DEVELOPMENT OF HOT MELT ETHYLENE VINYL ACETATE (EVA) ADHESIVE FOR PACKAGING INDUSTRY

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MOHD SYAHMI HAFIZI BIN GHANI

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

In The Name of Allah, Most Gracious, Most Merciful

Love special dedicated to
special inspiring and special encouraging of my lovely parent

Ghani B Mahadiah and Siti Mariam Bt Ibrahim,
my siblings,
and
also my truly best friends,
those who has influenced my life on the right course
Thank you so much

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Alhamdulillah, praise be to Allah, the most gracious and the merciful. With His strength, guidance, and only by this assistance, this study has reached its end. My gratitude specially dedicated to my supervisor, Prof. Dato’ Dr.Rosli B Mohd Yunus upon his sincere consistent encouragement, advice and guidance throughout ensuring the success of this study.

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Not to be left, I almost thought for my beloved mum and dad Ghani b Mahadiah,Siti Mariam Bt Ibrahim and my family who have been firing up my spirit.

Last but not least my appreciation to all my friends who always be my side and always give suggestion to improve my performance in studying. Also to all who are involved directly or indirectly in ensuring the smoothness of this research either through your ideas, advices, support, energy or time consuming. Nice to have cooperation and working with all of you.

ABSTRACT

Hot-melt adhesives have been commercially available for a long time and they are used in a wide range of applications. In recent years, packaging industry prefers to use hot melt adhesive based on polyolefin because polyolefin provide ease of processing, low off-taste, low smell and heat seal ability. In this research, it is intended to develop the formulation for Ethylene Vinyl Acetate (EVA) based hot melt adhesive with the same properties of polyolefin based hot melt adhesive since EVA offers low cost than polyolefin. To develop new formulation of EVA hot melt adhesive (HMA), EVA copolymers with various melt index were blended together with resin, wax and antioxidant in the molten state. The performance of new formulations was compared with commercial polyolefin hot melt adhesive. Three formulations of EVA hot melt adhesive have been developed. The thermal properties such as glass transition temperature and melt viscosity were studied by using differential scanning calorimeter (DSC) and Brookfield Viscometer. From DSC curve, the result indicated that three new formulations and commercial polyolefin has a glass transition temperature between -20 ^{0}C and -25 ^{0}C. Implying, the EVA copolymer blend with resin is compatible. The peak observed on the heating curve corresponded to the melting point, Tm. EVA-HMA 1 and EVA-HMA 3 is comparable with commercial polyoelfin based on identical broad peak. The melt viscosity of all EVA HMA formulation and commercial polyolefin HMA decrease with increasing the temperature. Hot melt adhesive with lower viscosity will have more flexibility to flow out, indicating that it has better wetting properties when applied to the substrate. EVA-HMA 3 have the best performance to be made the hot melt adhesive for the packaging industry because of comparable thermal properties and viscosity at desired temperature with commercial polyolefin adhesive. Further research needs to be conducted on EVA-HMA 3 for other properties to confirm its viability in replacing the commercial polyolefin based hot melt adhesive in packaging industry.

ABSTRAK

Pelekat panas mencairkan telah lama wujud secara komersial dan ia digunakan dalam pelbagai aplikasi. Akhir-akhir ini, industri pembungkusan lebih banyak menggunakan pelekat leburan panas polyolefin kerana polyolefin menyediakan kemudahan pemprosesan, bau yang rendah dan keupayaan kedap haba. Dalam kajian ini, ia bertujuan untuk membangunkan formulasi untuk Ethylene Vinyl Acetate (EVA) berdasarkan leburan panas pelekat dengan sifat-sifat sama polyolefin kerana leburan panas pelekat EVA menawarkan kos yang rendah dari polyolefin. Untuk menghasil formulasi baru EVA pelekat leburan panas (HMA), EVA kopolimer dengan pelbagai indeks leburan telah dicampur bersama-sama dengan resin, lilin dan antioksidan dalam keadaan lebur. Prestasi formulasi baru akan di bandingkan dengan komersial polyolefin mencairkan pelekat panas. Tiga formulasi EVA panas mencairkan pelekat telah dibangunkan. Ciri-ciri haba seperti suhu peralihan kaca dan mencairkan kelikatan telah dikaji dengan menggunakan differential scanning calorimeter (DSC) dan Brookfield Viscometer.Daripada graf DSC, hasilnya menunjukkan bahawa tiga formulasi baru dan polyolefin komersial mempunyai suhu peralihan kaca antara -20 ^{0}C dan -25 ^{0}C.Oleh itu, hasil gabungan EVA kopolimer dengan resin adalah serasi. Puncak diperhatikan pada lengkung pemanasan sepadan dengan takat lebur, Tm. EVA-HMA 1 dan EVA-HMA 3 adalah setanding dengan polyoelfin komersial berdasarkan puncak luas yang hampir sama. Kelikatan leburan semua EVA HMA dan polyolefin komersial HMA menurun dengan peningkatan suhu. Pelekat panas cair dengan kelikatan yang lebih rendah akan mempunyai lebih banyak fleksibiliti untuk mengalir keluar, menunjukkan bahawa ia mempunyai ciri-ciri yang lebih baik membasahkan apabila digunakan ke atas bahan. EVA-HMA 3 mempunyai prestasi terbaik untuk dibuat pelekat panas cair untuk industri pembungkusan kerana sifat haba setanding dan kelikatan pada suhu yang dikehendaki dengan komersial pelekat polyolefin. Kajian lebih lanjut perlu dijalankan ke atas EVA-HMA 3 untuk mengesahkan daya maju dalam menggantikan polyolefin dalam industri pembungkusan.

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LIST OF ABBREVIATIONS

CSTR	Continuous stirred reactor
DSC	Differential scanning calorimeter
EVA	Ethylene Vinyl Acetate
HMA	Hot melt adhesive
MW	Molecular weight
MWDs	Molecular weight &stributions
MSDS	Material safety data sheet
PE	Polyethylene
PP	Polypropylenes
SEC	Size Exclusion Chromatography
RPM	Rotation per minute
VA	Vinyl acetate

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

In this developed world today, engineers have brainstormed the idea to design and specify fasteners and other mechanical tools to assemble and maintain equipment used in the production of their products. Adhesive is one successful technology they develop to accelerate the process of product assembling. Hot-melt adhesives as a thermoplastic material in solid condition at room temperature, when heated above their melting point, they become fluid and able to wet the surface to which they applied (Dexehmier and Vertnik, 1983). Hot-melt adhesives have been commercially available for a long time and they are used in a wide range of applications for bookbinding, packaging, product assembly, tapes and labels, floor and tile, textile, furniture to specialty adhesive (Paine, 1991). The composition of a hot-melt adhesive usually includes a thermoplastic polymer backbone and a diluent system. Since hot-melt adhesives need to be applied in the molten state, polymers with adequate resistance to heat degradation such as polyethylene, polyvinyl acetate or ethylene-vinyl acetate copolymers are typically used as the backbone polymer (Cagle, 1973). The diluent system in a hot-melt adhesive can include materials such as wax, tackifier, plasticizer and antioxidant. By adding these materials accordingly, the properties of hot-melt adhesives can be modified and customized to a specific end usage (Li et al, 2008). The diluent system can help to lower the viscosity of the molten polymer making it more convenient to apply onto surfaces as well as to increase the wetting ability and adhesive strength. It also can provide molten tack and modify the physical properties of hot-melt adhesives. However, in order for the diluent system to be effective, the components need to be selected with care to ensure compatibility of the whole system (Tse, 1998). The advantage of hot melt adhesives is that they typically provide for short setting times, e.g. below 5 seconds, such that the substrates need only be pressed together for a short time after gluing a short pressing time. At the end of the pressing time, the adhesive strength should be high enough to hold the substrates together. Furthermore, hot melts are able to bond many different types of substrates, including permeable substrates and non-permeable substrates. Hot-melt adhesives are usually water-insoluble therefore insensitive to water (Li et al, 2008), and they can be used as gap filler in many applications (Cagle, 1973). The disadvantage of hot melt is that they are inherently temperature sensitive. Hot melts become soft at elevated temperatures and become brittle at low temperatures. At elevated temperatures hot melts are susceptible to joint movement or creep, which can result in bond failure (Europe Patent No. EP2622034 A1, 2013).

Hot melt adhesive with lower viscosity will have more flexibility to flow out, which makes it easier for the adhesive to fully wet the substrate. This provides an opportunity for the adhesive material molecules orient themselves onto the substrate surface, hence forming a bond with the substrate. Adhesive with higher molten viscosity will have a harder time to flow out and completely wet the substrate, hence the adhesive material molecules will have less chance to orient themselves onto the substrate surface to form a bond. Ideally, at application temperature, the viscosity of the molten adhesive should stay low long enough for the substrate to be brought into contact and then rise rapidly to set the band in minimum time (Macosko, 1977). The glass transition temperature (Tg) is used for determining compatibility of polymer blends. It has usually been associated with the onset of segmental mobility in the amorphous phase of an amorphous or semi crystalline polymer (Chen et al, 2001). Open time is an important concept in the adhesive industry. Open time can be defined as the time lapse between applying the molten adhesive onto the substrate and the transformation to the solid state, at which point the hot melt adhesive loses its ability to wet the substrate (Cagle, 1973).

In recent years, packaging industry prefers to use hot melt adhesive based on polyolefin because polyolefin provide ease of processing, low off-taste, low smell and heat seal ability. Polyolefin is also a good barrier against moisture and water vapor, and excellent chemical resistance against polar solvents and solutions including acids, bases, and alcohols. In this research, it is intended to develop the formulation for Ethylene Vinyl Acetate (EVA) based hot melt adhesive with the same properties of polyolefin based hot melt adhesive since EVA offers low cost than polyolefin.

To prepare the EVA hot melt adhesive, they must follow four main basic components. First is EVA polymer as the backbone, second is tackifier used to increase the wetting of the surface, to alter the adhesion and to change the polymer flexibility (Kalish et al, 2014), third are low molecular waxes used to reduce the high viscosity of the hot melt adhesive to an applicable range and lastly is an antioxidant to prevent the resin from oxidizing and to aid in processing (Park and Kim, 2003). The performance of EVA hot melt adhesive will be analyzed and tested by using the viscometer and differential scanning calorimeter (DSC). The performance of EVA hot melt adhesive will be compared with the performance of commercial polyolefin hot melt adhesive.

1.2 Problem Statement

The main problem in hot melt adhesive in the packaging industry is to find the suitable raw material. In recent years, packaging industry prefers to use hot melt adhesive based on polyolefin because polyolefin provide ease of processing, low off-taste, low smell and heat seal ability. Polyolefin is also a good barrier against moisture and water vapor, and excellent chemical resistance against polar solvents and solutions including acids, bases, and alcohols. In this research, it is intended to develop the formulation for Ethylene Vinyl Acetate (EVA) based hot melt adhesive with the same properties of polyolefin based hot melt adhesive since EVA offers low cost than polyolefin.

1.3 Objectives of research

The objectives of this research are:

1. To develop a new hot melt adhesive for packaging industry utilizing Ethylene Vinyl Acetate (EVA) copolymer
2. To compare the performance of this new development Ethylene Vinyl Acetate (EVA) based adhesive with commercial polyolefin based adhesive

1.4 Scope of this research

To achieve the objectives; the scopes of this research are:

1. To formulate Ethylene Vinyl Acetate base hot melt adhesive for case and carton sealing
2. To characterize physical properties of Ethylene Vinyl Acetate (EVA) base hot melt adhesive by using kinematic viscosity and differential scanning calorimeter (DSC)

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This research presents to develop a new formulation of hot melt adhesive for packaging industry utilizing ethylene vinyl acetate (EVA) and compared with commercial polyolefin based adhesive. The parameter use of the experimental is melt viscosity, glass transition temperature and adhesion strength. To develop the hot melt adhesive, they have four components, polymer, tackifier, waxes and antioxidant (Kalish et al, 2014). There are various types of polymers to develop hot melt adhesive such as ethylene vinyl acetate (EVA), polyolefin, polyamide and reactive urethanes (Park et al., 2005). Other than that, in this chapter also describe the equipment used to find the parameter, e.g. Brookfield Viscometer and Diffential Scanning Calometry (DSC).

2.2 Hot Melt Adhesive

Hot-melt adhesives as a thermoplastic material in solid condition at room temperature, when heated above their melting point, they become fluid and able to wet the surface to which they applied (Dexehmier and Vertnik, 1983). During the cooling process, the adhesive composition regains its solid form. The hard phase formed upon cooling, the adhesive composition imparts all of the cohesion such as strength, toughness, creep and heat resistance of the final bond. Hot melt adhesive compositions does not use any type of solvent include water. The adhesive composition will cure by a chemical crosslinking reaction upon exposure to suitable conditions such as exposure to moisture. Before curing the adhesive composition remains thermoplastic and can be remelted and solidified. The cross-linked adhesive composition provides strength, toughness, creeps and heat resistance to the final bond. Hot melt curable adhesive compositions can provide higher strength and heat resistance compared to non- curable hot melt adhesive compositions. (International Publication PCT Patent No. WO2014116398 A1, 2014). The origin of hot melts probably started with the use of sealing wax used to seal documents and letters with a signature ring or stamp, but the art of hot melts was not pursued until the 1960. (Nicholsan, 1991). Hot melts adhesive become popular because it's fast processing, efficient shipment and storage. Hot melt adhesive also popular because they are convenient and satisfy environmental requirements (Young and Hyun, 2003). The advantage of hot melt adhesives is that they typically provide for short setting times, e.g. below 5 seconds, such that the substrates need only be pressed together for a short time after gluing a short pressing time. At the end of the pressing time, the adhesive strength should be high enough to hold the substrates together. Furthermore, hot melts are able to bond many different types of substrates, including permeable substrates and non-permeable substrates. The disadvantage of hot melt is that they are inherently temperature sensitive. Hot melts become soft at elevated temperatures and become brittle at low temperatures. At elevated temperatures hot melts are susceptible to joint movement or creep, which can result in bond failure. A further disadvantage of hot melts is that they typically have a high application temperature of between 140 - 180 °C. Such high temperatures may be undesirable with respect to energy consumption and operational safety and may further be undesirable to use in certain applications, for example, when one of the substrates to be glued is a heat-sensitive substrate. (Europe Patent No. EP2622034 A1, 2013). Hot melt can generally categorize by one or more of the following characteristics such as their type of base polymer, viscosity at a given temperature, speed of set, heat resistance, tensile strength and heat stability. The main type of chemistries for hot melt is Ethylene Vinyl Acetate (EVA) based adhesive, polyolefin based adhesive, styrene copolymer based adhesive, polyurethane based adhesive, polyamide and polyester based adhesive (Rolando, 1998). Hot melt adhesives for packaging are generally extruded in bad form onto a substrate using a piston pump or gear pump extrusion equipment.

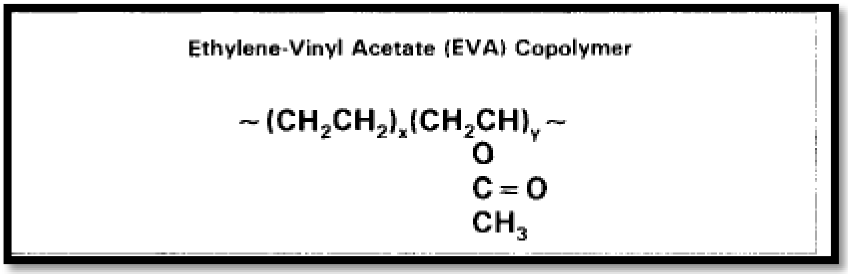
Wheel applicators are also commonly used for applying hot melt adhesives, but are used less frequently than extrusion equipment. Hot melts are required to have sufficient adhesion to the substrates to firmly hold the package together, and in many cases, end users of hot melt adhesives require full fiber tearing bonds, meaning substantially all the fiber is removed from the substrate along the entire length of the adhesive application when the bond is separated by hand. Generally, in order to get full fiber tearing bonds, hot melt need to be applied at temperatures of 175°C or greater. This increases the open time of the adhesive and lowers the viscosity for better penetration into the substrate. Open time refers to the amount of time that the adhesive can form a bond to the substrate. (United State Patent No. 6319979 B1, 2001). In addition to bonding requirements, customers are demanding higher performance in other areas, such as thermal stability. Good thermal stability means that the product will not darken in the glue pot with prolonged exposure to high temperatures, will not produce char, skin or gel, and will not exhibit a substantial viscosity change over time. High application temperatures, along with exposure to oxygen, can increase the degradation of the hot melt adhesives. This problem is most commonly alleviated with the use of antioxidants such as Irganox® 565, 1010 and 1076, which are hindered phenolic antioxidants. Another way to reduce charring, skin, gel formation, discoloration and viscosity changes, is to lower the application temperature of the hot melt adhesive. In addition to improving thermal stability, lowering the application temperature also reduces the risk of severe burns to hot melt equipment operators, decreases the amount of electricity required to heat the adhesives which can result in energy cost savings, decreases maintenance costs, and reduces the amount of odors due to volatiles coming from the adhesives. Decreasing the odor and fumes coming from the adhesive is particularly appealing to customers, and to the employees who work in plants utilizing hot melt adhesives on a regular basis (Europe Patent No. 0912646 B1, 2002). Besides use in packaging, hot melt adhesive also use for bookbinding, footwear, wood industries and textile (Hussey and Wilson, 1996). Although various hot melt adhesives have been developed for specific applications to different substrates for use in different environments, but they must follow four main basic components. First is a polymer, second is tackifier, third are low molecular waxes and lastly is an antioxidant (Kalish et al, 2014).

2.3 Polymer

Polymer is the main component in hot melt adhesive. Functional polymer is the backbone of the hot melt adhesive, it can increase the potential for adhesion of polymers in contact with a solid surface (Ebnesajjad, 2012). They can be either homopolymers or copolymers with various functional groups specific to application needs (Kalish et al, 2014). Polymer also contributes strength and toughness for hot melt adhesive. Usually, in hot melt adhesive, its use around 40%-45% of the polymer. There are various types of polymers such as ethylene vinyl acetate (EVA), polyolefin, polyamide and reactive urethanes (Park et al., 2005)

2.3.1 Ethylene vinyl acetate (EVA)

EVA is a co-polymer made from two different monomer types being ethylene and vinyl acetate. The chemical structure of EVA is given in Figure 2-1 (Henderson, 1993). The first ethylene copolymers, including EVA, were synthesized and patented in the 1930s at IC1 in Great Britain in the same laboratories where polyethylene was discovered (United State Patent No. 2,200,429, 1940). The EVA copolymer is synthesized through the copolymerization of ethylene and vinyl acetate by a high pressure, high temperature and bulk polymerization process. (Stael and Tavares, 1998). Bulk polymerization is the technique most widely used to produce the EVA copolymers containing up to 50% vinyl acetate by weight. The properties of EVA copolymer can determined by three structural attributes which is the weight percent of vinyl acetate, molecular weight and distribution and molecular branching. Weight percent (%) of vinyl acetate content has two fundamental effects that influence the properties of EVA copolymers. The first effect is to disrupt the crystalline regions formed by the polyethylene segments of the copolymer (Henderson, 1993). Higher vinyl acetate content tends to make the polymer softer and more rubbery, while lower vinyl acetate content tends to make the polymer harder and more crystalline (Shen and Yu, 2014). Low and medium density polyethylenes, produced by the high pressure bulk process typically exhibit degrees of crystallinity in the range of 40-65% as measured by X-ray diffraction and confirmed by differential scanning calorimetry. This is progressively reduced by increasing VA content. If vinyl acetate exceeds 45 %, the cristallinity of the EVA will be lost. The ability to vary the degree of crystallinity of semi-crystalline EVA copolymers has significant interest in regulating properties for specific end uses and is largely responsible for versatility of these products (Henderson, 1993). The common grades for EVA copolymer have vinyl acetate contents ranging from 1%~50% by weight, depending upon the application (Arsac et al., 1999).In hot melt adhesive, EVA copolymers used 18– 40 % by weight of vinyl acetate content and their melt indices are 2–400 dg/min. Melt indices means the melt flow property of polymer materials at fixed pressure and temperature. The domain structure of EVA copolymers consists of stiff and partially crystalline polyethylene blocks, and flexible, soft and polar amorphous vinyl acetate blocks. (Park et al., 2005). The second effect of vinyl acetate content results from the polar nature of the acetoxy side chain. The vinyl acetate content increases, the polarity of the copolymer also increase. Although less obvious than the reduction in crystallization, the increase in polarity also raises some interesting features and important, it's responsible for the wide diversity of applications for EVA copolymers. For the example, the compatibility with polar resins and plasticizers will be increased because of increased polarity due to increasing vinyl acetate content. Molecular weight (MW) has a major influence on other properties besides the melt viscosity, although, it should be appreciated that the effect is invariably modified by the influence of other structural features. The most important properties affected by increasing molecular weight are illustrated in Table 2-1. Today MWs and molecular weight &stributions (MWDs) of EVA are most conveniently measured by high temperature (145°C) Size Exclusion Chromatography (SEC) in solvents such as 1-2-4 trichlorobenzene. For the molecular branching, in EVA, short chain branches with less than six carbon atoms are differentiated from long chain branches with six carbon atoms that become part of the crystalline network. The effect of short chain branches on EVA copolymer properties is similar to weight percent of vinyl acetate but to a much lesser extent is due to the relatively low number of short branches. The primary influence of long chain branches, formed by chain transfer of a growing polymer radical, is to increase the melt elasticity of the EVA copolymer. The long chain branches tend to entangle and increase the elastic response of the melt. (Henderson, 1993). Due to its good compatibility with a wide range of tackifiers and wax, EVA can be formulated to fulfill very broad performance requirements.



$$\sim(CH_2CH_2)_x(\underset{\underset{\underset{CH_3}{C=O}}{O}}{CH_2CH})_y\sim$$

Figure 2-1: Molecular Formula of Ethylene Vinyl Acetate

Table 2-1: Changes in physical properties of EVA copolymers as a function of increasing Molecular weight

Properties	Physical Changes
Viscosity	Increase
Softening point	Increase
Tensile strength at break	Increase
Solubility	Decrease

A low cost and wide formulation window provide excellent advantages for EVA to compete with other type hot melt adhesive (Mittal and Pizzi, 2009). Another advantage is EVA has a good adhesion strength and good adhesion to a variety of materials (Young and Hyun, 2003). The primary applications for EVA copolymers are in packaging film, adhesives or paper coatings, wire and cable insulation, carpet backing, molding and extrusion, foam, and sound barrier sheet. In general, EVA-based hot melt adhesive are widely used in various substrates such as paper, wood, plastics, rubbers, metals and painted metals. (Jung et al., 2010). A typical formulation range of EVA-based hot melt adhesive is shown in Table 2-2 (Mittal and Pizzi, 2009).

Table 2-2: Formulation of an EVA Hot Melt Adhesive

Ingredient	Weight percent (wt %)
EVA polymer	10-50
Tackifier resin and wax	30-80
Antioxidant	10-50

Base on material safety data sheet (MSDS) for EVA copolymer from International Polymer Company, Saudi Arabia, the physical and chemical properties of EVA copolymer summarized in the table below:

Table 2-3: Physical and chemical properties of EVA copolymer

Physical State	**Solid**
Color	clear, opaque, off-white
Melting Point	80-120 °C
Boiling Point	228 °C
Specific Gravity	0.92 -0.95

2.3.2 Polyolefin

A simple definition of polyolefin is a polymer obtained from Olefin as monomers. Olefins are typically ethylene, propylene, and butylene (Fourrier, 2014). Polyolefin only consist of carbon and hydrogen atom and the monomer are easily available. Considering the environmental aspect, clean disposal can be achieved by burning or by pyrolysis. In 2003, 55 million tons of polyethylene (PE) and 38 million tons of polypropylenes (PP) were produced. This product is used for packaging material, receptacle, pipes, domestic article, foils and fibers (Kaminsky, 2005). PE is homopolymers of ethylene or copolymers of ethylene with up to 20% of other commoners like 1-butene, 1-hexene, and 1-octene. PP is homopolymers of propylene or copolymers of propylene with up to 10% copolymerized ethylene (Chun and Swogger, 2008). By copolymerization of ethane and propene with the higher n-olefin, cyclic olefin or polar monomers, product properties can be varied considerably, thus extending the field of possible application. For this reason, polymers of the ethylene and propylene n-olefin type are the polymer with the greatest potential. The existence of several types of polyethylene as well as blend these polymers provide the designer with an unusual versatility in resin specification. Polyethylene technology has progressed from its dependence on one low-density polymer to numerous linear polymers, copolymer and blends that will extend the polyethylene to many previously unacceptable applications. Polypropylene also shows the versatility and unusual growth potential. The main advantage is improved susceptibility to degradation by outdoor exposure. (Kaminsky, 2005). Polyolefin typically comes in the form of pellets that are extruded, blow molded, injection molded, or rot molded to fabricate products. Extrusion processes produce films, sheets, fibers, profiles, foams and coatings. Blow molding produces containers and parts. Injection molding produces smaller containers and parts. Rot molding produces parts in a huge variety of shapes and sizes (Chun and Swogger, 2008). Polyolefin based hot melt adhesive comprise of polyethylene (PE) and atactic polypropylene (APP) as well as some polymer based product with polyethylene. APP is a tacky product that is not easily formulated and is generally used as a neat resin or extended with a small amount of wax or polymer to provide hot tack. PE hot melt adhesive are generally lower MW species, none or slightly modified or formulated and used in packaging application such as case and carton sealing and corrugated container. The MW of the polyolefin generally influences the properties of the adhesive. In general, when MW is increased, the heat seal strength of the adhesive is increased. Additionally, when MW is increased, the hot tack and melt viscosity also increased. Conversely, MW decrease, the flexibility and low temperature performance are increased. Polyolefin can be modified with small amount of tackifier and waxes. General type use for tackifier is hydrocarbon based while the type of waxes is paraffin based or microcrystalline. Waxes are used to lower costs and alter block resistance, softening point and open time properties. Polyolefin hot melt adhesive are used for many packaging such as carton and case sealing, non-woven, and laminating e.g. paper, film and aluminums foil application (Rolando, 1998). This hot melt technology provides superior adhesion to polypropylene, a good barrier against moisture and water vapor, and excellent chemical resistance against polar solvents and solutions including acids, bases, and alcohols. When compared with EVA and polyamide hot melt adhesives, polyolefin offer extended open times for positioning of parts. (Tremblay, 1999)

2.4 Resin

Resins or tackifiers are used to increase the wetting of the surface, to alter the adhesion and to change the polymer flexibility (Kalish et al., 2014). Tackifiers are commonly added to impart tack to the HMA and pressure-sensitive adhesive based on EVA and styrenic block copolymers (Class, 1985). Tack is required in most adhesive formulations to allow for proper joining of articles prior to the hot melt adhesive solidifying (United State Patent No. 6890982, 2005) .The tackifier must be reasonably compatible with the base polymer, have a very low molecular weight relative to the base elastomer, and have a glass transition temperature (Tg) that is higher than that of the base elastomer. Therefore, the addition of tackifiers modifies viscosity, rheology and adhesion properties (Park et al., 2005). Resin can divide into two groups which is natural and synthetic resin. Natural resin is defined as resins of vegetable or animal origin. Synthetic resin is defined as reins resulting from controlled chemical reaction such as polyaddition or polycondensation. Synthetic resin also obtained by polymerization of unsaturated monomer. Hydrocarbon resin is one of the subgroups of synthetic resin (Mildenberg, 2008). The hydrocarbon resins, which are used as tackifiers in HMAs, can be classified according to whether they contain primarily aromatic, aliphatic, or dicyclopentadiene (DCPD) monomers. These are also referred to as C9, C5, and C10, respectively, corresponding to the average number of carbon atoms per monomer molecule. (Lee et al. , 2010).

2.5 Wax

The low viscosity of the wax is used to reduce the high viscosity of the hot melt adhesive to an applicable range. Large amounts of wax are also required to set the time control since wax helps control the set time (Rodriguez et al., 2010). The wax also plays a major role in increasing the blocking point of the final adhesive, preventing the adhesive pastilles from sticking together during transport and storage (sasolwax.com, 2014). The use of a wax having a low but relatively sharp melting point leads to a hot melt adhesive composition which liquefies at a temperature lower than that of commercially available hot melt adhesives, but still retains good set speed characteristics. The ratio of polymer to tackifier to wax is generally specific to a particular application's need. In general, the percent wax is minimized and added in sufficient quantities to achieve desired viscosity and set speeds. The level of wax is generally in the range of 15 to 35% by weight of the formulation. Generally, hot melt adhesive formulations are heated to 140-170 ^{0}C prior to application in order to reduce viscosity. The wax must be stable at these temperatures to allow for extended periods as a molten product prior to application. (United State Patent No. 6890982, 2005). There are few types of wax such as petroleum base, made on purpose polyethylene (PE), polypropylene (PP) and Fischer-Tropsch. Petroleum base is obtained from the distillation and cracking of crude oil such as paraffin and micro-crystalline. Type of made on purpose polyethylene (PE), polypropylene (PP) is obtained from the polymerization of ethylene or propylene. Fischer-Tropsch obtains from catalytic conversion of coal or natural gas to produce linear alkanes. (Brown et al, 2012).

2.6 Antioxidant

Function antioxidants are to prevent the resin from oxidizing and to aid in processing (Young and Hyun, 2003). Antioxidant have two major classes and they differentiated based on their machasism of inhibition of polymer oxidation which is primary antioxidants and hydroperoxide-decomposing secondary antioxidant (Klemchuk, 1985). The majority of primary antioxidant is hindered phenol or secondary aryl amines. Hindered phenol is nonsatining ,nondiscoloring and are available in a wide range of molecular weights and efficiencies. A typical hindered phenol primary antioxidant is AO-1(2,6-di-*tert*-butyl-*para*-cresol). Due to its lower cost, AO-1 is widely use in as an antioxidant. In addition, this antioxidant show higher activity,compatibility and resistance toward the formation of colored byproduct during compounding and application temperature of hot melt adhesive (Pizzi and Mittal, 2003). Suitable amounts of antioxidants in the adhesive composition of the invention are preferably within the range of 0.005 wt % to 5 wt %, more preferably within the range of 0.01 wt % to 1 wt %, and most preferably within the range of 0.05 wt % to 0.5 Wt %, of the adhesive composition. (Botros et al., 2011)

2.7 Viscosity

Viscosity is a fundamental characteristic property of all liquids. When liquids flow, it has an internal resistance to flow. Viscosity is a measure of this resistance to flow or shear. Viscosity can also be termed as a drag force and is a measure of fractional properties of liquids. Viscosity is a function of temperature and pressure. Common unit for viscosity are centipoise (cP) (Vismanath, et al., 2007). In terms of adhesive, the viscosity adhesive decrease with increasing temperature. Figure 2-2 shows this viscosity reduction as a function of temperature (Licari and Swanson, 2011).

In processing, the viscosity must be fairly low at application temperature to allow good substrate penetration. If it is too low, it runs off the substrate or produces a thin film which results in voids when two substrates are joined. The hot melt viscosity should remain low enough for the opposite substrate to be brought into contact and then rise rapidly to set the bond in a minimum time. The molten viscosity of most adhesive polymers (low molecular weight) is proportional to its molecular weight.

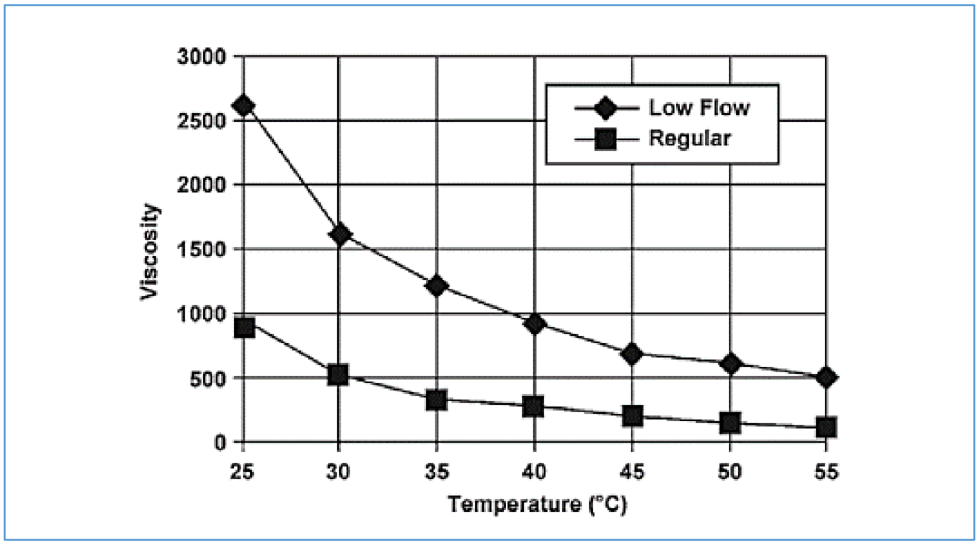


Figure 2-2 Viscosity (cP) as function temperature

The measurement of viscosity is important in academia or in industry. From the book of *Viscosity of Liquids: Theory, Estimation, Experiment, and Data* by Vismanath et al. in 2007,there are several types of instrument used to measure the viscosity of liquid, it can be broadly classified into seven categories:

1) Capillary viscometer
2) Orifice viscometer
3) High temperature,high shear rate viscometer
4) Rotational viscometer
5) Falling ball viscometer
6) Vibrational viscometer
7) Ultrasonic viscometer

A number of viscometer also available that combine the features of two or three types of viscometer notes at above such as Brookfield Viscometer, Friction tube and Norcross. The most common equipment used to test viscosity is Brookfield Viscometer. Brookfield Viscometer have three models, Model LVF for low-viscosity material, Model RVF for medium viscosity formulation and Model HVF for high viscosity formulations. (Licari and Swanson, 2011). To measure the viscosity of adhesive at elevated temperatures, it prefers to use Brookfield Viscometer with thermosel system. Figure 3 shows the Brookfield viscometer with termosel system to measure the viscosity at elevated temparature.

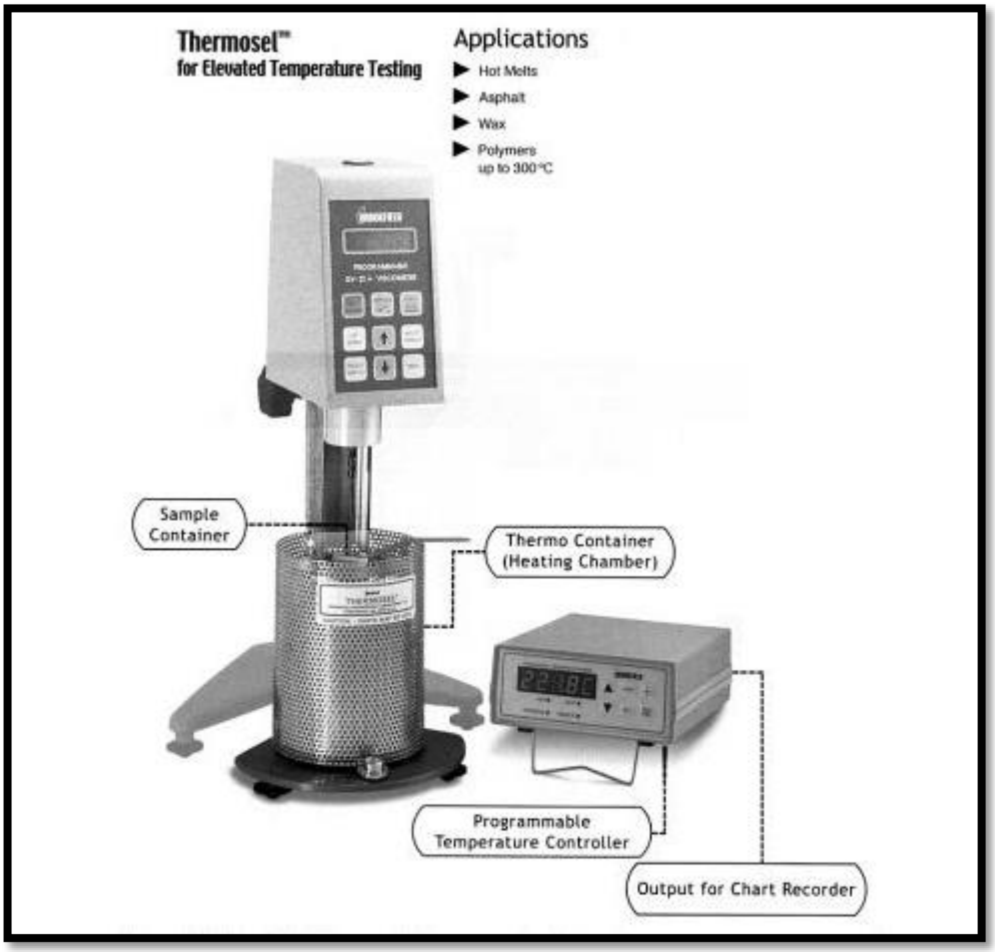


Figure 2-3 Brookfield Thermosel Viscometer for elevated temperature measurement of viscosity

2.8 *Differential Scanning Calometry (DSC)*

Differential scanning Calomtery (DSC) means the measurement of the change of the difference in heat flow rate in the sample and to a reference sample while they are subject to control program (Höhne et al., 2003). DSC is use to characterized physical properties of polymer, e.g. melting temperature, heat melting, percent crystallinity and glass transition temperature (flemingptc.co.uk, 2014). Figure 4 shows the typical scan of DSC.

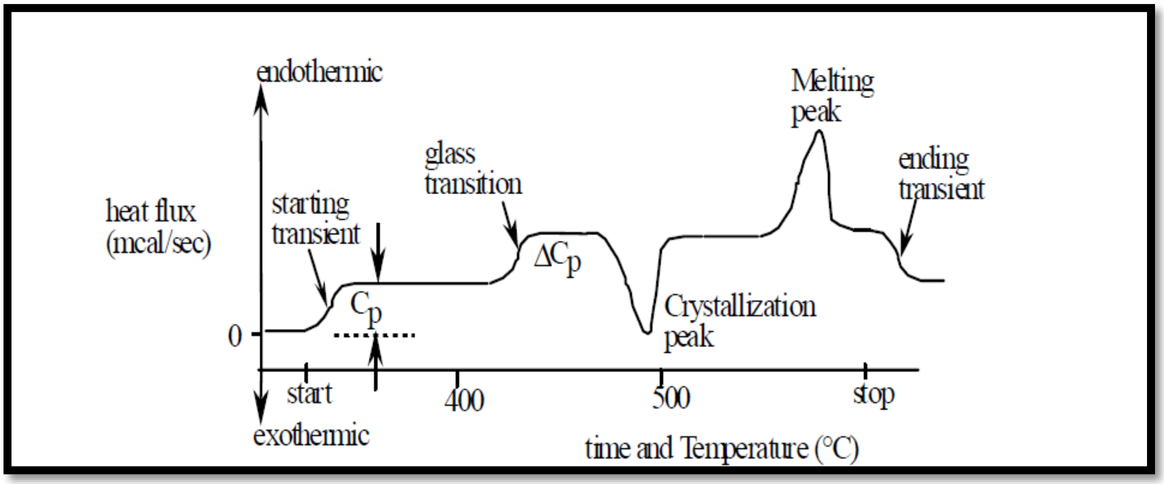


Figure 2-4: Typical scan of DSC

The information can obtained from a DSC curve is the temperature at which a certain process occurs, for example, the melting point of a polymer. The temperature at which a reaction, such as decomposition, may start is another important parameter. The peak temperature is associated with the temperature at which maximum reaction rate occurs. A special case in which the temperature of a phase transformation is of great importance in polymers is the glass transition temperature, T_g. This is the temperature at which amorphous (noncrystalline) polymers are converted from a brittle, glasslike form to a rubbery and flexible form. Crystallization is a typical exothermic process and melting a typical endothermic process (colby.edu, 2014).DSC is widely used in the pharmaceutical and polymer industries. For the polymer chemist, DSC is a handy tool for studying curing process, which allows the fine tuning of polymer properties. The cross-linking of polymer molecules that occurs in the curing process is exothermic, resulting in a positive peak in the DSC curve that usually appears soon after the glass transition. (flemingptc.co.uk, 2014).

2.8.1 Glass Transitions Temperature

Glass transitions can only take place in an amorphous material. A glass transition has no latent heat associated with it, and such transitions are referred to as second order transitions. The heat flow vs. temperature for a glass transition is as shown in Figure 2.5. In this case, the heat capacity has increased and the molecules have become more mobile, and so the material is now in a state where its atoms/molecules have more energy. In order to keep the heat rate constant, the sample pan heater needed to increase heat flow. The material is still amorphous but has undergone a transition from a lower energy state to a higher energy state. The temperature at which the material undergoes a glass transition is known as the glass transition temperature (T_g), and as seen in Figure 2.5, the T_g is assigned to the midpoint temperature of the range of temperature during the transition (Lukas and KLeMaire, 2009)

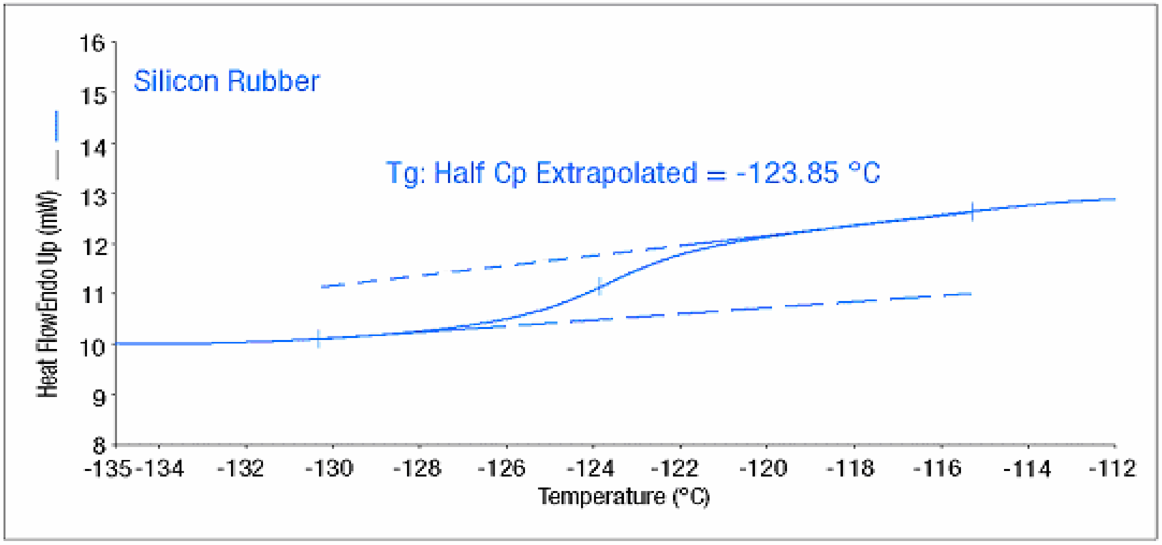


Figure 2.5. Glass transition temperature (T_g)

CHAPTER 3

MATERIAL AND METHODOLOGY

3.1 Material

Three types of ethylene vinyl acetate were used in this study. Some characteristics of EVA copolymers, such as density and melting point, are shown in Table 1.

Table 3.1: Properties of EVA copolymers

Code	Density (g/cm^3)	Melting Point (^{o}C)
EVA- 1	0.95	63
EVA-2	0.95	66
EVA-3	0.95	68

Three types of resin were used in this study. Table 2 indicates the softening point and molecular weight of the tackifier.

Table 3.2: Properties of resin

Code	Softening Point (^{o}C)	Molecular weight (g/mol)
Resin 1	105.0	670
Resin 2	124.0	660
Resin 3	103.0	800

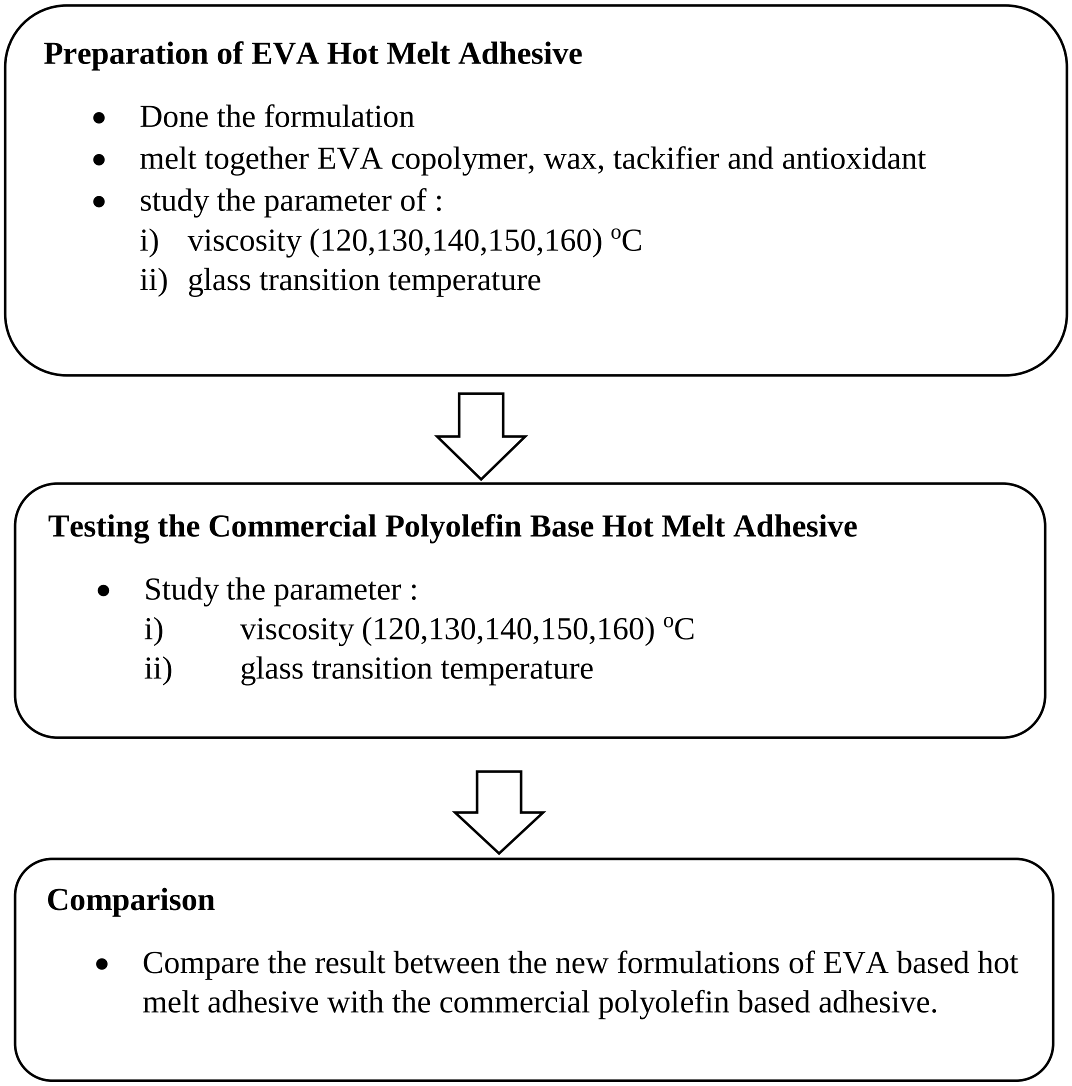
To reduce the high viscosity of the polymer and resin to ensure efficient mixing, the wax was used in this study.

To reduce the thermal degradation of HMAs during melt process, 0.4 parts by weight of antioxidant were used as a thermal stabilizer.

To compare the performance of EVA hot melt adhesive with the commercial adhesive, one type of polyolefin hot melt adhesive is used in this study.

3.2 Methodology

In this study, it wants to develop the new hot melt adhesive utilizing ethylene vinyl acetate and will be compared with the commercial polyolefin based adhesive. The experiment involves three stages, preparation of EVA based hot melt adhesive, testing for commercial polyolefin based hot melt adhesive and lastly compares the result between the new developments of EVA based hot melt adhesive with the commercial polyolefin based hot melt adhesive. The flow of the experiment is summarized in the flow chart.



Preparation of EVA Hot Melt Adhesive

- Done the formulation
- melt together EVA copolymer, wax, tackifier and antioxidant
- study the parameter of :
  i) viscosity (120,130,140,150,160) ^{o}C
  ii) glass transition temperature

Testing the Commercial Polyolefin Base Hot Melt Adhesive

- Study the parameter :
  i) viscosity (120,130,140,150,160) ^{o}C
  ii) glass transition temperature

Comparison

- Compare the result between the new formulations of EVA based hot melt adhesive with the commercial polyolefin based adhesive.

Figure 3.1*:* Overall Methodology Flow Chart

3.2.1 Preparation of EVA Hot Melt Adhesive

To prepare the EVA hot melt adhesive, the items needed are hot plate, glass beaker and glove to prevent from the hot surface.

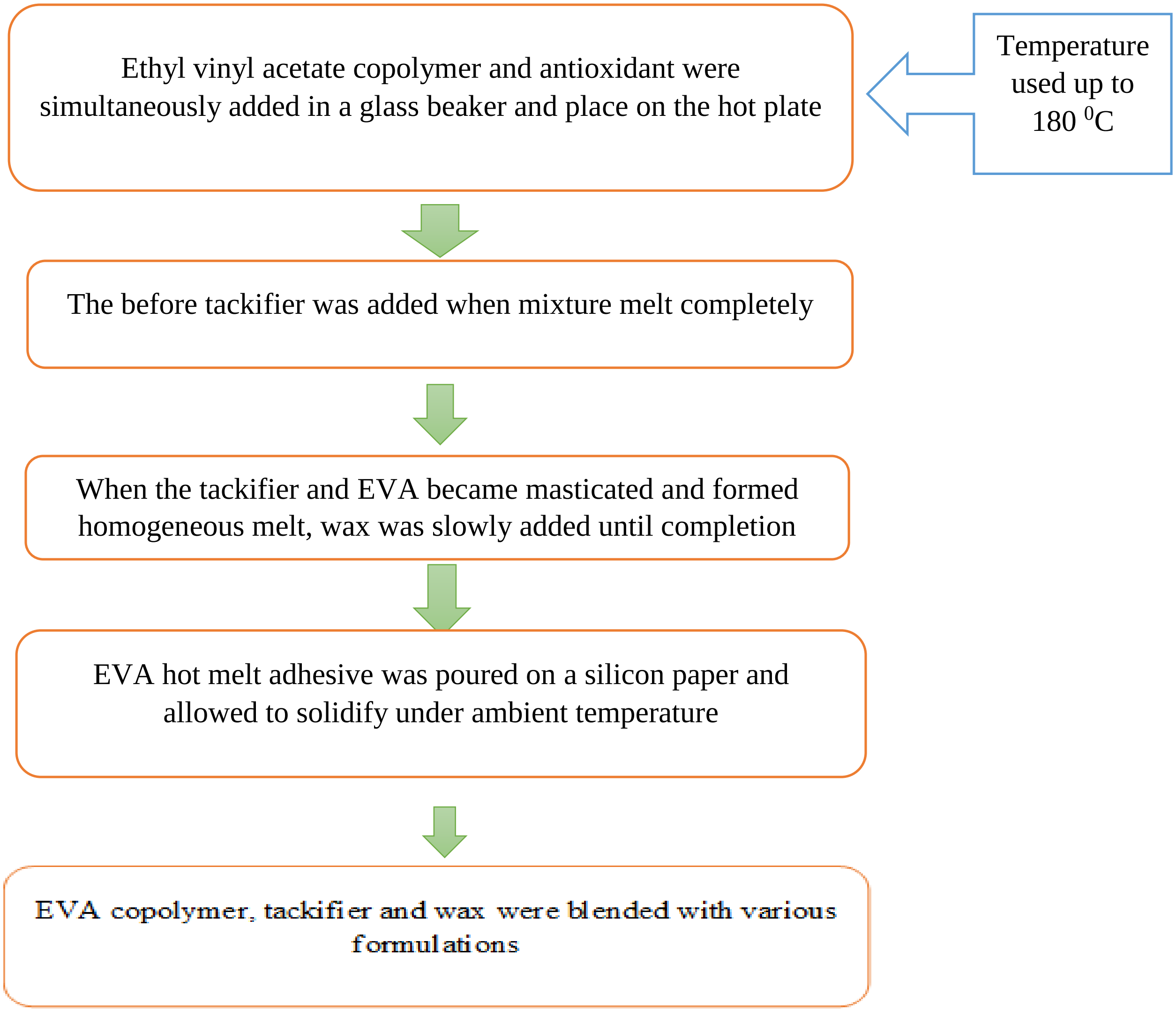


Figure 3.2: Flow diagram of Preparation of EVA Hot Melt Adhesive

3.3 Characterization of Hot Melt Adhesive

Ethylene vinyl acetate (EVA) base hot melt adhesive and the commercial polyolefin based hot melt adhesive was characterized by using melt viscosity, glass transition temperature and adhesion strength. Melt viscosity was measured by using the Brookfield Viscometer, glass transition temperature was measured using differential scanning calorimetry (DSC)

3.3.1 Melt viscosity

Melt viscosity was measured using a Brookfield Viscometer Model DV-II+ with a Brookfield Thermosel System, which allows the measurements under controlled high temperature. Viscosity obtains at temperatures of 120 ^{0}C, 130 ^{0}C, 140 ^{0}C, 150 ^{0}C and 160 ^{0}C. A SC4-21 spindle at a rotational speed of 100 rpm was used to measure a viscosity range of 250–5,000,000 cP.

3.3.2 Glass Transition Temperature

The glass transition temperatures (Tg) were measured using differential scanning calorimeter (DSC). The first samples are cooled to -80°C, and then heated to 120°C at 10°C/min. Then, the samples were cooled to -80°C and scanned to 120°C at 10°C/min. The glass transition temperature (Tg) values were determined from the DSC curves obtained in the second heating run. (Lee et al., 2010)

CHAPTER 4

RESULT AND DISCUSSION

4.1 Formulation EVA Hot Melt Adhesive

Table 4.1: Formulation of EVA hot melt adhesive (weight percent)

Code	EVA-HMA 1	EVA-HMA 2	EVA-HMA 3
EVA 1	25	30.4	25.4
EVA 2	14.6	11	11
EVA 3	-	-	5.0
Resin 1	15.0	30.0	30.0
Resin 2	15.0	8.1	8.1
Resin 3	15.0	2.1	2.1
Wax	15.0	18.0	18
Antioxidant	0.4	0.4	0.4

4.2 Differential scanning calorimeter

The glass transition temperature (Tg) measured by DSC is most the widely used for determining compatibility of polymer blends. It has usually been associated with the onset of segmental mobility in the amorphous phase of an amorphous or semi crystalline polymer (Chen et. al, 2001).

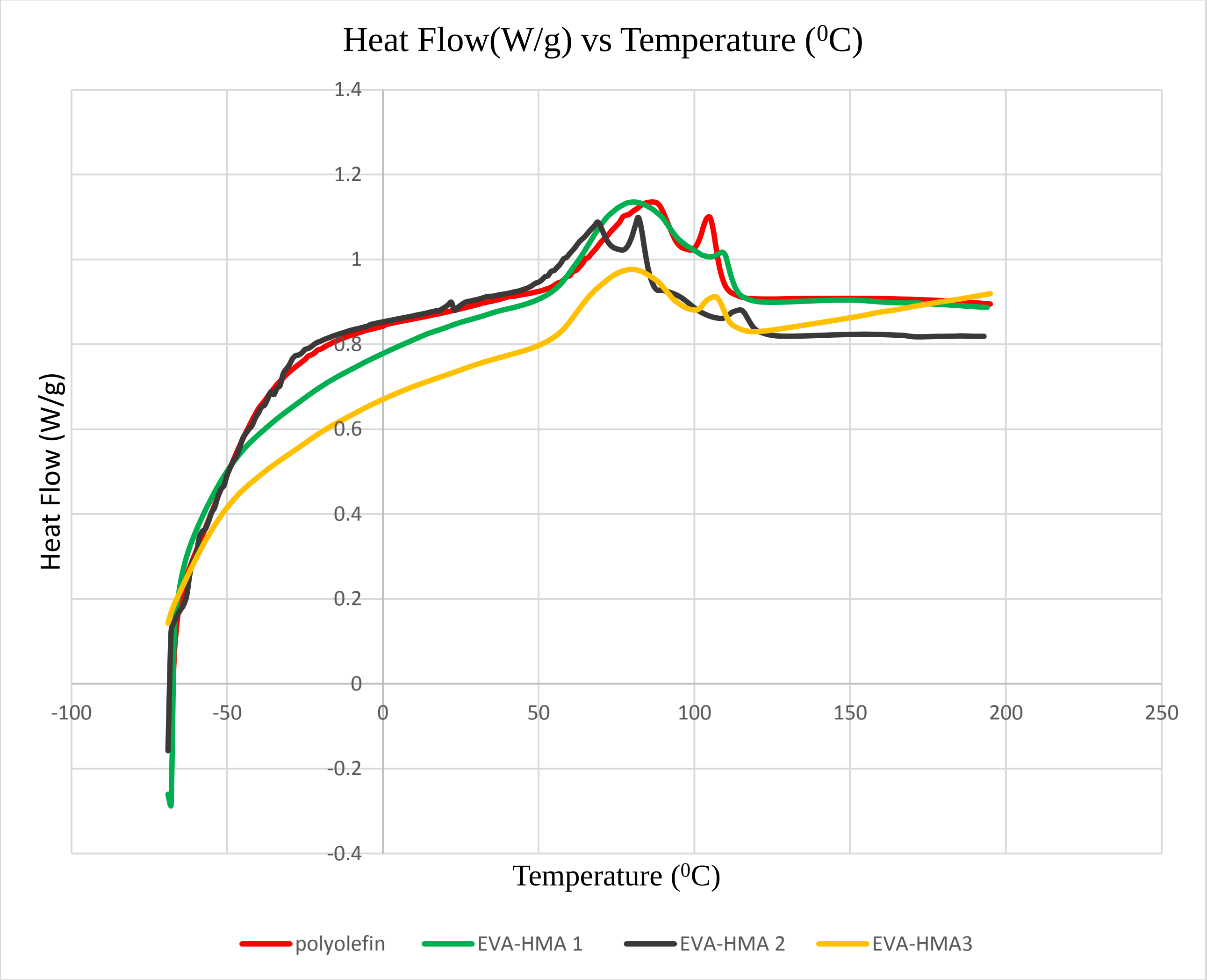


Figure 4.1: DSC curve

Table 4.2: Melting Temperature

Adhesive	Melting Temperature 1, Tm (^{0}C)	Melting Temperature 2, Tm (^{0}C)
Polyolefin (commercial)	87	105
EVA-HMA 1	81	109
EVA-HMA 2	70	82
EVA-HMA 3	80	106

The thermal properties of EVA adhesive and polyolefin (commercial) were determined using modulated DSC. The curve in Figure 1 show glass transition temperature, T_g and melting point, T_m. From DSC curve, the result indicated that three new formulations and commercial polyolefin has a glass transition temperature between -20 ^{0}C and -25 ^{0}C. The glass transition temperature usually just take the middle of the incline line (Makromolekülen, 2015).

The glass transition temperature is related with resin we use to blend the EVA adhesive. According Park and Kim in journal hot melt adhesive properties of EVA/aromatic resin blend showed the result of glass transition temperature is between -25 and -30.Implying, the result T_g of the new formulation is acceptable and the blend of four materials is compatible .

The peak observed on the heating curve corresponded to the melting point, T_m. It can be seen, all the four adhesive had different thermal behavior from each other. From the curve, all the adhesive has two peak point. Melting point 1 was used as the result. In general, melting point of EVA adhesive was affected by vinyl acetate content of EVA copolymers, but less affected by melting index (MI) of EVA copolymers (Arsac et al, 1999). EVA-HMA 2 gave sharp peak indicating that the thermal event occurred in a short temperature span while EVA-HMA 1, EVA-HMA 3 and commercial polyolefin adhesive gave similar broad and shallow peak, it indicates that the thermal occurred in a long temperature span.

The width and height of the peak observed from heat flow curve seemed to reflect the open time range suggested for each adhesive supplier (Le, 2011).Open time can be defined as the time lapse between applying the molten adhesive onto the substrate and the transformation to the solid state, at which point the hot melt adhesive loses its ability to wet the substrate (Cagle, 1973). EVA-HMA 2 deemed to have short open time because it has sharp peak. EVA-HMA 1 and EVA-HMA 3 is comparable with commercial adhesive base on the peak, it is supposed to have a long open time. It means the EVA-HMA 1 and EVA-HMA 3 is suitable to do EVA hot melt adhesive for packaging industry based on the thermal properties.

4.3 Viscosity

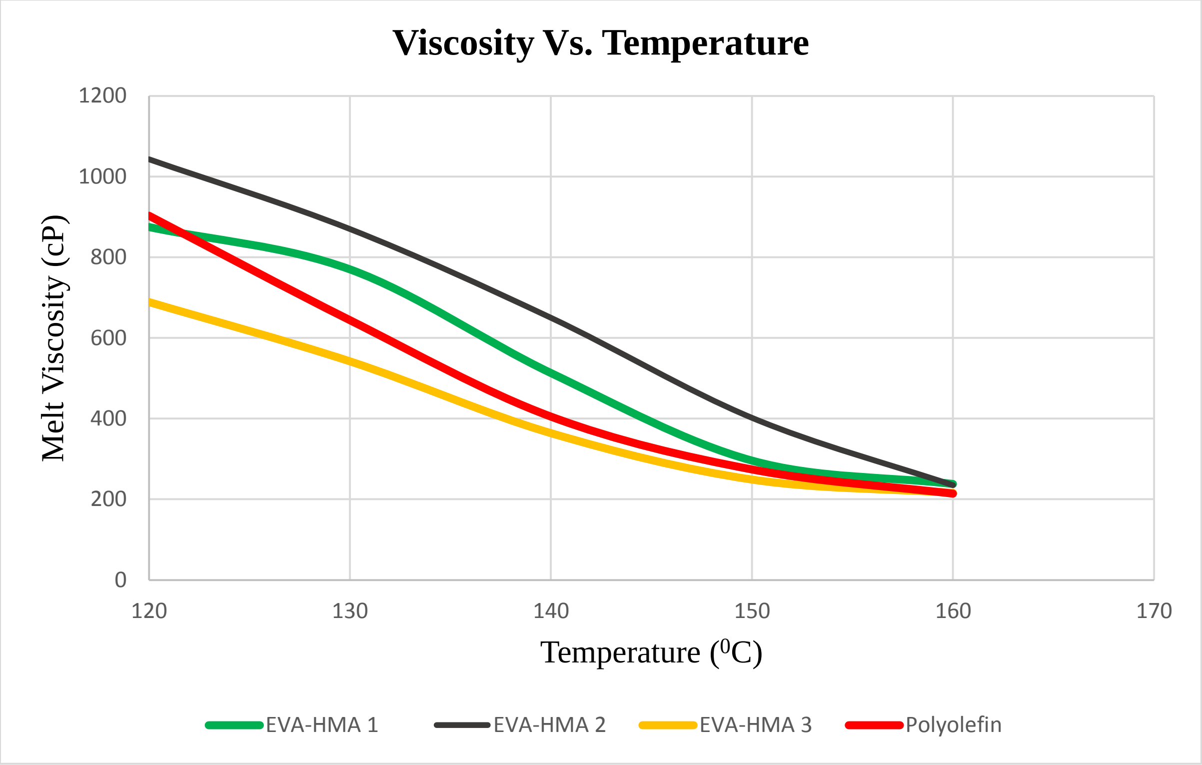


Figure 4.2: Melt viscosity Vs. Temperature

For the manufacture of hot melt adhesive, the materials used need to be sufficiently stable both during storage and processing as well as during their application. In particular, the most important of hot melt adhesive is thermal stability. Figure 2 shows the melt viscosity of three formulations of EVA hot melt adhesive and commercial polyolefin hot melt adhesive. A decrease of melt viscosity means thermal degradation of the adhesive. The increase of viscosity at the application temperature develop problems for the end user of the adhesive, resulting in unscheduled interruptions in production, because of plugged transfer lines and applicators (Colegrove et .al, 1998) .Usually,melt viscosity of EVA hot melt adhesive was affected by molecular weight of EVA copolymer, vinyl acetate and concentration (Qian et.al, 1997).

From the graph, at the beginning of measurement, the viscosity is slightly decreasing and lastly became stabilized. The melt viscosity decrease with increasing temperature and softening point of the adhesive also decrease (Park and Kim, 2003). EVA-HMA 1 and EVA-HMA 2 shows a relatively high melt viscosity compared with commercial polyolefin hot melt adhesive. EVA-HMA 2 shows the highest melt viscosity because the weight percent of EVA copolymer use EVA-HMA 2 is highest compared other formulations. It proved that the molecular weight of EVA copolymer will affect the melt viscosity. A rubbery polymer provides the elastic component, while the low molecular weight of resin constitutes a viscous component (Gierenz and Karman, 2001). Thus, the melt viscosity decrease as the content of weight percent increase use in the formulation. From the table 3, EVA-HMA 1 have a lower range of weight percent of resin compared to EVA-HMA 3. It proved base of the graph, EVA-HMA 3 has low melt viscosity compared to EVA-HMA 1.

Based on the graph, EVA-HMA 3 has lower melt viscosity compared to the commercial polyolefin hot melt adhesive at temperature 120 ^{0}C until temperature 140 ^{0}C and similar melt viscosity at temperature 140 ^{0}C - 160 ^{0}C. The melt viscosity is depend on the application. Hot melt adhesive with lower viscosity will have more flexibility to flow out, which makes it easier for the adhesive to fully wet the substrate. This provides an opportunity for the adhesive material molecules orient themselves onto the substrate surface, hence forming a bond with the substrate. Adhesive with higher molten viscosity will have a harder time to flow out and completely wet the substrate, hence the adhesive material molecules will have less chance to orient themselves onto the substrate surface to form a bond. Ideally, at application temperature, the viscosity for molten adhesive should stay low long enough for the substrate to be brought into contact and then rise rapidly to set the bond in minimum time (Macosko, 1977).Hence, EVA-HMA 3 can use as hot melt adhesive for the packaging due to melt viscosity.

CHAPTER 5

CONCLUSION

5.1 CONCLUSION

The performance of three formulations of EVA hot melt adhesive and commercial polyolefin hot melt adhesives were characterized by DSC and Viscometer. The thermal performance of the adhesives was conducted using DSC. All the three formulations of EVA hot melt adhesive have same glass transition temperature with commercial polyolefin. It proves the four materials used to produce EVA hot melt adhesive is compatible. EVA-HMA 1 and EVA-HMA 3 have a similar broad peak with commercial polyolefin, it indicates the hot melt adhesive has a long open time. The melt viscosity of all hot melt adhesive decrease with increasing temperature. The melt viscosity Formulation 3 is matched with the melt viscosity of commercial polyolefin at temperature 140 ^{0}C to 160 ^{0}C. Thus, from the three formulations, EVA HMA 3 have the best performance to be made the hot melt adhesive for the packaging industry because it's comparable for thermal properties and viscosity at a certain temperature. Further research needs to be conducted on EVA-HMA 3 for other properties to confirm its viability in replacing the commercial polyolefin based hot melt adhesive in packaging industry.

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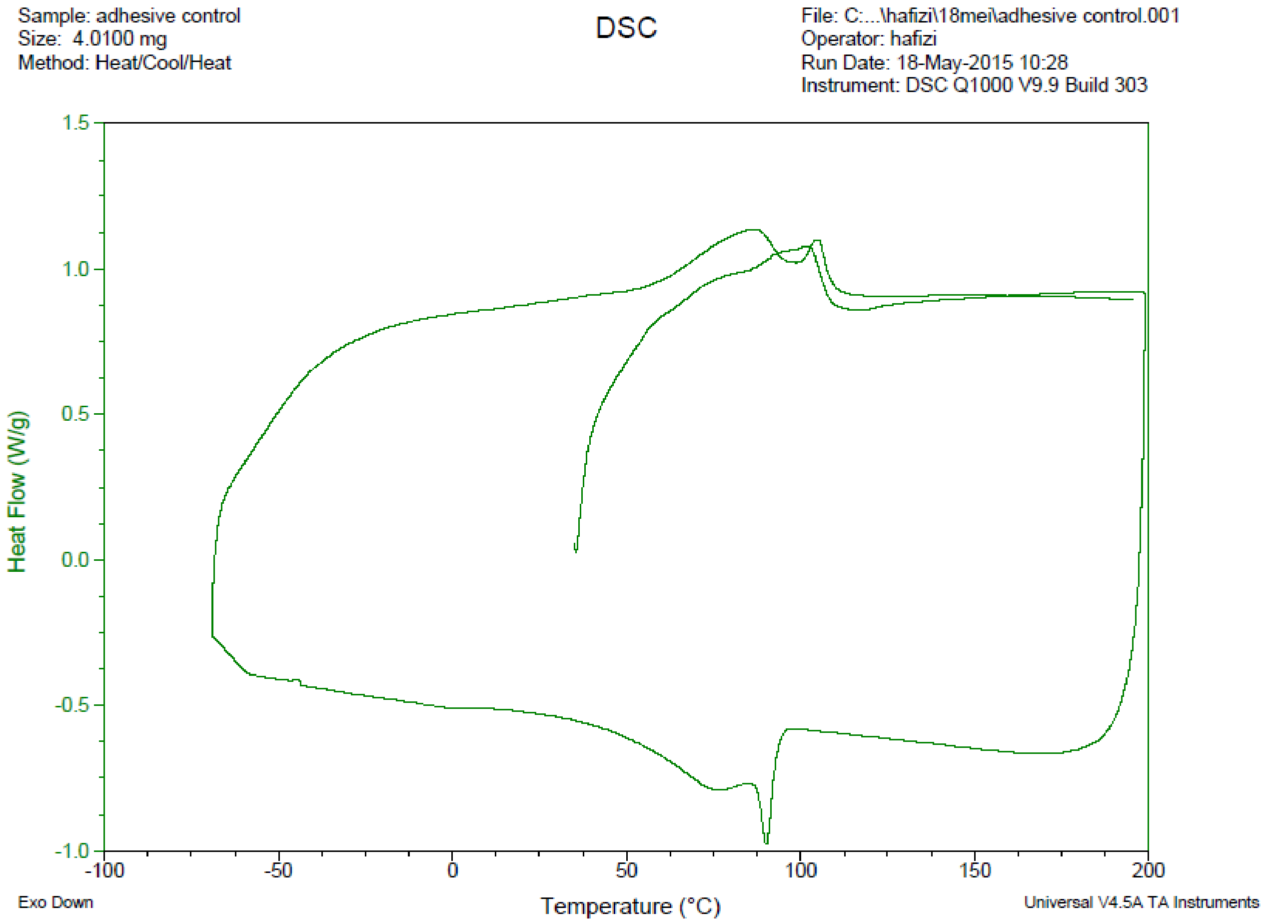
APPENDICES

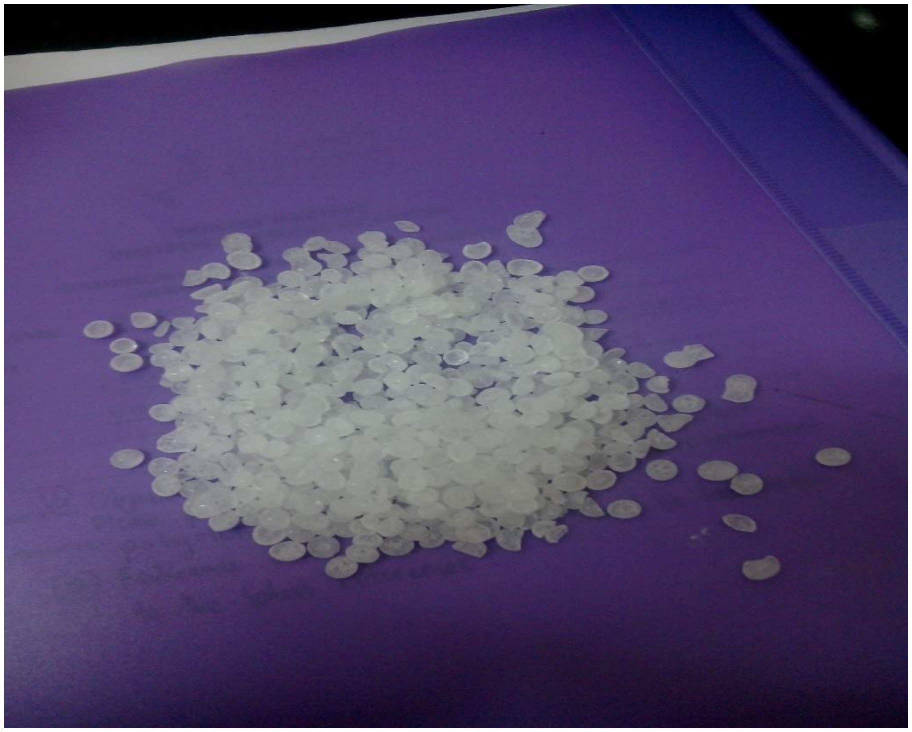
Appendix A – DSC with heating/cooling rate for polyolefin adhesive



Appendix B: Polymer

Appendix B.1: EVA copolymer

Appendix B.2: Wax



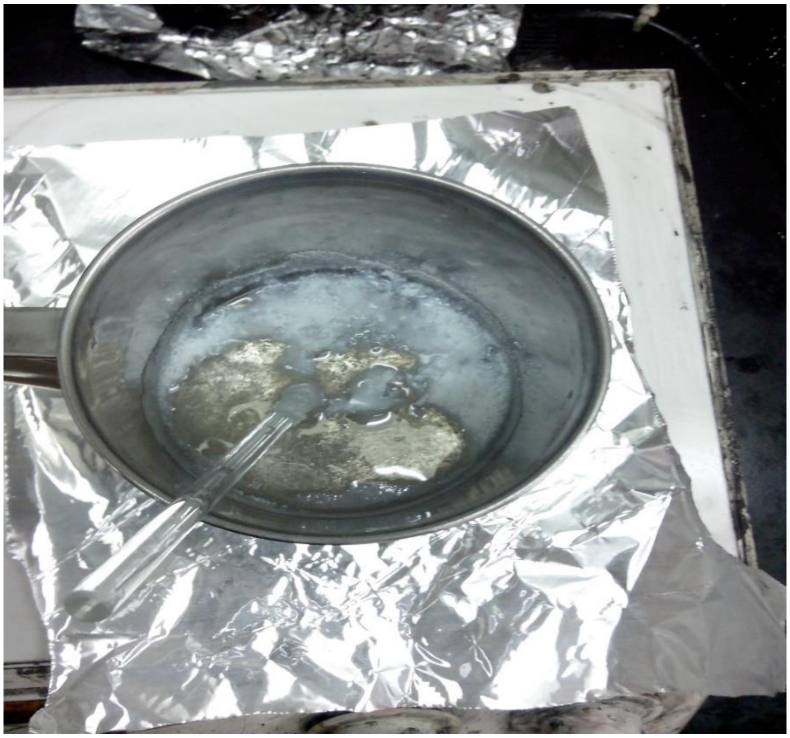
Appendix B.3: Resin

Appendix B.4: Polyolefin adhesive

Appendix C: Apparatus

Appendix C.1: Brookfield Viscometer used to determined melt viscosity

Appendix C.2: Apparatus setup to prepare EVA hot melt adhesive



Appendix C.3: All polymers blend together

Appendix C.3: EVA hot melt adhesive on silicon paper at ambient temperature