Fabricate the Raw Material and Cutting Process

In this project, ABS raw material was fabricated by using Hot Press Machine and the mould used is not in the needed size. The ABS material needs to be cut by using some cutting machine in order to get the desired size and dimension. The cutting process was done by using Laser Machine. Laser machine used very high heat in order to cut the samples properly. In this case, the sample was exposed with the heat from Laser Machine and it can affect the characteristics in that sample. The dimension of the sample also could be affected by this machine because the sample was melted when the cutting process occurs and this case makes the dimension of the sample affected. The smoke from the laser machine made the surface of sample become dark and not nice. The best way to fabricate the ABS sample is by using injection moulding because this process required specific mould with the desired shape and size. So, there are no needs to do cutting process after fabricated this material.

#### 6.2.2 Thermal Degradation Process

In this process, the temperature used is 50°C and 80°C as a heat treatment for the samples. When the door of Humidity Oven was opened, the temperature will drop immediately. In this case, the temperatures that were tested are not accurate because the beginning temperature was not achieved desired temperature. It is better to close the door quickly after put the sample in that Oven in order to obtain best result. Moreover, after the heat treatment test, it is better to test the sample by using tensile test immediately because the temperature from outside of Oven can affect characteristics of sample. The result obtained also can show more differences between samples. Tensile machine in Fasa B was not complete because there are some tensile machine have temperature chamber on it. For the future, better test the sample in the tensile machine that have temperature chamber on it because when the sample still in desired temperature while the test conducted and it can show the best result.

6.2.3 Tensile Strength

In this research, the results of tensile strength from all of samples are not shows big differences. It is difficult to compare the strength of each sample with differentiate condition. One of the factors is the method to grips the sample before doing tensile testing. It has possible that the position of sample was not fit properly and its must have sufficient force capacity so that it will not damage during testing (P.M.Hosford, 1992). When the sample was not grips properly, the result obtained was not perfect and it also can make the fracture occurs not in the middle of sample.

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## APPENDICES

## Appendix A

## t-distribution

		Confidence Level									
	60%	70%	80%	85%	90%	95%	98%	99%	99.8%	99.9%	
		Lovel of Significance									
2 Tailed	0.40	0.30	0.20	0.15	0.10	0.05	0.02	0.01	0.002	0.001	
1 Tailed	0.20	0.15	0.10	0.075	0.05	0.025	0.01	0.005	0.001	0.0005	
1 Hunde	0.20	0.10	0.10	0.010	0.00	0.010	0.01	0.000	0.001	0.0000	
df	If MALATSIA										
1 💊	1.376	1.963	3.133	4.195	6.320	12.69	31.81	63.67			
2	1.060	1.385	1,883	2.278	2.912	4.271	6.816	9.520	19.65	26.30	
3	0.978	1.250	1.637	1.924	2.352	3.179	4.525	5.797	9.937	12.39	
4	0.941	1.190	1.533	1.778	2.132	2.776	3.744	4.596	7.115	8.499	
5	0.919	1.156	1.476	1.699	2.015	2.570	3.365	4.030	5.876	6.835	
6	0.906	1.134	1.440	1.650	1.943	2.447	3.143	3.707	5.201	5.946	
7-	0.896	1.119	1.415	1.617	1.895	2.365	2.999	3.500	4.783	5.403	
8	0.889	1.108	1.397	1.592	1.860	2.306	2.897	3.356	4.500	5.039	
9	0.883	1.100	1.383	1.574	1.833	2.262	2.822	3.250	4.297	4.780	
10	0.879	1.093	1.372	1.559	1.813	2.228	2.764	3.170	4.144	4.586	
11	0.875	1.088	1.363	1.548	1.796	2.201	2.719	3.106	4.025	4.437	
12	0.873	1.083	1.356	1.538	1.782	2.179	2.682	3.055	3.930	4.318	
13	0.870	1.079	1.350	1.530	1.771	2.160	2.651	3.013	3.852	4.221	
14	0.808	1.070	1.340	1.523	1.701	2.140	2.625	2.911	3.100	4.141	
16	0.865	1.074	1.341	1.517	1.735	2.131	0.584	2.947	2.687	4.075	
17	0.863	-1.060	1.337	1.512	1.740	2.120	2.567	2.521	3.646	3 065	
18	0.862	1.067	1.330	1.504	1 734	2.101	2.553	2.879	3 611	3 922	
19	0.861	1.066	1.328	1.500	1.729	2.093	2.540	2.861	3.580	3.884	
20	0.860	1.064	1.325	1.497	1.725	2.086	2.529	2.846	3.552	3.850	
21	0.859	1.063	1.323	1.494	1.721	2.080	2.518	2.832	3.528	3.820	
22	0.858	1.061	1.321	1.492	1.717	2.074	2.509	2.819	3.505	3.792	
23	0.857	1.060	1.319	1.489	1.714	2.069	2.500	2.808	3.485	3.768	
24	0.857	1.059	1.318	1.487	1.711	2.064	2.493	2.797	3.467	3.746	
25	0.856	1.058	1.316	1.485	1.708	2.060	2.486	2.788	3.451	3.725	
26	0.856	1.058	1.315	1.483	1.706	2.056	2.479	2.779	3.435	3.707	
27	0.855	1.057	1.314	1.482	1.703	2.052	2.473	2.771	3.421	3.690	
28	0.855	1.056	1.313	1.480	1.701	2.048	2.468	2.764	3.409	3.674	
29	0.854	1.055	1.311	1.479	1.699	2.045	2.463	2.757	3.397	3.660	
30	0.854	1.055	1.310	1.477	1.697	2.042	2.458	2.750	3.386	3.646	
40	0.851	1.050	1.303	1.468	1.684	2.021	2.424	2.705	3.307	3.551	
50	0.849	1.047	1.299	1.462	1.676	2.009	2.404	2.678	3.262	3.496	
60	0.848	1.045	1.296	1.458	1.671	2.000	2.391	2.661	3.232	3.460	
70	0.847	1.044	1.294	1.456	1.667	1.994	2.381	2.648	3.211	3.435	
80	0.846	1.043	1.292	1.453	1.664	1.990	2.374	2.639	3.196	3.417	
90	0.846	1.042	1.291	1.452	1.662	1.987	2.369	2.632	3.184	3.402	
100	0.845	1.042	1.290	1.451	1.660	1.984	2.365	2.626	3.174	3.391	
$\infty$	0.842	1.036	1.282	1.440	1.645	1.960	2.327	2.576	3.091	3.291	