# **CHAPTER 1: INTRODUCTION**

#### **1.1 Background**

In the world of electrical engineering, the heat shrinkable polymers can be considered as versatile products that have been manufactured. Its wide application in wire insulating for conductors, connections, joints and terminals, had offered big opportunities for manufacturers to open new market by producing heat shrink tubing with additional properties such as luminosity and ultra-violet (UV) reactive varieties.

Heat shrink tubing (or commonly "heat shrink") is a tube which shrinks in diameter when heated. Its diameter and thickness can vary, and there are three main categories, thin-wall, medium-wall and thick-wall. It is rated by its expansion ratio, a comparative of the differences in expansion and recovery rate.

The shrinkage behavior of this kind of polymers might influence by several factors such as temperature, time exposure, the dimensions and the materials used.

With some additional chemical constituents in the material, it will add extra abilities for the material such as flame retardant, an anti-oxidant, a vinyl stabilizer, and an inert, inorganic carrier. Thus, improve the performance of the material as well as increasing the applications of the material.

#### **1.2 Problem Statement**

Heat shrinkable polymers have been manufactured since late 1950s. With its wide application especially in wire insulation, this kind of invention had increased the product quality as well as the performance of the equipment in various ways.

Since the product was obtained from the existing market, every information and technologies of the products are private and confidential. Thus, it is quite difficult to find the details version of the studies from the manufacturer.

#### 1.3 Objectives and Scope of Study

For this study, the student will use the existing product (heat shrinkable material) that were obtained from the market and apply the concept of reverse engineering by discovering the technological principles of the product through analysis of its microstructure, function and operation.

The aims of this study are:

- 1. Get the effect of heating parameter (temperature & duration of flame exposure) through the microstructure of Commercial Heat Shrinkable Polymeric Material (CHSPM) and through the crystallinity of CHSPM based on the differentiation of metric study.
- 2. Establish the elemental and chemical composition of CHSPM on spectroscopic data.
- 3. Define the mechanism of the shrinkage process of CHSPM.

The knowledge on the following courses is very essential for this study; Introduction to Material Science & Engineering (IMSE), Engineering Materials (EM), and Advanced Engineering Polymers, Ceramics & Composites (AEPCC). All these courses help in better understanding of the material structure and its characterization.

# **CHAPTER 2: LITERATURE REVIEW**

# 2.1 What is Polymer?

Polymer as a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds (Wikipedia, 2010). There are millions of polymer products in the world categorized as either thermoplastics or thermosets depending on its applications and demand requirements.

# 2.2 Characteristics of Heat Shrinkable Material

This product is said to be a versatile product as it has very unique characteristics. When this product is exposed to any heat source at moderate temperature, it will shrink and capable to form a good seal.

(Barthell, 1967) said that, at moderate temperature in the order of 275°F, this material does not split or rupture while shrinking over irregular objects. It will shrink over 50% of its own diameter, retain excellent dielectric and mechanical strength while maintaining flexibility, and also can be made flame retardant.

# 2.3 The Heat Shrinkable Polymeric Material as Crosslinked Polymers

The heat shrinkable polymeric materials have complex manufacturing process to suit its application as an insulation product for commercial used. A process called crosslinking is one of the mechanisms involved when this material is subjected to heat source.

(Yang, Silverman and Wozniak, 1985) said that the crosslinked polymers are produced by irradiating the substances from a high energy source such as high voltage electrons or gamma rays, in order to enhance their physical or mechanical properties such as infusibility or solubility.

#### 2.4 Shrink-wrap as an Application of Heat Treatment in Polymers

The application of heat to seal or insulate the object can be considered as the heat treatment process that will certainly enhance the properties of the products.

(Callister, 2007) had discussed on the application of heat treatment in polymers such as the shrink-wrap used in packaging. Shrink-wrap is a polymer film, usually made of poly (vinyl chloride), polyethylene, or polyolefin (a multilayer sheet with alternating layers of polyethylene and polypropylene). It is initially plastically deformed (cold drawn) by about 20-300% to provide a prestretched (aligned) film. The film is wrapped around an object to be packaged and sealed at the edges. When heated to about 100 to 150°C, this prestretched material shrinks to recover 80-90% of its initial deformation, which gives a tightly stretched, wrinkle-free, transparent polymer film.

## 2.5 Several Types of Crosslinked Thermoplastic Polymers

Heat shrinkable polymers are considered high performance polymeric materials that have the ability to shrink due to the crosslinking process undergone during thermal reaction. Recent studies have shown that there are several polymeric products that possessed this kind of ability.

(D. Nyberg, 1972), described the examples of thermoplastic polymers which have been crosslinked or which inherently possess the property of heat recoverability are polyolefins, such as polyethylene, ethylene-vinyl acetate copolymer, ethylene-ethyl acrylate copolymer or other ethylene copolymers, polyvinylidine difluoride, polyvinyl chloride, etc.

# **CHAPTER 3 : METHODOLOGY**

Methodology refers to more than a simple set of methods; rather it refers to the rationale and the philosophical assumptions that underlie a particular study relative to the scientific method. Figure 1 below showing the methodology flow chart of the project.



Figure 1 : Methodology Flow Chart.

#### **3.1 Information Collection**

This project will cover on how the shrinkage of the polymers occurs when it is being imposed to heat at moderate temperature.

The study is discussing on the existing products available in market right now which is the heat shrinkable polymeric materials. The purpose of gathering the product's background is to aid in the process of interpreting the results at the end of this project. The information on type of materials, the general behavior of the materials when it is being heated and other constituent materials of the products are very important for these studies.

There are 2 samples being used throughout the studies. All of these samples have their own labels but can easily being determined by its size. However, for the ease of writing this report, short-terms are very essentials instead of using those lengthy labels:

- SALIPT S-901 E209436 VW-1 LR209028 CSA OFT 125°C (12Ø) = SAMPLE A
- E203950 WOER RSFR TUBE  $125^{\circ}$ C VW-1 (2.0Ø) = SAMPLE B

Currently, there are lacks of information explaining the properties of the product. Since the samples were manufactured by different company (SALIPT for Sample A, WOER for Sample B), any kind of information gathered from the website of the manufacturers are very helpful in getting the overview of the products' properties.

Generally, both samples (Sample A and B) are type of CHSPM that specially designed for the formulation of high polymers, through cross-link by electronic accelerator and continuous expansion.

CHSPM has an excellent flame-retardant heat-shrinkable tubing, insulation performance, very soft and flexible, low temperature shrinking, and can shrink very fast. It can be widely used in the field of electronics, communication, automobile, and wirely applied for connecting or end-harding, electric wire, insulating and harness of electric wire, corrosion and rust-proof of metallic rods or tubes, antenna protection and marking for other products.

Under the action of the high-energy rays, the linear polymer will form crosslinked three-dimensional network structure. This crosslinked structure will greatly improve its mechanical strength, resistance to temperature, chemical solvents and anti-aging especially in acid and alkaline solution.

Table 1 below shows some important features of Sample A and B. This information will help in predicting the results from the experiment and analysis.

Properties	Sample A (Ø12 mm)	Sample B (Ø2 mm)					
Manufacturer	SALIPT	WOER					
Available Size	Ø 0.06 to Ø 180 mm	Ø 0.06 to Ø 180 mm					
Temperature	-55°C to 125°C	-55°C to 125°C					
Range		55 0 10 125 0					
		Initial T <sub>s</sub> is 70°C.					
Shrinkage	Initial T <sub>s</sub> is 70°C.	Completely shrink at 110°C for					
Temperature, T <sub>s</sub>	Completely shrink at 120°C.	thin-wall and 120°C for normal-					
		wall.					
Radial	2.1	2.1					
Shrinkage Ratio	2.1	2.1					
	Black, red, yellow, green, blue,	Black, red, yellow, green, blue,					
Available Color	white, purple, grey, brown,	white, purple, grey, brown,					
Available Color	other (based on the customer's	other (based on the customer's					
	requirement)	requirement)					
Standards	UL224 VW-1,	UL224 VW-1,					
Stalluarus	C-UL CSA C 22.2 OFT	C-UL CSA C 22.2 OFT					

Table 1: The Properties of CHSPM for Sample A and B.

#### **3.2 Gas Flame Temperature Profile**

One of the major activities involved in these studies is the heating process of the materials. Since every material behaves differently at different temperature profile, the calibration of the temperature used for heating process prior to the experiment must be conducted.

A Bunsen burner with needle valve that produces a single open gas flame will be used for heating process.

With the use of thermocouple, the student will record the temperature profile for every flame types of the Bunsen burner. The time of heat exposure will also be taken into consideration.

By comparing the information obtained in previous methodology, the suitable temperature region will be used to heat the products.

#### **3.3 Experimental**

A proper experiment session will be conducted. Basically, the samples will be heated with any source of heat (lighter, oven or heating gun) with short period of heating exposure. For these studies, the student will use Bunsen burner as the heating equipment for the experiment.

The experiment will be conducted with care to avoid unnecessary results. Every single data and observation obtained during experiment will be recorded.

#### 3.4 Microscopic Examination and Results Measurement

There are two (2) areas of the specimens that need to be examined which are the internal and external surfaces.

The experimented results will be used in order to examine the microstructure of the specimens by using the following microscopic examination devices:

# 3.4.1 Optical Microscopy Analysis

The optical microscope, often referred to as the "light microscope", is a type of microscope which uses visible light and a system of lenses to magnify images of small samples. Optical microscopes are the oldest and simplest of the microscopes. Figure 2 below shows the optical microscope use for this study:



Figure 2 : Optical Microscope.

## 3.4.2 Scanning Electron Microscope (SEM)

SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern.

The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The specimens used for these studies are expected to have additional constituents that might involve in the shrinkage formation.

Figure 3 below shows the SEM with Energy Dispersive X-Ray (EDX) detector as located in Material Lab, Universiti Teknologi PETRONAS.



Figure 3 : Scanning Electron Microscope with Energy Dispersive X-Ray Detector.

## 3.4.3 Energy Dispersive X-Ray (EDX) Analysis

EDX is an analytical technique used for the elemental analysis or chemical characterization of a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

EDX is performed together with SEM device as in Figure 3 above.

# 3.4.4 Fourier Transform Infrared Spectroscopy (FTIR)

Polymers which experienced shrinkage due to heat influenced are said to be degrade. Many polymer degradation mechanisms can be followed using infrared spectroscopy.

Fourier transform infrared (FTIR) spectroscopy is a measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator), the IR light is guided through an interferometer. After passing through the sample, the measured signal is the interferogram. Performing a mathematical Fourier transform on this signal results in a spectrum identical to that from conventional (dispersive) infrared spectroscopy.



Figure 4 : Fourier Transform Infrared Spectroscopy.

In a practical way, it is almost impossible to penetrate black and dark surface specimens with infrared. However, if we can produce KBr pellets with finely grinded specimens (as small as one dot of 0.7mm ball point tip), it is possible to get the results from FTIR.

The results obtained from FTIR will be analyzed. The data from the graph (wavenumber, transmittance percentage) will give some information on the shrinkage mechanism of the material.

#### **3.5 Gantt Chart**

A Gantt Chart is very important in order to organize the overall project flow. See Appendix A to see the Gantt Chart of this study.

# **CHAPTER 4 : RESULTS AND DISCUSSION**

#### 4.1 Gas Flame Temperature Profile

The student had done calibrating the gas temperature profile of a Bunsen burner. Figure 6 below shows three main regions being calibrated which are the inner core, interconal gases and outer diffusion flame or outer cone.



Figure 5 : Three Main Regions of Bunsen Burner's flame. Courtesy: Encyclopedia Britannica, Inc.

All the regions are being calibrated by measuring the temperature every two seconds for a total of 20 seconds. The results were taken 3 times to increase the accuracy of the results obtained.

The graphs in Figure 7, 8 and 9 show the temperature profile of inner core, interconal gases and outer core flame of the Bunsen burner.



Figure 6 : Temperature Profile for Inner Core of the Bunsen Burners flame.



Figure 7 : Temperature Profile for Interconal Gases of the Bunsen Burners flame.



Figure 8 : Temperature Profile for Outer Core of Bunsen Burners flame

Based on the results obtained from three graphs above, the interconal gases temperature profile is being extended to 40 seconds time exposure as in Figure 10 below.



Figure 9 : Extended Temperature Profile for Interconal Gases of Bunsen Burners Flame.

From the results obtained, the interconal gas of Bunsen burners flame will be chosen as the heating region for the experiment because of its consistency in temperature profile as well as achieving the moderate temperature at a given time exposure.

Based on the fact that CHSPM will start to shrink at 50°C and fully shrink at 120°C, the heating region of 100°C till 200°C, around 8 to 10 seconds time exposure will be used for the experiment.

## **4.2 Experiment**

#### Objective:

The objective of the experiment is to observe the properties of CHSPM based on its dimension, and appearance after a short period of heating exposure.

#### Apparatus:

Two samples of CHSPM (Sample A and B), Bunsen burner, thermocouple K-type, stopwatch, lighter and a clipper.

## Procedure:

- 1. All the apparatus are setup and calibrated.
- 2. The Bunsen burner is light up and adjusted the air flow to the valve until we get yellowish or orange flame.
- 3. By using a clipper, Sample A is exposed to the flame. At the same time, the thermocouple electrode is exposed to the flame and start the stopwatch. Observe the temperature and time. Either of them reaches 200°C or 10 seconds, the sample is pull back from the flame. Stop the Bunsen burner flame.
- 4. The heated sample is observed for any changes in its dimension, surface roughness and hardness.
- 5. Step 1 till Step 4 are repeated for Sample B.

Results and Discussion:

The results of the heated region have shown significant changes on its dimension and texture. Figure 11 below shows the different between the heated (right side) and non-heated (left side) regions of CHSPM for both samples.



Figure 10: Heated and Non-Heated Regions of Sample A and B.

From the experiment, several observations have been made:

- 1. The samples had major changes in term of its shape and the thickness of the shrinked region.
- 2. The total length of the specimens is not significantly change.
- 3. The thickness of the shrinked area is thicker than the original condition.
- 4. The surface of the heated region is more grainy and stiffer than before being heated.

The final diameter and original diameter of the samples are measured and the percentage of shrinkage was calculated as in Table 2 below.

Sample	Original Diameter, D <sub>o</sub>	Final Diameter, D <sub>f</sub>	% Shrinkage
А	12	7	41.67
В	2	1.5	25.00

Table 2: The Shrinkage Percentage of Sample A and B.

Based on the shrinkage percentage calculated, the shrinkage ratio is less than 2:1 for both samples.

# 4.3 Optical Microscopy Analysis

The results from optical microscope are very useful for a quick "look see" and the most familiar tool for the study of the morphology of materials. Figure 12, 13, 14 and 15 will give us some description on the surface (internal and external) of the polymers (Sample A and B), for the condition of before and after being heated.

Internal Surface:



Figure 11 : Internal Surfaces of Sample A, Before (Left Picture), and After (Right Picture) Being Heated at 50x Magnification.



Figure 12 : Internal Surfaces of Sample B, Before (Left Picture), and After (Right Picture) Being Heated at 50x Magnification.

From Figure 12 and Figure 13, qualitatively we can observe that, Sample A has more grainy surface if compare to Sample B. Furthermore, Sample A has some obvious

crystal-like particles on its surface. There are some of the crystal-like and orange particles for Sample B before it is being heated, but the particles seem to be reduced after heated.

**External Surface:** 



Figure 13 : External Surfaces of Sample A, Before (Left Picture), and After (Right Picture) Being Heated at 50x Magnification.



Figure 14 : External Surfaces of Sample B, Before (Left Picture), and After (Right Picture) Being Heated at 50x Magnification.

Based on Figure 14 and 15 above, both are having the crystal-like particles on their external surfaces. However, for Sample A, the particles seem to be reducing after it is being heated. For Sample B, the crystal-like particles blended in the surface.

For internal and external surfaces of Sample A and B, qualitatively both samples have grainy textures after being heated.

# 4.4 Scanning Electron Microscope

Figure 16 and 17 below show some of the microscopic images at the magnification of 500x using SEM before experiment.

Internal surface:



Figure 15 : Internal Surfaces of Sample A (Left Picture) and Sample B (Right Picture) Before Experiment.

External surface:



Figure 16 : External Surfaces of Sample A (Left Picture) and Sample B (Right Picture) Before Experiment.

From Figure 16 and Figure 17 above, at 500x magnification, qualitatively Sample A has more grainy texture if compare to Sample B.

## 4.5 Elementary Composition Using EDX

Energy dispersive detectors are solid state devices which measure the energy of the xrays. Each X-ray photon produces a voltage pulse proportional to the energy, hence identifying the element from which it originated. A pulse height analyser with rapid counting capability measures the rate of each different energy so that data for all elements are gathered simultaneously.

The analysis has been run on EDX detector that is integrated with SEM as in Figure 3 and the results is tabulated as in Table 3 below.

Element	Weight and	Sample A	Sample B					
	Atomic %							
	Weight %	63.7	61.49					
CK	Atomic %	77.67	73.58					
OK	Weight %	17.32	25.2					
UK	Atomic %	15.85	22.64					
Mak	Weight %	6.78	0					
NIG K	Atomic %	4.09	0					
	Weight %	0	4					
AIK	Atomic %	0	2.13					
S; V	Weight %	1.29	0.4					
SIK	Atomic %	0.67	0.2					
Dr V	Weight %	6.49	6.3					
DIK	Atomic %	1.19	1.13					
Shi	Weight %	4.42	2.62					
SUL	Atomic %	0.53	0.31					

Table 3 : The Elementary Composition by Weight and Atomic Percentage for SampleA and B.

Based on Table 3, Sample A and Sample B have just a little different on their elementary composition in which Sample A contains Mg element rather than Sample B, Al element.

The EDX Spectrum (EDS) are shown as in Figure 18 and 19 for Sample A and B respectively.



Figure 17: EDS Spectrum of Sample A.



Figure 18 : EDS Spectrum of Sample B.

By comparing EDS spectrums in Figure 18 and Figure 19 for Sample A and Sample B respectively, there are major different from 1-2 keV scale. Figure 18 shows three (3) significant peaks of Mg, Br and Si elements. In Figure 19, there are high peaks of Al and Br elements, and a very low peak of Si element.

Another significant observation is for C element spectrum. For EDS spectrum in Figure 2, it shows a very high peak if compared to the spectrum in Figure 1 for Sample A.

#### 4.6 Chemical Composition Using FTIR

The results of taken from FTIR analysis, are plotted. There are three (3) peaks to be analyzed by determining their vibrating group based on their wavenumbers. The percentage of transmittance change is calculated from the graph. All the data being analyzed are tabulated accordingly.

There are four (4) results that should be taken into considerations for this analysis:

- 1. Sample A before and after being heated.
- 2. Sample B before and after being heated.
- 3. Sample A and B before being heated.
- 4. Sample A and B after being heated.

The importance of comparing the results obtained for Sample A and B for both conditions is to detect any interesting observations that might have some relationships with the results from other analysis (OM, SEM, and EDX).

Figure 20 below shows the IR spectrum of Sample A, for before and after being heated conditions.



Figure 19 : IR Spectrum of Sample A, Before and After Being Heated.

The three peaks of interest are analyzed and tabulated as in Table 4.

**Assigned Vibrating** Transmittance, %T Change, Wavenumber, Peak  $\bar{v}$  (cm<sup>-1</sup>) %T Group (%) A1 5.474229 1627.808621 6.72 C = C stretching A2 4.378341 1627.808621 5.41 **B**1 14.957291 B – H stretching 12.32 2358.779554 **B**2 6.006717 2358.779554 vibration 6.42 O – H stretching C1 28.477316 3442.699512 28.00 C2 19.676938 vibrations 3442.699512 20.27

Table 4 : The Assigned Vibrating Group and %T Change (%) for Three Peaks ofInterest of Sample A, Before and After Being Heated.

Based on the data in Table 4, all the values for the transmittance and %T change are higher for the sample before being heated.

Figure 21 below shows the IR spectrum of Sample B, for before and after being heated conditions.



Figure 20 : IR Spectrum of Sample B, Before and After Being Heated.

The three peaks of interest are analyzed and tabulated as in Table 5.

Table 5 : The Assigned Vibrating Group and %T Change (%) for Three Peaks ofInterest of Sample B, Before and After Being Heated.

Doolz	Transmittance,	Wavenumber,	Assigned Vibrating	%T Change,
Геак	%T	<b>v</b> (cm <sup>-1</sup> )	Group	(%)
D1	5.931315	1627.808621	C - C stratabing	5.00
D2	4.549892	1627.808621	C = C succoming	4.84
E1	27.763748	2358.779554	B – H stretching	28.13
E2	20.057189	2358.779554	vibration	20.32
F1	20.871426	3438.842146	O – H stretching	20.63
F2	19.021346	3438.842146	vibrations	17.90

Based on the data in Table 5, all the values for the transmittance and %T change are higher for the sample before being heated.

Figure 22 below shows the IR spectrum of Sample B, for before and after being heated conditions.



Figure 21 : IR Spectrum of Sample A and B, Before Being Heated.

The three peaks of interest are analyzed and tabulated as in Table 6.

Peak	Transmittance, %T	Wavenumber, $\bar{\upsilon}$ (cm <sup>-1</sup> )	Assigned Vibrating Group	%T Change, (%)
D1	5.931315	1627.808621	C = C stratabing	5.00
A1	5.474229	1627.808621	C = C succoming	6.72
E1	27.763748	2358.779554	B – H stretching	28.13
B1	14.957291	2358.779554	vibration	12.32
F1	20.871426	3438.842146	O – H stretching	20.63
C1	28.477316	3438.842146	vibrations	28.00

Table 6 : The Assigned Vibrating Group and %T Change (%) for Three Peaks ofInterest of Sample A and B, Before Being Heated.

Based on the data in Table 6, all the values for the transmittance and %T change are higher for Sample A (Peak A1 and Peak C1) if compared to Sample B (Peak D1 and Peak F1). However, the value for the transmittance and %T change are higher for Sample B (Peak E1) if compared to Sample A (Peak B1).

These different in %T might be due to the Br element contain in the samples. By referring to Table 3, the weight percentage of Br for Sample A is 6.49%, whereas Sample B is 6.3%.

By having only 0.19% in weight percentage, it reduced the transmittance percentage of almost Sample A by 15.81%.



Figure 23 shown below is the IR spectrum of Sample A and B after being heated.

Figure 22 : IR Spectrum of Sample A and B, After Being Heated.

The three peaks of interest are analyzed and tabulated as in Table 7.

Table 7 : The Assigned Vibrating Group and %T Change (%) for Three Peaks ofInterest of Sample A and B, After Being Heated.

Peak	Transmittance, %T	Transmittance, $\%$ TWavenumber, $\bar{v}$ (cm <sup>-1</sup> )Assigned Vi Grou				
D2	4.549892	1627.808621	C = C stratabing	4.84		
A2	4.378341	1627.808621	C = C succoming	5.41		
E2	6.006717	2358.779554	B – H stretching	20.32		
B2	20.057189	2358.779554	vibration	6.42		
F2	19.676938	3438.842146	O – H stretching	17.90		
C2	19.021346	3438.842146	vibrations	20.27		

Based on the data in Table 4, all the values for the transmittance and %T change are higher for Sample A (Peak A2 and Peak C2) if compared to Sample B (Peak D2 and Peak F2). However, the value for the transmittance and %T change are higher for Sample B (Peak E2) if compared to Sample A (Peak B2).

These different in %T might be due to the Br element contain in the samples. By having only 0.19% in weight percentage, it reduced the transmittance percentage of Sample A by 13.9%.

Based on the result obtained from FTIR, the three peaks of interest are belonging to three groups of vibrating groups; C = C stretching, O - H stretching, and B - H stretching:

#### 4.6.1 C = C stretching

Those peaks that belong to the wavenumber within 1680 to  $1630 \text{ cm}^{-1}$  are said to be in alkenes group.

(Smith, 1998) said that, the intensity of this vibration is variable. For double bonds that are nearly symmetrically substituted, the dipole moment change is zero, and the C=C stretching band does not appear in their spectra. For double bonds that are nearly symmetrically substituted, the intensity of the C=C stretching band can be weak. On the other hand, if one of the substituents has a large dipole moment, the C=C stretching band can be relatively strong. This means the C=C stretch is useful within limits.

The reduction of the transmittance may be due to the reduction of C=C bond in order for crosslinking to take part during the reaction. The crosslinking processes between two or more adjacent molecules will reduce the inter-chain density and affect the results shown in IR spectrum.

#### 4.6.2 **O** – **H** stretching

According to (Mohan, 2004), hydroxy compound, containing active hydrogen grouping, undergo self association and their spectra are accordingly very dependent on the state of the sample.

Inter-molecular hydrogen bonding increases as the concentration of the solute in solution increases and additional bands start to appear at lower frequencies near  $3550 - 3200 \text{ cm}^{-1}$  at the expense of the free hydroxyl band.

Hydroxy compounds, in solid and pure liquid states, normally exist as polymeric aggregates held together by hydrogen bonds which break up on dilution with non-polar solvents, first to trimers (polymer molecules consisting of three identical monomers) or dimmers and finally on large dilution to monomers.

## 4.6.3 **B** – **H** stretching

(Vansant, Voort and Vrancken, 1995) have discussed that, in coordination compounds of boranes, the B-H stretching vibrations shift to lower wavenumbers and absorb in the  $2270 - 2440 \text{ cm}^{-1}$  region. Boronhynide ions absorb only in the  $2100 - 2300 \text{ cm}^{-1}$  region. So based on the observed wavenumbers, information is gained about the possible surface structures present after modification.

#### 4.7 Other Discussions

Quantitatively, it is almost impossible to measure the roughness and hardness of the sample before and after being heated. There are two major reasons why this method is not applicable for this study:

- 1. The thickness of the samples is too small and very soft that make it difficult to use the indenter of the hardness tester.
- 2. The samples have curved surface that make it hard or almost impossible to point the stylus of the profilometer onto the surface. Eventhough there are non-contact technique to measure the roughness, they have some critical limitation in which it is limited to the frequency of their wavelength. A black and dark colours of the samples will make it impossible to perform that technique.

# **CHAPTER 5 : CONCLUSION AND RECOMMENDATION**

## 5.1 Conclusion

The special characteristics of heat shrinkable polymers had given manufacturers the opportunities to wide range of potential market right now.

CHSPM shrinks when it is being heated. The shrinkage formation leads to the other changes on the material itself such as its thickness, diameter and the surface textures and stiffness. The shrinked CHSPM will have thicker thickness, smaller diameter, rougher and harder surface. Based on these results, the mechanical properties of the CHSPM is said to be increased.

The elemental composition of the samples leads to the different in the properties of CHSPM. The results in FTIR proved that higher Boron, B element composition will reduce the IR transmittance of the material. A higher B element composition will sharply increase the ability of thermal resistance of Sample A.

The shrinkage phenomenon might be influenced by one of the process called crosslinking by the additive inside the samples. These can be proved from the FTIR results where %T transmittance reduces after it is being heated. During the heating process, chemical reaction takes place, in which the linear polymer will form crosslinked three-dimensional network structure. This process of cross-linking will reduce the interchain distance of the polymer chain and affect the IR transmittance.

#### 5.2 Recommendation

The CHSPM is said to be degraded when it is shrinked after being heated. Thus, the enhancement of the study on the mechanism of the polymer degradation is very useful for this purpose. Few recommendations have been discussed in order to improve the quality of the study for future use:

1. The use of Differential Scanning Chalorimetry (DSC)

DSC used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures  $T_g$ .

Melting points and glass transition temperatures for most polymers are available from standard compilations, and the method can show up possible polymer degradation by the lowering of the expected melting point,  $T_m$ , for example.  $T_m$  depends on the molecular weight of the polymer, so lower grades will have lower melting points than expected.

2. Perform the Thermogravimetric Analysis (TGA)

TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change.

3. Perform the Differential Thermal Analysis (DTA)

DTA is a thermoanalytic technique, similar to differential scanning calorimetry. In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference.

4. Perform X-Ray Diffraction (XRD) Analysis

X-ray diffraction finds the geometry or shape of a molecule using X-rays. X-ray diffraction techniques are based on the elastic scattering of X-rays from structures that have long range order.

## REFERENCES

- F.E Barthell, December 19, 1967, "Heat Shrinkable Components With Meltable Insert Liner", assigned to Electronized Chemicals Corporation, Burlington, Dracut, Mass.
- Hou-Ching Yang, Joseph Silverman and John J. Wozniak, February 1, 1985, "Low Temperature Heat Shrinkable Polymer Material", assigned to The Johns Hopkins University, Baltimore, University of Maryland, College Park, both of Md.
- William D. Callister, 2007, "Shrink-Wrap Polymer Films", Material Sciences and Engineering: An Introduction, Pg. 541, John Wiley & Sons (Asia) Pte Ltd., New York.
- David D. Nyberg, September 1, 1972, "Heat-Shrinkable Laminate", assigned to Raychem Corporation, Menlo Park, Calif.
- Brian Smith, 1998, "Hydrocarbons, Alkenes", Infrared Spectral Interpretation, A Systematic Approach, Pg. 45, CRC Press LLC, Boca Raton, New York Washington, D.C.
- Jag Mohan, 2004, "Organic Spectroscopy, Principles and Applications", *Infrared Spectroscopy*, Pg. 38, Alpha Science International Ltd., Harrow, U.K.
- E.F. Vansant, P. Van Der Voort and K.C. Vrancken, 1995, *Characterization and Chemical Modification of the Silica Surface*, Elsevier Science B.V, AE Amsterdam, Netherlands.
- Wikipedia, The Free Online Encyclopedia, 12 May 2010 < <u>http://en.wikipedia.org/wiki/Polymer</u>>

# Appendix A: Gantt Chart

	0	Task Name	Duration	Start	Finish	3 Jul '09	9   10	Aug '09	07 Sep '09	05 Oct '0	9 02 Nov	'09 i	30 Nov '09	28 Dec '	09 25.	Jan '10	22 Feb	) <b>'10</b>  1	22 Mar '1(	0  19 A	\pr '10	17 May	/ '10 14
	-					17 28	3 08	19 30	10 21	02 13 2	4 04 15	26	6 07 18	29 09	20 3	11	22 0	5 16	27 07	18	29 1	0 21 0	J1 12
1	$\checkmark$	Final Year Project I	91 days	Wed 22/07/09	Wed 25/11/09	-																	
2	$\checkmark$	Selection of project topic	6 days	Wed 22/07/09	Wed 29/07/09	1	100%																
3	$\checkmark$	Preliminary research work	16 days	Thu 30/07/09	Thu 20/08/09			100%															
4	$\checkmark$	Submission of Preliminary Report	1 day	Fri 21/08/09	Fri 21/08/09		•	21/08	3														
5	$\checkmark$	Project work	69 days	Fri 21/08/09	Wed 25/11/09							1	00%										
6	$\checkmark$	Submission of Progress Report	1 day	Wed 09/09/09	Wed 09/09/09				09/09														
7	$\checkmark$	Seminar I	1 day	Wed 16/09/09	Wed 16/09/09				🔶 16/0														
8	$\checkmark$	Submission of Interim Report Final Draft	1 day	Mon 26/10/09	Mon 26/10/09					•	26/10												
9	$\checkmark$	Oral Presentation	1 day	Fri 13/11/09	Fri 13/11/09						🔶 1	3/11	l										
10		Semester Break	43 days?	Thu 26/11/09	Mon 25/01/10						1	-			-								
11		Final Year Project II	91 days	Mon 25/01/10	Mon 31/05/10										-			_		1			
12	$\checkmark$	Project work continues	83 days	Mon 25/01/10	Wed 19/05/10																	100%	á
13	$\checkmark$	Submission of Progress Report 1	1 day	Fri 19/02/10	Fri 19/02/10											•	19/02						
14	$\checkmark$	Submission of Progress Report 2	1 day	Mon 22/03/10	Mon 22/03/10													•	22/03				
15	$\checkmark$	Seminar II	1 day	Fri 26/03/10	Fri 26/03/10													•	26/03				
16	$\checkmark$	Poster submission	1 day	Mon 12/04/10	Mon 12/04/10														•	12/04	ŧ.		
17	$\checkmark$	Dissertation draft submission	1 day	Mon 03/05/10	Mon 03/05/10																03	/05	
18	$\checkmark$	Oral presentation	1 day	Thu 13/05/10	Thu 13/05/10																•	13/05	
19		Hardbound dissertation submission	1 day	Mon 31/05/10	Mon 31/05/10																	•	31/05

# Appendix B: CHSPM Manufacturer Profile: Shenzhen Woer Heat-Shrinkable Material Co., Ltd.

Shenzhen Woer Heat-Shrinkable Material Co., Ltd. is located in Woer Industrial Park, Xili, Nanshan District, Shenzhen, China, as a high-tech enterprise approved by Shenzhen Science & Technology Bureau, Woer company has been always receiving energetic supports from Shenzhen Municipal Government and Shenzhen Hi-Tech Industrial Investment Service Co., Ltd., which is one of our financially powerful shareholders. We specialize in R&D, manufacturing and sale of wide range of special new electronic, electric materials and equipments.

Woer Company owns four sets of most advanced electronic accelerators, worth of more than USD 5,000,000, which guarantee the production efficiency and the quality. We have fully realized the management of computerization, standardization and people-connecting humanization through the application of the most advanced ERP management software. Our company has a very aggressive and innovative group of more than 1,000 employees, with and area of about 50,000 m<sup>2</sup>.

The main products include heat shrinkable tube, heat shrinkable bus bar tubing, heat shrinkable power cable accessories, cold shrinkable power cable accessories, Cable Branch Box, Ring-net Switch Cupboard, High and Low voltage Switchgear. Silicone rubber insulated wire, PTFE tube, etc., altogether 9 series, 2500 types. Currently, the annual output of heat shrinkable tube has reached 1.5 billion meters, ranked first in mainland, second in the world. With national authorization, our products have barcoding printed on the heat shrinkable tube, which is generally used in international business. All the products have separately received the UL, CUL and SGS Approval, We have many national patents. Meanwhile, our quality system has been certified to meet the requirements of ISO:9001.

#### **Appendix C: CHSPM Manufacturer Profile: Dongguan Salipt Co. Ltd.**

Dongguan Salipt Co.,Ltd. founded in 1999 and located in Sanlian Technological Park, Liaobu Town, Dongguan, near Dongguan Songshanhu Technological Industrial Park, is a technological foreign owned enterprise.

The company owns over 200 personnel, covers an area of 20,000sq.m and has building area of 10,000sq.m. It is a modern garden enterprise.

The company, a high-tech enterprise integrating the R&D, manufacturing and sale of radiation cross-linking polyolefin heat-shrinkable tube and PTFE tubing, is the earliest enterprise in the domestic manufacturing halogen-free heat-shrinkable tubes with electronic accelerator, the key equipment, and all the manufacturing equipment and property testing devices of heat-shrinkable tubing. The formula, extrusion, irradiation, and expansion of the products own the independent intellectual property. With the enterprising and innovative spirit, the company develops effectively and persistently.

Radiation cross-linking polyolefin heat-shrinkable tube, a kind of new type functional polymeric material, is made and used by the "Elastic memory" function of polymer. Due to its features of good strength, low weight, favorable electrical property, and convenience, etc. It is used widely in electronic appliance and machinery industry, such as the connection of wire, insulation of welding point, end treatment of wire, insulation of resistance and capacitor, sign and end of wire, rust proof of metal pipe or bar, and antenna protection, etc. PTFE tube, made of polystetrafluroroethylene (PTFE), is featured by high temperature resistance, corrosion resistance, high insulation, and good mechanical strength, etc. It is used widely in the important technological industry of electron, computer, electric heating, aviation, military, and communication, etc, such as miniature transformer and others. This kind of product is popular among both at home and abroad, especially in Zhujiang Delta and Changjiang Delta.

The company builds up the market-oriented product and technology innovative mechanism, and has attracted a group of R&D and management talents, who are

mainly doctors, masters, and senior engineers. In the new material field, the company researches and develops halogen-free heat-shrinkable tubes, keeping ahead in the similar industry. With complete category and spec, and high quality, "SALIPT" halogen-free heat-shrinkable tube accords with the requirements of European RoHS and the environmental and technological standard of SONY SS-00259.

Adhering to the quality policy of "Human-oriented and self-transcended; quality product and sincere service", the company is striving to create a harmonious society for human beings and the nature. Relying on the stable technological resource and effective management system, the company sells its products in more than 20 provinces all over the country. And the company has won the titles of "High-Tech Enterprise" by Department of Science & Technology of Guangdong, and the certification of American UL, Canadian CSA, ISO9001: 2000, and SONY Green Partner.

# Appendix D: WOER Technical Data for Halogen Free Flame-Retardant Thin Wall Heat Shrink

Technical Da	ta:									
	PROPERTY		Test Met	hod	Standard					
	Tensile Strength(MPa)			GB/T1040	1040 ≥10.4					
	Elongation(%)			GB/T1040	GB/T1040 ≥200					
Physical	Tensile Strength after Aging	(MPa)		UL 224 158□×168h	ır	≥7.3				
Physical	Elongation after Aging(%)			UL 224 158□×168h	ır	≥100				
	Heat Resisitance			UL 224 250□×4hr		No viscidity, No cracking				
	Cold Blend		UL 224 -30□×4hr		No cracking					
El a studiera l	Dielectric Strength(kv/mm)			GB/T1408		≥15				
Electrical	Dielectro Withstand	UL 224		No breakdown for 1500V						
		UL 224		No breakdown for 2500V						
	Volume resistance(Ω.cm)			GB/T1410	GB/T1410 ≥1×10 <sup>14</sup>					
	Anti Corrosion			UL 224 158□×168h	nr	PASS				
Chemical	Conpper stability			UL 224 158 × 168h	ır	PASS				
	Flammability			UL 224		VW-1	W-1			
Environment	Friendly Characteristics									
Hazardous element	s Test Method Result(mg/kg)		Hazardous element		Test Method	Result(mg/kg)				
Cd	EN1122:2001Method B	≤5 A		As	EPA 3	052	≤50			
Pb	EPA 3050 B	≤90 5		Se	EPA 3	052	≤25			
Sb	EPA 3050 B	≤60		F	EN 14	582 Method B	≤200			
Ba	EPA 3050 B	≤1000		CI	EN 14	582 Method B	≤800			
Cr	EPA 3050 B	≤5		Br	EN 14	582 Method B	≤800			
Ha	EPA 3052	2 ≤5			EN 14	582 Method B	≤200			