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MISCIBILITY AND REINFORCING ABILITY OF ALLYLIC MONOMERS IN POLYSTYRENE

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles **“Miscibility and Reinforcing Ability of Allylic Monomers in Polystyrene”**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
DAOP	Diallyl Ortho-phthalate
DCP	Dicumyl Peroxide
DSC	Dynamic Scanning Calorimetry
DMTA	Dynamic Mechanical Thermal Analysis
IUPAC	International Union of Pure and Applied Chemistry
PC	Polycarbonate
PPE	Poly(2,6-dimethyl-1,4-phenylene ether)
PEI	Polyetherimide
PPO	Polyphenylene Oxide
PS	Polystyrene
PVC	Polyvinyl Chloride
TP	Thermoplastic
TS	Thermoset
THF	Tetrahydrofuran
PP	Polypropylene

LIST OF EQUATIONS

Equation 4.1	$\delta^2 = E_{coh} / V$
Equation 4.2	$E_{coh} = F^2 / V$
Equation 4.3	$E_{coh} = \delta^2 V$
Equation 4.4	$\frac{1}{Tg} = \frac{w1}{Tg1} + \frac{w2}{Tg2}$

LIST OF SYMBOLS

℃	Degree Celcius
%	Percent
g/cm^3	Grams per centimetre cube
g/mol	Grams per mole
J/mol	Joules per mole
MPa	Mega Pascal
T_g	Glass Transition Temperature
wt%	Weight percentage

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ABSTRAK

Penggunaan diallil otho-ftalat (DAOP) sebagai pemplastik reaktif dalam adunan polisterina/ diallil ortho-ftalat (PS/DAOP) telah dikaji. Parameter kelarutan, suhu peralihan kaca (T_g) dan morfologi adunan 100wt% PS dan 80PS/20DAOP bersama pelbagai komposisi pemplastik reaktif telah disiasat. Dikumil peroksida (DCP) telah digunakan untuk memulakan proses pematangan DAOP. Pematangan DAOP dengan 3 phr daripada DCP menggunakan DSC menunjukkan satu puncak eksotermik. T_g adunan 80PS/20DAOP, 80PS/20DAOP-DCP belum matang dan pelbagai 80PS/20DAOP-DCP campuran matang telah diperoleh melalui imbasan DSC dan keputusannya telah dibandingkan dengan persamaan Fox. Pengiraan parameter kebolehlarutan mengikut Hildebrand telah digunakan untuk menentukan kebolehlarutcampuran PS dan DAOP dengan menggunakan kaedah Fedor, Small dan Van Krevelan. Untuk melarutkan PS, parameter kebolehlarutan seperti toluene dan tetrahidrofuran (THF) juga telah dikira. Dalam sistem termoplastik/pemplastik, T_g berkurang dengan peningkatan jumlah pemplastik mencadangkan kebolehprosesan yang bertambah baik dengan penurunan sifat termomekanikal. Sementara itu, dalam pemplastik reaktif -termoplastik, ia menunjukkan pemplastik reaktif dalam termoplastik biasanya mempunyai keupayaan untuk mengekalkan sifat-sifat termomekanikal (T_g) termoplastik pada DSC pematangan DAOP dengan DCP sebagai pemula. Selain itu, morfologi akhir dan sifat-sifat campuran dipengaruhi oleh beberapa faktor seperti komposisi dan suhu pematangan. Bukti pemisahan fasa dan perubahan dalam morfologi adalah penting untuk menentukan T_g dan meneliti morfologi campuran matang.

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ABSTRACT

The use of diallyl-ortho phthalate (DAOP) as reactive plasticiser of Polystyrene/diallyl-ortho phthalate blends (PS/DAOP) was studied. The solubility parameters, glass transition temperature (T_g) and morphology of the 100wt% PS and reactive plasticized 80PS/20DAOP blends over a wide range of compositions were investigated. Dicumyl peroxide (DCP) was used to initiate the cure reaction of DAOP. Curing of DAOP with 3phr of DCP using DSC indicated single exothermic peak. T_g's of the 80PS/20DAOP, 80PS/20DAOP-DCP uncured and various 80PS/20DAOP-DCP cured blends were obtaining through the DSC scan and the result was compared with Fox equation. The solubility parameter calculation according to Hildebrand has been used to determine the miscibility of PS and DAOP by using Fedor's, Small and Van Krevelan method. In order to dissolved PS, the solubility parameter of solvent such as toluene and tetrahydrofuran (THF) also have been calculated. In thermoplastic-plasticizer system, T_g reduced with increasing amount of plasticizer suggesting that processibility improve with the expense of reduction of thermomechanical properties. While, in thermoplastic-reactive plasticizer, successful application of reactive plasticizer in thermoplastic normally shown by the ability to retain the thermomechanical properties (T_g) of the thermoplastic on DSC curing of DAOP with DCP initiator. In other hand, the final morphology and thus properties of blends affected by a few factors such as compositions and cure temperature. Evidence of phase separation and changes in the morphology that is important to determine the T_g and examine morphology of cured blends.

CHAPTER 1

INTRODUCTION

1.1 Overview

Traditional methods of reducing polymer viscosity instead of increasing processing temperature, include reducing their molecular weight, adding inert plasticizer and also blending with more processable polymers. One example of the successful application of the last method is blending of polyphenylene oxide (PPO) with polystyrene (PS). PPO is miscible with PS in all proportions due to the favourable interaction between their aromatic rings. Mixtures of PPO and PS provided amourphous and segmentally miscible blends of commercial importance (Wang et al., 2002). The blends of PPO with PS or its derivatives such as high-impact PS resulted in tough materials with good processability and flame retardance.

According to Kutz (2011), a plasticizer is an additive that when added to another material makes that material softer and pliable. Although this definition can be applied to a variety of products, the word “plasticizer” generally refers to materials used in plastics. In 1951, The Council of the International Union of Pure and Applied Chemistry (IUPAC) adopted the following definition of plasticizer: a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability or distensibility. In addition, it is found that a plasticizer may reduce the melt viscosity, lower the temperature of a second order transition, or lower the elastic modulus of the product, but it does not alter the chemical nature of the macromolecule (Grossman, 2008).

However, these traditional methods of reducing viscosity by adding inert plasticizer or blending with more processable polymers usually result in low strength and heat distortion temperature of the thermoplastic (Liang et al., 2009).

In order to avoid the effect, a few researchers (Venderbosch, 1994, Rusli & Cook, 2014) reported the addition thermoset monomers which acts as reactive plasticizer in thermoplastic to improve processibility without reducing the thermomechanical properties of thermoplastic. Most of the research on the application of a thermosetting monomer as a reactive plasticizer for thermoplastics used thermosetting monomers that can undergo gelation at relative high conversion such as epoxy (Liang et al., 2011) and allylic (Rusli et al., 2011), monomers.

In the system, the thermoset is the main component and the monomer, prior to their polymerization, acts as reactive plasticisers/reactive solvents that may improve processability at the early stage of processing thermoset/thermoplastic blends. The presence of two components with different physical and chemical properties results in a complex system. For example, even for an initially homogenous blend of thermoplastic and thermoset monomer, phase separation may occur at certain stage in the reaction due to the cure of the thermoset component of the blend (Liu et. al., 2010).

Allylic monomer which undergo elation at relatively high conversion and have been found to be useful as reactive plasticizers to improve the processing of PPO (Rusli et al., 2011), Epoxy resin and diallylic monomers such as diallyl phthalate and triallyl cyanurate are the most common thermosetting monomers that have been used as reactive plasticizers for thermoplastics such as poly (2,6-dimethyl-1,4-phenylene ether) (Yang et al., 1998), poly(-methyl methacrylate) (Aouachria et al., 2014), polycarbonate (PC) (Liang, 2011) and polyvinyl chloride(PVC) (Liang, 2009) because these monomers have a relatively low viscosities which aids the processing, high boiling temperatures to minimize evaporation, and low reactivity at high temperatures (with proper selection of curatives or initiator).

Meanwhile, most of the research on improving processibility of thermoplastic in the presence of thermosets studied the effect of thermoset on viscosity and morphology of the blends. However, not much research has been done on the properties of the thermoset as both reactive plasticizer and reinforcement or toughener in thermoplastic system. Allylic monomers are reported to be miscible with PPO at high concentrations of PPO (Rusli et al., 2011). Meanwhile, PPO is normally blended with PS to improve processibility but cause reduction on the thermomechanical (T_g) of the blend. To the best of our knowledge, no research has been done on the properties of PS and allylic monomer blends. It would be interesting to determine the effect of allylic monomers on the properties of PS which is known to be miscible with PPO.

1.2 Problem Statement

To be an effective plasticizer, the monomer should be readily miscible with thermoplastic and not form a network at an early stage of cure or react too quickly at the processing temperature of the blend. The use of these monomers successfully improved the processing of the thermoplastics without sacrificing the useful thermomechanical properties of the thermoplastics.

However, miscible blends are difficult to obtain. One ways to estimate whether a polymer miscible with other polymer, plasticizer or soluble in solvent is based on solubility parameter value. Normally, PS, DAOP and solvent calculated by the Hildebrand solubility parameter which is widely used in a range of applications was applied. The solubility parameters were calculated by using the group additivity approach with the assumption that the contributions of different functional groups to the thermodynamic properties are additive and equivalent to the solubility of its repeat unit (Grulke, 1999).

One of the rule in application of thermoset as reactive plasticizer in thermoplastic, a monomer should miscible with thermoplastic at early stage of processing, so that viscosity can be reduced. In order to obtain an indication of the relatively miscible

PS/DAOP blends, it should obtain a single-phase transition T_g since a single T_g of a blend implies complete miscibility between the polymer pairs in their amorphous fractions. A few study reported miscibility of thermoset-thermoplastic blends affected by composition and temperature (Rusli et al., 2011). However, different systems of thermoset/thermoplastic will have different miscibility/immiciblity behaviour.

In thermoplastic-plasticizer system, T_g reduced with increasing amount of plasticizer suggesting that processibility improve with the expense of reduction of thermomechanical properties. While, in thermoplastic-reactive plasticizer, successful application of reactive plasticizer in thermoplastic normally shown by the ability to retain the thermomechanical properties (T_g) of the thermoplastic on DSC curing of DAOP with DCP initiator. In other hand, the final morphology and thus properties of blends affected by a few factors such as compositions and cure temperature. Evidence of phase separation and changes in the morphology that is important to determine the T_g and examine morphology of cured blends.

1.3 Research Objectives

The purpose of this project is to examine whether DAOP could be an effective reactive plasticizer and/or reinforcement in PS. In order to do that, the research is done based on objectives, which are:

a. To estimate miscibility of PS and DAOP using solubility parameters.
b. To examine the T_g of various concentrations PS/DAOP blends which could be related to their miscibility.
c. To determine the T_g and morphology of PS/DAOP cured blends.

In order to achieve the objective, a few experimental procedures need to be accomplished. The estimation of miscibility of PS and DAOP will be obtain using solubility parameter calculation according to Hildebrand which include Fedor's, Small and Van Krevelan method. While, the T_g of the various concentrations PS/DAOP blends will be observed from second heating scan of DSC curve in order to obtain single-phase transition T_g which stated the miscibility. For cured blends PS/DAOP, DCP used as the initiator to initiate the DAOP while the samples cured at 160°C for 5 hours. However, the morphology shows here are phase separation in thermoplastic/thermoset blends although its obtain single-phase transition T_g.

1.4 Scope of Work

Chapter 1 consists of introduction of the thesis. It covers brief introduction about research background, problem statements, research objectives and also scope of all chapters in the thesis.

Chapter 2 contains the literature review. It covers general overview of thermoplastic, polymer blends and allylic monomers as reactive plasticizers. The chapter concludes the importance of this research.

Chapter 3 includes the information about the materials specifications, equipment, experimental procedures and testing conducted in this study.

Chapter 4 covers results and discussion of this study. The effect of allylic monomers on the miscibility and properties of PS blend will be presented.

Chapter 5 concludes the finding in Chapter 4 with suggestions for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1. Polymers

Polymers are classified as either natural that resulted from natural biosynthesis or synthetic. The natural for examples polysaccharides, protein, nucleic acids and natural rubbershave been used for tens of thousands of years. The term synthetic polymer refers equally well to linear, saturated mascromolecules (i.e., *thermoplastics*), to unsaturated polymers (i.e., *synthetics*) or to any substance based on crosslinkable monomers, macromers, or pre-polymers (i.e., *thermosets*) (Utracki, 2002). According to Rudin (1999), a thermoplastic is a polymer which oftens and can made to flow when it is heated. It hardens on cooling and retains the shape imposed at elevated temperature. This heating and cooling cycle can usually be repeated at many times if the polymer is properly compounded with stabilizers. Some of the polymers listed which are thermoplastics are polystyrene, polyvinyl chloride, polyethyleneteraphthalate, polyethylene and etc. Whereas thermoset plastic is a solid polymer that cannot be dissolved or heated to sufficiently high temperatures to permit continuous deformation because chemical decomposition intervenes at lower temperatures. Vulcanized rubber such as styrene butadiene (SBR) is an example.

2.1.1 Thermoplastic

Thermoplastic polymer can be further divided into three categories which are commodity, engineering and high performance plastics. Commodity thermoplastic are known as widely used commercial plastics with low to moderate strength (Krishnamurthy et al., 2014). Polymeric families that belong to commodity plastics are polystyrene (PS), polyethylene, polypropylene, polyvinyl chloride. These thermoplastics constitute more than 50% of thermoplastic material. Commodity thermoplastic typically have average mechanical properties and low prices. They are used in large quantities because of their cost effectiveness. Polymeric families that considered as engineering thermoplastics are polyamides (e.g. nylons), thermoplastic polyester, polysthylene terapthalate (e.g. PET), polycarbonates, polyoxymethylenes and polyphenylene ethers (Utracki, 2002). Thermoplastics which are categorized as engineering thermoplastic have above average mechanical and extraordinary properties and these make them have higher prices than commodity thermoplastics. Such extraordinary properties include higher moduli of elasticity, higher heat distortion temperature, higher impact strength, etc. Engineering plastics also often defined as those thermoplastics that maintain dimensional stability and most mechanical properties above 100^oC or below 0^oC. Engineering thermoplastics have low consumption volumes due to their high prices for example nylon which is the most used engineering thermoplastic materials have a total U.S. consumption volume of only about 0.8 billion pounds per year (Ibeh, 2011). Whereas Pritchard (1999) suggested that high performance plastics are classified due to their superior tolerance of high temperature. High performance thermoplastic include polyphenylene sulfide resin, sulfone polymers, aromatic ketone polymers and polyetherimide.

2.1.2 Thermoset

Thermoset plastics are synthetic materials that hardened and strengthen when being heated, but cannot be reshaped and reheated after their initial heat-forming. Unlike thermoplastics, which is soften when applied heat and hardened after cooling. Thermoplastics can be heated, shaped and cooled as often as necessary without causing a change, while thermosetting plastics will burn when heated after the initial molding. Usually, thermoplastics tend to be easier to mold compared to thermosetting plastics, which also take much more longer time to produce due to the time it takes to cure the heated material (Emmanuel Rotimi Sadiku , 2016).

Thermosetting plastics, however they have a number of advantages. Unlike thermoplastics, they can retain their properties and shape even being heated which will makes thermosetting plastics well-suited to the production of permanent components and large, solid shapes. These components have excellent strength attributes and will not become weaker when the temperature increases (Ming, 2017). Meanwhile, thermoset plastic products are typically produced by heating liquid or powder within a mold, allowing the material to cure into its hardened form. These products then can be removed from the mold even without being cool. To produce thermosetting plastic products is not always the result of heating, and is sometimes performed by interaction between specialized materials. Typical types of thermosetting plastics are epoxies, polyesters, silicones and phenolics. Vulcanized rubber is also an excellent example of a thermosetting plastics (Reynolds & Williams, 2015)

Each type of thermosetting plastic has a unique set of properties. For examples, epoxies exhibit elasticity and exceptional chemical resistance, which are relatively easy to cure. Phenolics, while fairly simple to mold, are brittle, strong and hard. Because of their wide range of characteristics, thermosetting plastics find use in an extensive variety of applications, from electrical insulators to car bodies (Yahua & Zhenhao, 2016).

2.2 Polystyrene

Nowdays, together with the vast stores of knowledge and experience that had been accumulated, became the spur for further polystyrene development, and resulted in the production of the low cost commodity resin that we are familiar with today. The developments in materials technology continued throughout the years, creating the wide range of material grades that are available and thrust the materials into a wide sphere of applications. Today polystyrene is the fourth most important commodity plastic in the world, in tonnage terms, after polyethylene (PE), polyvinylchloride (PVC) and polypropylene (PP) (Brydson, 1999).

2.2.1 Structure and Properties

Polystyrene (PS) is a synthetic aromatic polymer made from the monomer styrene, a liquid petrochemical. Polystyrene can be rigid or foamed. General purpose polystyrene is clear, hard and brittle. It is a very inexpensive resin per unit weight. It is a rather poor barrier to oxygen and water vapor and has relatively low melting point. Polystyrene can be naturally transparent, but can be colored with colorants.

PS has the simple repeating structure shown in Figure 2.1 as expected from a linear polymer of thermoplastic. The specific position of the benzene ring is sufficiently random to inhibit crystallization. Because of the chain-stiffening effect of the benzene ring, the T_g of polymer in range of 90 – 100^{o}C. A consequence of this Tg value plus the amorphous nature of the polymer, PS is hard and transparent at room temperature. They are also somewhat brittle (Brydson, 1999).

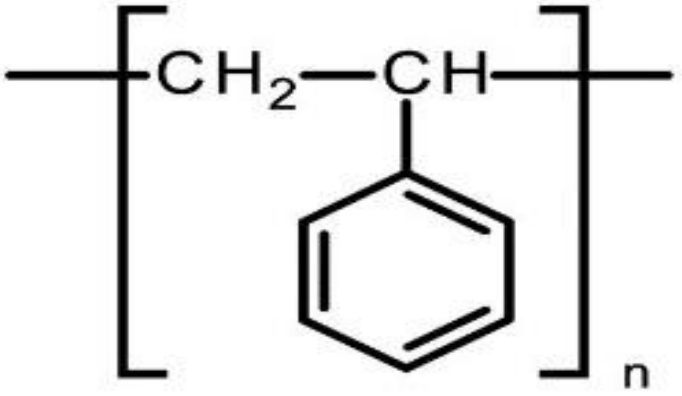


Figure 2.1: Chemical structure of polystyrene (Strobl, 2004)

The main advantages of PS are its low cost, ease of processability, good dimensional stability, low moisture absorption, low taste and odour characteristics, transparency and gloss, and excellent colouring properties. However, in its unmodified state it is an extremely rigid and brittle thermoplastic material that exhibits poor impact properties and poor weathering resistance, and has a relatively low softening point

(Hudson, 1955). In order to overcome some of these property shortcomings, a number of modified grades have been developed over the years, the most significant of which are noted below.

- General purpose grades – a balance of good heat resistance and flow properties with moderate impact strength
- High molecular weight grades – improve impact strength without compromising clarity but at the expense of flow properties
- Heat-resistant grades – increases the softening temperature by around 5 –10% by means of reducing residual monomer contents.

2.2.2 Manufacturing of Polystyrene

Recently there are two types of PS which are crystal that is clear, amorphous resin with good stiffness and electrical characteristics, and impact which contains varying levels of polybutadiene to improve toughness and impact resistance. The process to produced PS can be categorized into three types that usually used which are suspension, solution and mass (bulk) polymerization. In the solution process, in which it produced low residual monomer content and high purity polymers. Meanwhile, suspension process produced polymers of different molecular weights and can be specialist crystal and high impact grades of polystyrene. For mass process it will produced the clarity and excellent colour of the resins (James, 2011).

The building block - monomer - of PS is styrene. The raw materials to produced styrene are obtained from crude oil. A step of processes such as distillation, steam-cracking and dehydration are required to transform the crude oil into styrene. At the end the process PS is produced by polymerized styrene. The final product available in the form of pellets. PS pellets are extruded and injection moulded in order to obtain the final articles (Wunsch, 2000). Figure 2.2 shows the manufacturing process of Polystyrene.

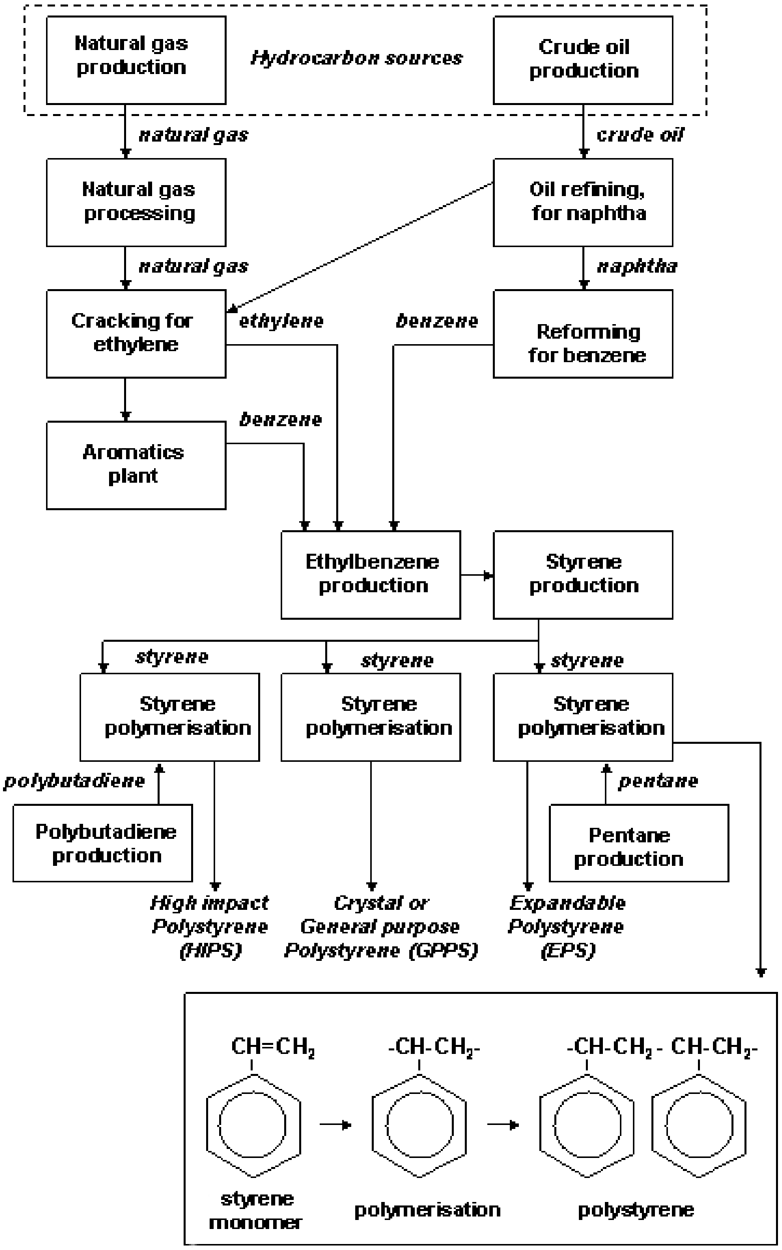


Figure 2.2: Manufacturing process of Polystyrene (http://www.plasticseurope.org, 29th January 2017)

2.2.3 Modification of properties of PS

The brittleness of PS has influence to the development of modified high-impact polystyrene (HIPS) and to the complex acrylonitrile butadiene styrene (ABS). Instead of the drawback, the pure hydrocarbon nature of polystyrene gives an excellent electrical, insulation properties, as a result both of the fundamentally good characteristics of material and to the low water absorption of such a hydrocarbon polymer. The insulation properties are well maintained in humid conditions (Brydson, 1999).

2.3 Processing of PS

Typical processing equipment for rigid and brittle PS:

- Extrusion
- Injection moulding

2.3.1 Extrusion

The moulding process indicate to a manufacturing operation which involves the creating of material using a rigid frame called a pattern. Extrusion moulding uses this process to form tube-shaped objects from a range of materials. Extrusion moulding extrudes, the materials through a die to produce such products as hoses, drinking straws, rods and pipes. A die is a manufacturing tool used to carve or cut material via a press, or machine that uses pressure to compact or otherwise reshape an object (Dominick & Donald, 2004).

Extrusion moulding is completed via an extrusion machine. The plastic materials then feed through the heater by the screw when the motor operate. The granules in the plastic melt converted into liquid, which is then pushed through the die tool. This forces the material into a tube shape determined based on the specific design of the die. The material forms a solid tube shape after cooling (Charles Harper, 2006).

2.3.2 Injection Moulding

Injection moulding is a process by which polymer is melted and injected in a mould cavity, which solidified after a cooling process into the shape of the mould. Common injection moulding applications are housing of televisions, jewel boxes for compact discs, toys and innumerable other uses.

In injection moulding process, the material feed up into the machine via a hopper. Using a heated barrel equipped with a reciprocating screw in an injection machine are needed to feeds the molten polymer into a temperature controlled mould by a channel system of gates and runners (Elsevier, 2004).

During injection phase, the screw melts the polymer into a molten state and also operate as a ram. The screw action also contributed to additional heating by an excellent shearing process on the polymer. The polymer is injected into a mold tool that characterizes the pattern of the molded part. The pressure of injection depends on the material being processed. Tools are made from steel, that can be hardened and plated. The usage of aluminium alloys also critical for increased cutting and hand polishing speeds (Sperling, 1984).

2.4 Polymer Plasticization

In order to improve processing of rigid thermoplastics such as polyvinyl chloride (PVC), polycarbonate (PC) and others, plasticizer normally added to the thermoplastic materials. Plasticizers decrease the interactions between segments of polymer chains, reduce glass transition temperature (Tg), melt viscosity, and elastic modulus. Plasticizers generally can be selected to be non-volatile materials and have good compatibility with the desired polymer (Ibert Mellan, 1961).

When the plasticizers compatible with a polymer, their molecule are able to move into the free volume around the polymer chains. This interaction results in a few possible process. In order to obtain free volume, the effects of secondary bonding forces will be decreases which tend to keep the polymer pack together. The intermolecular distance also will increase which results in some swelling and increased free volume. As a result of the increased the free volume and decreased secondary bonding forces, the plasticizer acts as an additive which enhances chain mobility which is the polymer molecules are more easily to move and slip past each other in response to an applied load (George Wypych, 2004).

A plasticizer is a substance usually liquid, but occasionally a low melting or softening point liquid, which solvates a polymer and therefore softens it, i.e. acts as a flexibilizer. To be practically useful a plasticizer must also exhibit permanence so that it must not be lost during use either by volatilization by extraction. Therefore, practical plasticizers are normally high boiling point, and hence high molecular mass, organic liquids which are of similar solubility parameter to the polymer and may be said to be compatible with the polymer being plasticized (Alger, 2012).

Aromatic polymers possess many desirable properties such as high toughness, strength and heat distortion but their rigid aromatic backbones mean that they have to be processed at a very high temperature where these polymers are prone to degrade.

Blending of these thermoplastics with a small amount of crosslinkable monomer is considered as a new method (Venderbosch, 1994) to improve the processability in which at the early stage, the viscosity reduced and thus lowering its processing temperature. Subsequently, the monomer can be polymerized at the end of processing and will phase separate. The morphology of the blends depends on the composition of the thermoset and thermoplastic and it will affect the final properties of the polymer blend. The thermo-mechanical properties of the thermoplastic could be regained when the final blend morphology is dispersed thermoset particles in the thermoplastic matrix (Cook & Schiller, 2014).

For this application, the thermoplastic and the thermoset monomer should be miscible at the early stage of processing to reduce the glass transition temperature (Tg) and thus reducing the processing temperature of the blend, while the thermosetting monomer should be able to react at high temperature with low reaction rate to avoid formation of network prematurely during the early stages of processing. As an example epoxy monomers, which can undergo reaction at high temperature with a suitable curative, is considered to be suitable reactive plasticizers (Rusli & Cook, 2014).

Blending of a small amount of polyetherimide (PEI) with epoxies (Bucknall & Gilbert, 1989) is normally done with a primary aim to improve toughness of the epoxies. The properties of the blends are very much affected by the type of epoxies and curatives used. Little research (Liang, Cook & Tcharkhtchi, 2011) has been done on the applicability of epoxy as reactive plasticizer in thermoplastics especially PEI. This preliminary research was conducted in order to determine theprocessibility of PEI in the presence of epoxy and thermo-mechanical properties of the blends.

2.5 Polymer Blends

According to Thomas (2005), a polymer blend is a mixture of two or more polymers that have been blended together to create a new material with different physical and mechanical properties. Generally, there are few main types of polymer blend which are thermoplastic-thermoplastic blends, thermoplastic-rubber blends, thermoplastic-thermosetting blends and rubber-thermosetting blend have been extensively studied. Polymer blending has drawn so much attention as an easy and profitable method of developing polymeric materials that have flexibility for commercial applications. In other words, the properties of the blends can be employed according to their use by correct selection of the component polymers. Today, the market pressure is so high that producers of plastics need to provide better and more economic materials with exceptional combinations of properties as a substitute for the traditional metals and polymers. Even through plastic raw materials are more expensive than metals in terms of weight, they are more economical in terms of the product cost. Moreover, polymers are corrosion-resistant, possess a light weight with a good toughness (which is important for good fuel economy in automobiles and aerospace applications), and are used for forming a wide range of goods that include household plastic products, automotive interior and exterior components, biomedical devices and aerospace applications (Scobbo et al., 2003).

Blending is also known as the combining of homopolymers to take advantage of the properties of each polymer. The homopolymer is defined as a polymer derived from one species of monomer. However, the word homopolymer is used to describe whose structure can be represented by multiple repetitions of a single type of a repeat unit which contain one or two species of monomer unit (Young & Lovell, 2011). Combining homopolymers to form a resin blend, also referred to as alloys, can result in a new or unique product with the best properties of each homopolymer.

The development and commercialization of new polymer usually require many years and is also extremely costly. However, by applying a polymer blending process which is also very inexpensive to perform it is possible to decrease the time to commercialization the new polymer (Scobbo et. al., 2003). As part of the substitution of traditional polymers, the production of the polymer blends symbolised half of all plastics produced in 2010. Today, the polymer industry is becoming increasingly sophisticated, with ultra-high-performance injection moulding machines and extruders are applicable that allow phase-separations and viscosity changes to be effectively discovered or manipulated during the processing stage (White & Bumm, 2011). An example of a blend would be combining a polycarbonate (PC) with a polyester like polybutylene terephthalate (PBT) to get a unique plastic that offers something more than what each individual polymer would have offered. This PC/PBT blend would offer good impact resistance, better than a PBT homopolymer, and very good chemical resistance, much better than PC homopolymer.

There are two important points to be taken into consideration in polymer blends: miscibility and compatibility. Both of these conditions are important for properties, morphologies and performance of polymer blends. Based on the state of miscibility and compatibility, polymer blends can be categorized into completely miscible blends, partially miscible blends and fully immiscible blends (Cor et al., 1998). According to Shonaike & Simon (1999), when plastics processors tried to blend polymer with each other, it was found that most of the pair plastics were immiscible and had very poor properties. However, some plastic chemist did discover some polymers pair that completely miscible to give homogenous single phase with properties proportional to the ratio of the two polymers in the blend.

In short, unique materials are developed through blending as far as its processability and performance are concerned. When two or more polymers are mixed, the phase structure of the resulting polymer can be either miscible or immiscible. Due to their high molecular mass, the entropy of mixing of polymers is relatively low and continuously specific interactions are necessary to achieve blends, which are miscible or homogeneous on a molecular level (Kannan, 2014). In the case of immiscible systems, the behavior depends critically on two demanding structural parameters which are a proper interfacial tension leading to a phase size small enough to allow the material to be considered as macroscopically homogenous and an interphase adhesion strong enough to assimilate stresses and strains without disruption of the established morphology (Cheremisinoff, 1997).

The term miscible is used to define polymer blends that have theoretical thermodynamic miscibility down to the segmental level (Sabu Thomas & Yves Grohens, 2014). Some of the polymer blends that are categorized into homogeneous (miscible on a molecular level) are PS-PPO (polyphenylene oxide) and poly(styrene-acrylonitrile) (SAN)-poly (methyl methacrylate) (PMMA). Moreover, miscible which has single phase blends are commonly optically transparent and homogenous to the polymer segmental level. Single-phase blends also experienced phase separation that is usually brought about by variations in temperature, pressure or in the composition of the mixture.

An example exhibiting miscibility in the whole composition range is PPO and PS. The Tg of a miscible blend is approximately described by the Fox equation:

$$\frac{1}{Tg} = \frac{w1}{Tg1} + \frac{w2}{Tg2} \qquad \boxed{(2.1)}$$

Where w(X) is weight fraction of component X (Konning et. al., 1993).

In partially miscible, a part of one component is dissolved in another. This type of blend which exhibits a fine phase morphology and satisfactory properties is indicated to as compatible. Both blend phases are homogeneous and have their own glass transition temperature (T_g). Both T_g's are changed from the values for the pure blend components towards the Tg of the other blend component (Hameed & Kareem, 2014). An example is the (polycarbonate) PC/ABS (acrylonitrile butadiene styrene) blends which combine the heat resistance and toughness of PC with the low-temperature impact, processability, stress cracking resistance and low cost of ABS. In this case, the interphase is wide and interfacial adhesion is good (Thomas et al., 2016). Therefore, compatibility consists of immiscible of two polymers in which will exhibit macroscopic uniform physical properties. A disperse phase with size and stability also being created and determined by interfacial interactions in which similar to toughening or reinforcement properties (Thomas et al., 2013). Compatibility in polymer blends is difficult to achieve and typically results in phase separation unless a very strong interaction presence between both components.

For fully immiscible, they have a coarse phase morphology, the interface is sharp and the adhesion between both blend phases each exhibiting the T_g of the pure blend component is poor, so that these blends are useless without being compatibilized (Cor et. al., 1998). The immiscible blend is known as heterogeneous and some of the blends examples are polypropylene (PP)-PS and polypropylene-polyethylene PP-(PE) (Parameswaranpillai et. al., 2014).

According to Arrighi & Cowie (2003), these phase behaviour of polymers, whether in solution or in mixture with other polymeric components, differs considerably from that of small molecules. This difference is a direct consequence of the large size of polymer molecules. For mixtures of small molecules, the driving force for miscibility is a result of the large gain in entropy that take place on mixing, but this is not the case for polymers. The entropy of mixing is particularly small for polymer/polymer mixtures and as a result, one-phase systems are obtained only in a limited number of cases. Here, the term miscibility is used to describe a mixture containing two or more components that form a one-phase solid or liquid system. In other hand, it is unequivocal as it corresponds to a precise thermodynamic description of the system, in practice for polymers the experimental determination of miscibility may rather ambiguous. This is because the latter depends on the specific experimental technique adopted and for example, while a system may appear one-phase if examined at sufficiently large length scales, it may not correspond to true miscibility at the molecular level. Moreover, blending of different polymers is an important way to prepare materials with optimized properties. Since the entropy of mixing approaches zero for high molecular weight polymers, which are mostly formed from building blocks whose interaction is not particularly favourable (Koning et al., 1993).

Many polymer pairs are not only immiscible but also incompatible which means that they show high interfacial tension that contributed to rough phase structure, poor mechanical characteristics, and poor adhesion at the interface. Compatibility occurring from thermodynamic interaction between the blend constituents, where it functions as their chemical and physical structure (Farheen et al., 2015). The main reasons lead to creating incompatibles systems that can be summarized as: absence of any specific interaction between their dissimilarity in their structure, broad differences in their viscosities and blend constituents (Ibrahim & Kadum, 2010).

Polymers blends often display phase diagram with an upper critical solution temperature (UCST) or lower critical solution temperature (LCST) even though some blends indicate more complex phase diagram. Only between two limits are the blends miscible. Figure 2.5 below shows the phase diagram for polymer blends (Rusli et al., 2013).

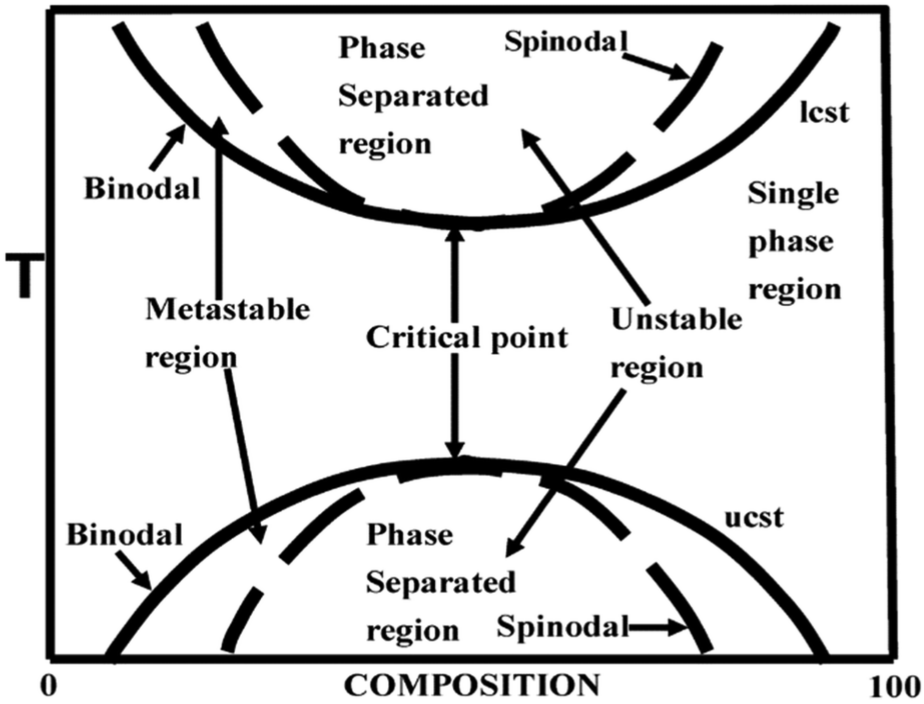


Figure 2.3: Phase diagram for polymer blends (Robeson, 2014)

There are several factors that affect the miscibility or immiscibility of polymer blends. One of the factors is polarity. Polymers that have identical structure and polarity are less likely to repel each other and more likely to form miscible blends. Diverging polarities usually will produce immiscibility for the polymer blend such as PP-PE blend. Others factors are molecular weight and crystallinity. The low molecular weight allows greater randomization on mixing and therefore greater gain of entropy which favours miscibility. More surprisingly polymers of a very much alike molecular weight are more miscible, while polymers of very different molecular weights may be crystallised, it already formed a two phase system. In polymer blends, when a polymer crystallised, this adds another phase to the system. If both polymers in a blend crystallise, they usually form two separate crystalline phases. It is rare for the two polymers to co-crystallize in a single crystalline phase (Shonaike & Simon, 1999).

In addition, the presence of strong interaction between two components can also contribute to miscibility. An example of the strong interactions includes hydrogen bonding (e.g. polyvinyl chloride (PVC)-polycaprolactone) and π-π interaction (e.g. polyphenylene oxide (PPO)-PS). Hydrogen bonding is a crucial for specific interaction often found in miscible polymer blends. Polymer blends comprised of one polymer with proton acceptor groups and another polymer with proton donor groups can have a much greater tendency to be miscible (Robeson, 2014).

2.5.1 Thermoset/thermoplastic Blend

Due to the difference in the properties of thermoplastic and thermoset, their blending has received much attention due to their capability of providing synergistic effects for specific applications. The blends give greater effect compared to its individual components as it will give rise to its mechanical properties and better processability.

Investigations of thermosets/thermoplastics blends are mainly driven by the need to toughen to brittle thermoplastic by the addition of small amount of ductile thermoset without sacrificing the excellent properties of the thermoplastic or the desire to improve the mechanical properties with a small amount of thermoset as a reactive plasticizer. The presence of two components with different physical and chemical properties results in a much more complex system. For example, even for an initially homogenous blend of thermoplastic and thermoset monomer, phase separation may occur at certain stage in the reaction due to the curing reaction of the thermoset component (Liu et. al., 2010).

In this system, for a blend of initially homogeneous crosslinkable monomer and thermoplastic, once the polymerization begins the molecular weight of the crosslinkable system will increase and thus reduce the entropy of mixing. Then, at a certain stage in the reaction, a homogeneous blend may no longer be thermodynamically favoured and phase separation may occur, producing thermoset-rich and thermoplastic-rich phases with various morphologies which affect the final properties of the blends. The process is schematically illustrated as Figure 2.4 for thermoplastic-thermoset blends:

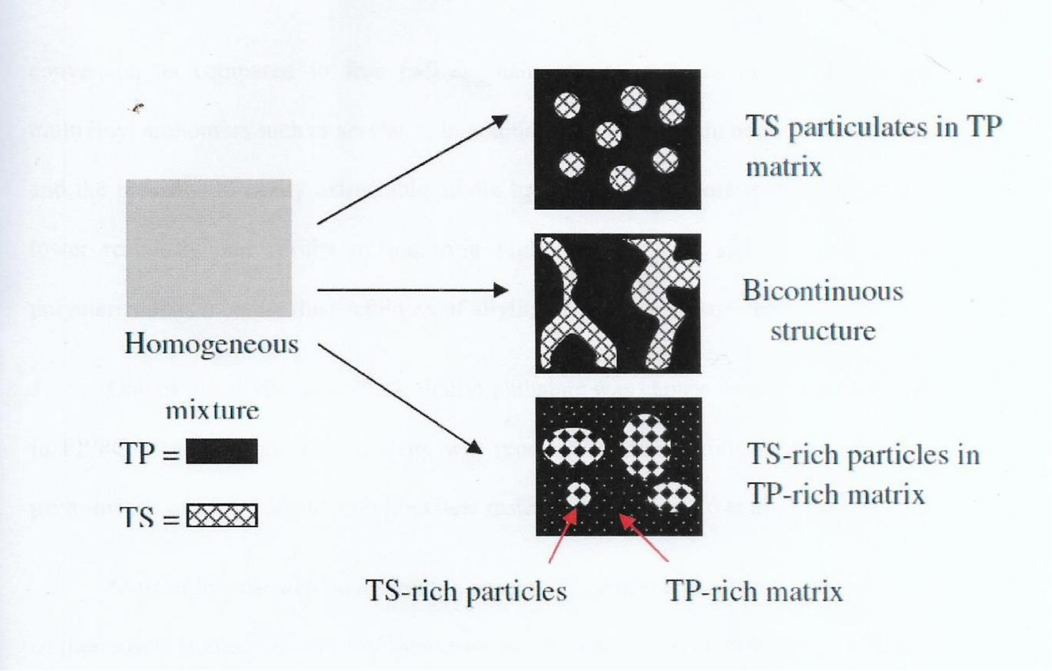


Figure 2.4: Reaction induce phase separation of thermoplastic-thermoset blends (Shonaike & Simon, 1999)

An example of widely used thermoset in an industrial application is vinyl ester resins. The main advantages of this material are the good resistance, thermal stability and mechanical strength. In addition, its low viscosity makes it very attractive for liquid composite moulding techniques as resin transfer moulding and vacuum assisted resin transfer moulding. However, vinyl ester has low ductility and poor fracture toughness, which limits its use as an engineering material (Ollier et. al., 2012).

In order to toughen thermosetting resins, the most widely used method is the incorporation of rubber and inorganic particles (Lee & Yee, 2001) into the thermoset. Rubber toughening can lead to a significant increase in toughness but this method generally leads to a lower in the materials stiffness and strength, which may be undesirable in many applications. Toughening with inorganic fillers on the other hand, can result in a more modest improvement of toughness but without significant loss of strength and even with an enhance in modulus (Kawaguchi & Pearson, 2003). The blending of a thermosetting matrix with a thermoplastic polymer that phase separates during the cure circle of the matrix is an alternative approach for toughening thermoset polymers. In general, the thermoplastic phase has good thermal stability and low water uptake compared with rubbers. For this application, normally a small amount of thermoplastic (<30 wt%) is incorporated into thermoset continuous phase. Various types of thermoplastics have been explored in order to modify thermoset resins. It has been indicated that the modifications need a fine phase separated structure and good adhesion between the two separated phases to achieve fracture toughness improvements (Ollier et. al., 2012).

On the other hand, recently few researchers are focusing on improving processing of thermoplastic with the addition of thermoset as some of the thermoplastics such as polyphenylene oxide (PPO) and polyvinyl chloride (PVC) are difficult to be processed in which the polymers are too viscous to be processed at low temperatures but easily degraded if processing temperature is raised. Traditional methods for reducing the polymer viscosity or processing temperature, include reducing their molecular weight, adding inert plasticize and also blending with more processable polymers. However, these methods usually result in low strength and heat distortion temperature. Common inert plasticizers that have been used are dioctylphthalate, diisononylphthalate, dioctyladipate and diisononyladipate (Liang et al., 2009).

Meanwhile, thermoset monomers may be added to engineering or specialty thermoplastics in order to modify processability and this area of research has not been widely explored. In this system, the thermoplastic is the main component and the monomer, prior to their polymerization, acts as reactive plasticisers/reactive solvents that may improve processability at the early stage of processing.

However, instead of removing the solvent after shaping step as usually done in common solvent blending, the reactive solvent is polymerized and phase separated during the final stage processing. As a consequence, the resulting morphology is either co-continuous or has crosslinked particles dispersed in the matrix of thermoplastic. The potential advantages of this system is that the desired properties of the thermoplastic can be retained because the thermoplastic forms the continuous phase and the crosslinked phase can either reinforce or toughen the blend, depending whether they are rigid or rubbery (Rusli et al., 2011).

Epoxy resin and diallylic monomers such as diallyl phthalate and triallyl cyanurate are the most common thermosetting monomers that have been used as reactive plasticizers for thermoplastics such as poly (2,6-dimethyl-1,4-phenylene ether) (Yang et al., 1998), poly(-methyl methacrylate) (Aouachria et al., 2014), polycarbonate (Liang, 2011) and polyvinyl chloride (Liang, 2009) because these monomers have a relatively low viscosities which aids the processing, high boiling temperatures to minimize evaporation, and low reactivity at high temperatures (with proper selection of curatives or initiator) to prevent from the early-stage gelation during processing (Liang et al., 2011).

Rusli et. al. (2011) reported that most of the studies on the use of thermoset monomer as reactive plasticizer for processing improvement that undergo step growth polymerization instead of chain growth polymerization. This is probably because chain growth polymerization results in early gelation and thus limited the processing time. Allylic monomers are said to undergo gelation at relatively high conversion as compared to free radical chain growth polymerization of common multivinyl monomers such acrylates. In addition, due to the chain transfer to monomer and the presence of easily extractable allylic hydrogen cause these monomers to have lower reactivity and results in requiring higher temperature and longer times to polymerize thus increase usefulness of allylic as reactive platicizers.

Most of the research on improving processability of thermoplastic in the presence of the thermosets studied the effect of the thermoset on viscosity and morphology of the blends. However, not much research has done on the properties of thermoset as both reactive plasticizer and reinforcement in thermoplastic system (Rusli et. al., 2011). Recently, diallyl phthalate was chosen as reactive plasticizer in PP/PC blend system. This strategy was reported to successfully developed a high performance of PP/PC blend with high heat resistance (Matsumoto et al., 2013).

CHAPTER 3

MATERIALS AND METHODOLOGY

This chapter provides the properties of the materials used in this research. In addition, this chapter presents methods of blending used to prepare different composition of the blends, solubility parameters, thermal analysis of the samples and morphological characterization on the sample in order to obtain the result that leads to the conclusion.

3.1 Materials

3.1.1 Polystyrene (PS)

The thermoplastic used in this study is Polystyrene (PS) which was purchased from Petrochemicals (Malaysia) Sdn. Bhd. The PS is in pellet form with a molecular weight of 104.1 g/mol and has a chemical formula of C_8H_8. PS is known as a synthetic aromatic polymer made from the styrene monomer, a liquid petrochemical. PS can be rigid or foamed. General purpose of PS is clear, hard and brittle. It is a very inexpensive resin per unit weight which is 1.05 (EUR/kg). It is a rather poor barrier to oxygen and water vapour and has relatively low melting point (NPCS,2014). PS has a T_g of about 100^oC (Rieger,1996). Figure 3.1 shows the chemical structure of PS.

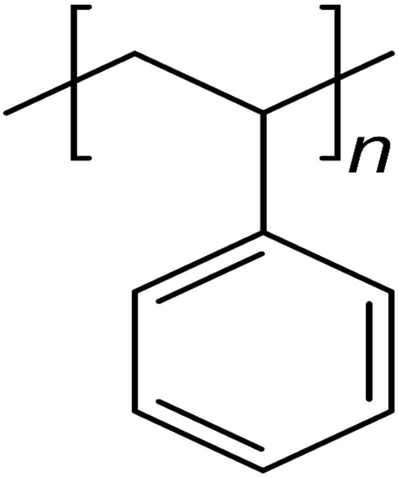


Figure 3.1: Chemical structure of PS

3.1.2 Diallyl Orthophthalate (DAOP)

Diallyl orthophthalate (DAOP) was purchased from Sigma-Aldrich in the form of liquid and has a chemical formula of C_6H_{4-}1 ,2-($CO_2CH_2CH=CH_2)_2$ with molecular weight of 246.26 g/mol. DAOP is reported to has a T_g of -91^oC (Dodiuk & Goodman, 1998).

DAOP normally chosen as a free-radical crosslinkable reactive plasticiser because DAOP has a high boiling temperature (290^oC) a relatively low reaction rate due to its degradative chain transition reaction and cyclization. DAOP has also been used as a reactive plasticiser for polycarbonate (PC) due to the low reactivity and high conversion at the gel point of DAOP and its high solubility in PC (Liang et al., 2008). Figure 3.2 depicted the chemical structure of DAOP.

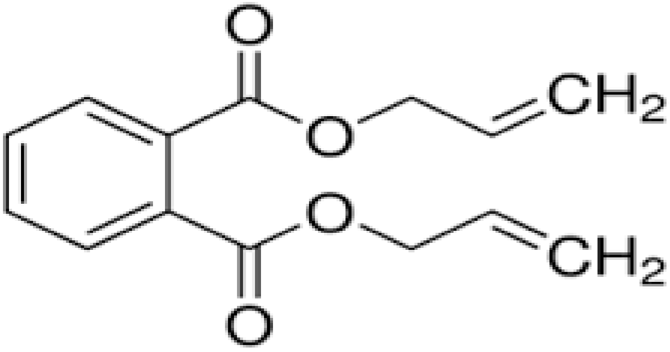


Figure 3.2: Chemical structure of DAOP

3.1.3 Dicumyl peroxide (DCP)

Dicumyl peroxide (DCP) which also known as cumene peroxide was used as an initiator to initiate chain growth polymerization of the allylic monomer. DCP is in the form of solid at room temperature and has density of 1.107 g/cm^3. The molecular formula of the peroxide is $C_{18}H_{22}O_2$ and was purchased from Aldrich.

DCP is one of the organic peroxides and it white solid substances at room temperature (under 37ºC) (Arkema, 2013). It is broadly applied as initiator and crosslinking agent for polyethylene, ethylene vinyl acetate copolymer, etc. and as a curing agent for unsaturated polystyrene. Figure 3.3 shows the chemical structure of DCP.

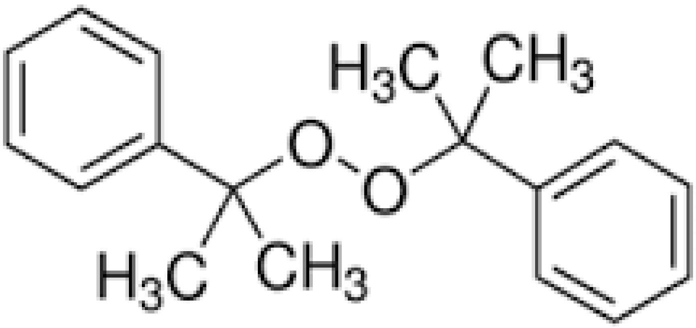


Figure 3.3: Chemical structure of DCP

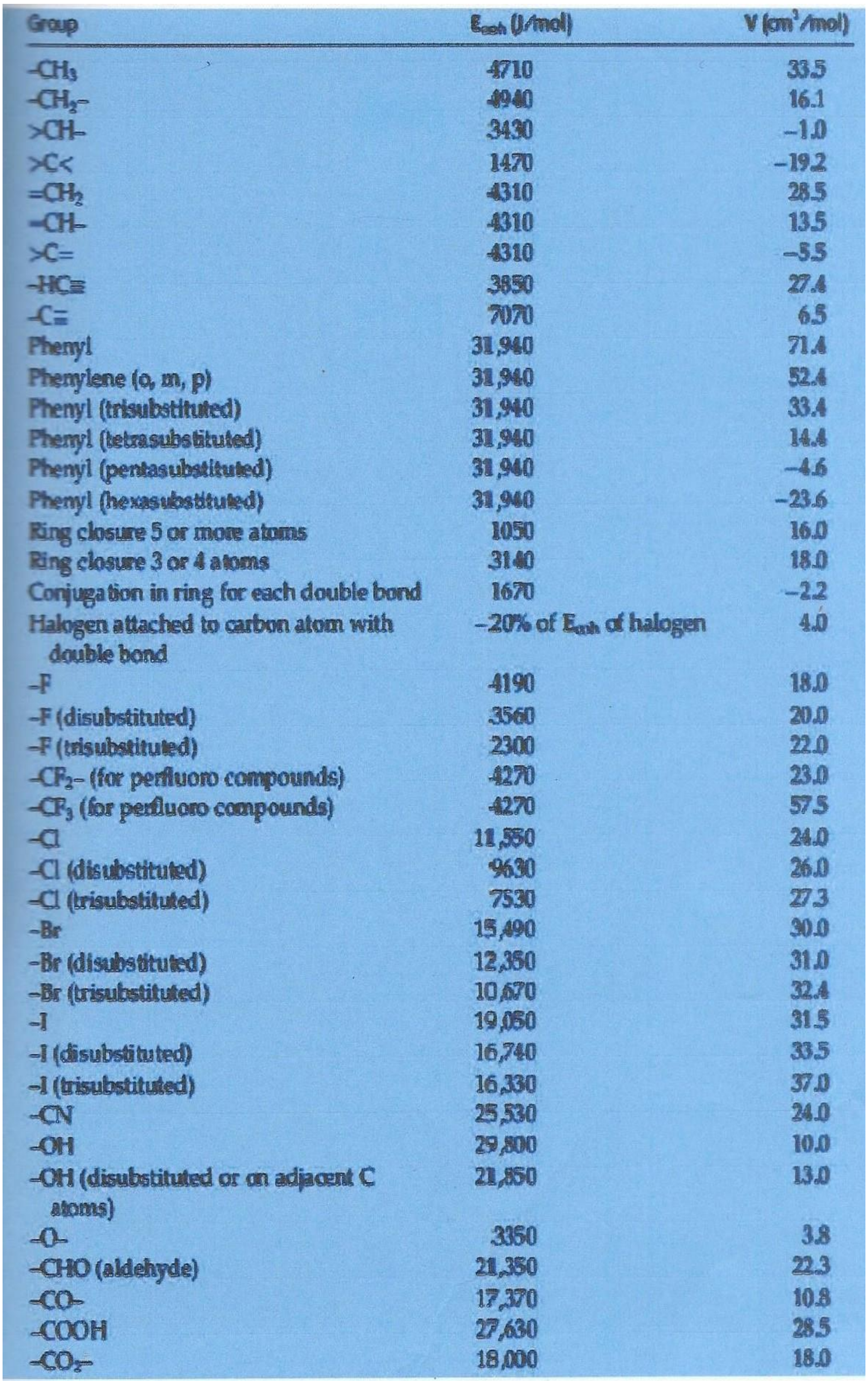
3.2 Solubility Parameters

The solubility parameter can be defined as the square root of cohesive energy density. It is widely utilized for correlating polymer solvent interactions.

To assess the likely solubility of DAOP with PS and thus DAOP ability to act as an effective plasticizer in PS, the solubility parameters of the DAOP and PS were compared. The Hildebrand solubility parameters was calculated using the group additivity approach. The calculation was done by assuming that the contributions of different functional groups of a polymer to the thermodynamic property are additive and equivalent to the solubility parameter of its repeating unit.

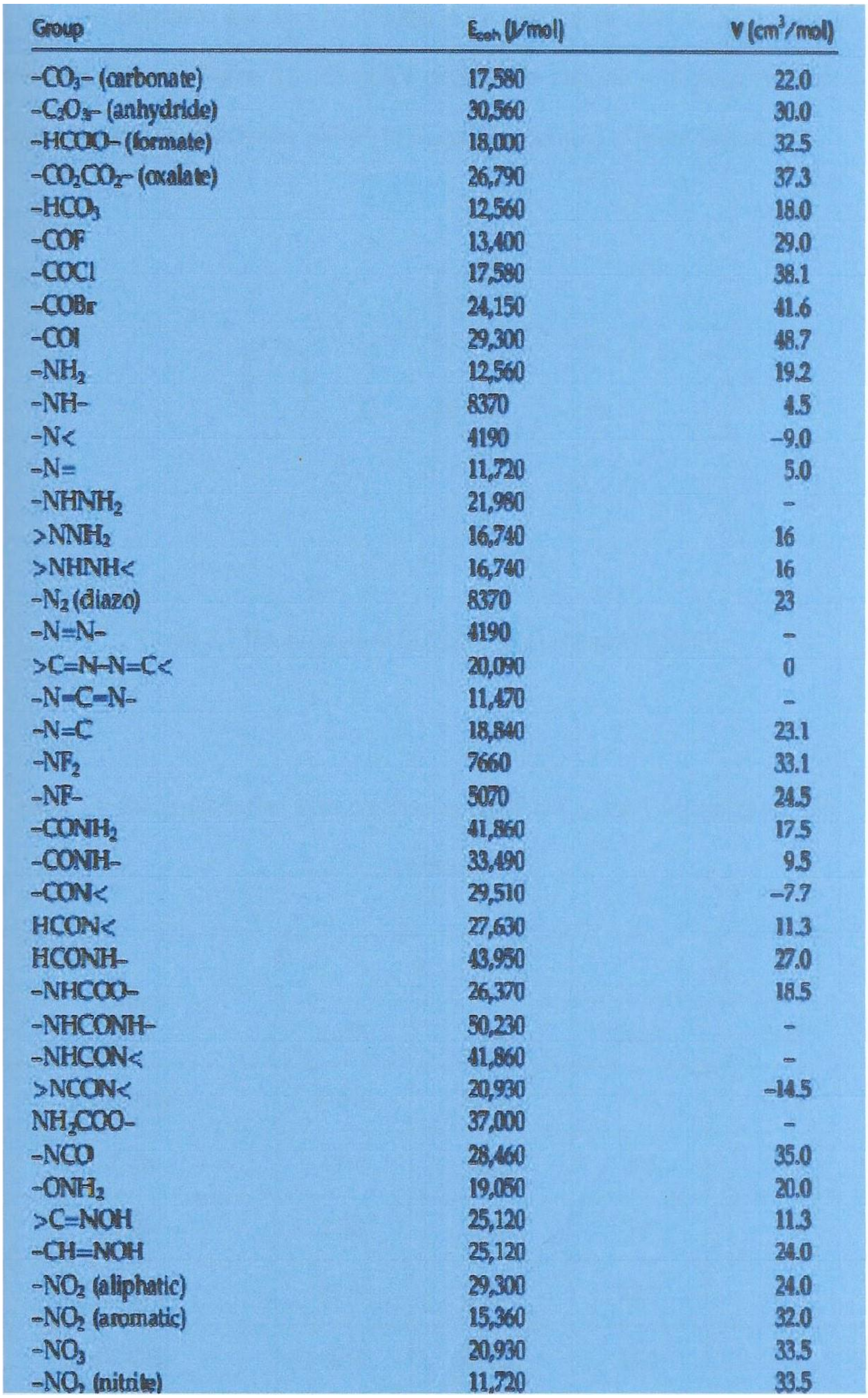
There are a few group contributions for calculating Hildebrand solubility parameter present in literature such as Small, Fedors and Van Krevelan. According to Hildebrand (1949), two substances with equal solubility parameters should be mutually soluble due to the negative entropy factor. This is in accordance with general rule that chemical and structural similarity favours solubility.

Evidently, the most important application of the solubility parameters to be discussed in this chapter is the prediction of the solubility of polymers in various solvents. The requirement of mutual solubility is that the solubility parameter of the polymer δ_p and that of solvent δ_s do not differ too much. Table 3.1 and 3.2 shows a group contibutions to E_{coh} and V.



Group	E_{coh} (J/mol)	V (cm^3/mol)
$-CH_3$	4710	33.5
$-CH_2-$	4940	16.1
$>CH-$	3430	−1.0
$>C<$	1470	−19.2
$=CH_2$	4310	28.5
$=CH-$	4310	13.5
$>C=$	4310	−5.5
$-HC\equiv$	3850	27.4
$-C\equiv$	7070	6.5
Phenyl	31,940	71.4
Phenylene (o, m, p)	31,940	52.4
Phenyl (trisubstituted)	31,940	33.4
Phenyl (tetrasubstituted)	31,940	14.4
Phenyl (pentasubstituted)	31,940	−4.6
Phenyl (hexasubstituted)	31,940	−23.6
Ring closure 5 or more atoms	1050	16.0
Ring closure 3 or 4 atoms	3140	18.0
Conjugation in ring for each double bond	1670	−2.2
Halogen attached to carbon atom with double bond	−20% of E_{coh} of halogen	4.0
$-F$	4190	18.0
$-F$ (disubstituted)	3560	20.0
$-F$ (trisubstituted)	2300	22.0
$-CF_2-$ (for perfluoro compounds)	4270	23.0
$-CF_3$ (for perfluoro compounds)	4270	57.5
$-Cl$	11,550	24.0
$-Cl$ (disubstituted)	9630	26.0
$-Cl$ (trisubstituted)	7530	27.3
$-Br$	15,490	30.0
$-Br$ (disubstituted)	12,350	31.0
$-Br$ (trisubstituted)	10,670	32.4
$-I$	19,050	31.5
$-I$ (disubstituted)	16,740	33.5
$-I$ (trisubstituted)	16,330	37.0
$-CN$	25,530	24.0
$-OH$	29,800	10.0
$-OH$ (disubstituted or on adjacent C atoms)	21,850	13.0
$-O-$	3350	3.8
$-CHO$ (aldehyde)	21,350	22.3
$-CO-$	17,370	10.8
$-COOH$	27,630	28.5
$-CO_2-$	18,000	18.0

Table 3.1: Group contributions to E_{coh} and V



Group	E_{coh} (J/mol)	V (cm^3/mol)
$-CO_3-$ (carbonate)	17,580	22.0
$-C_2O_3-$ (anhydride)	30,560	30.0
$-HCOO-$ (formate)	18,000	32.5
$-CO_2CO_2-$ (oxalate)	26,790	37.3
$-HCO_3$	12,560	18.0
$-COF$	13,400	29.0
$-COCl$	17,580	38.1
$-COBr$	24,150	41.6
$-COI$	29,300	48.7
$-NH_2$	12,560	19.2
$-NH-$	8370	4.5
$-N<$	4190	−9.0
$-N=$	11,720	5.0
$-NHNH_2$	21,980	–
$>NNH_2$	16,740	16
$>NHNH<$	16,740	16
$-N_2$ (diazo)	8370	23
$-N=N-$	4190	–
$>C=N-N=C<$	20,090	0
$-N=C=N-$	11,470	–
$-N=C$	18,840	23.1
$-NF_2$	7660	33.1
$-NF-$	5070	24.5
$-CONH_2$	41,860	17.5
$-CONH-$	33,490	9.5
$-CON<$	29,510	−7.7
$HCON<$	27,630	11.3
$HCONH-$	43,950	27.0
$-NHCOO-$	26,370	18.5
$-NHCONH-$	50,230	–
$-NHCON<$	41,860	–
$>NCON<$	20,930	−14.5
NH_2COO-	37,000	–
$-NCO$	28,460	35.0
$-ONH_2$	19,050	20.0
$>C=NOH$	25,120	11.3
$-CH=NOH$	25,120	24.0
$-NO_2$ (aliphatic)	29,300	24.0
$-NO_2$ (aromatic)	15,360	32.0
$-NO_3$	20,930	33.5
$-NO_2$ (nitrite)	11,720	33.5

Figure 3.2: Group contributions to E_{coh} and V

3.3 Sample Preparation

3.3.1 DAOP/DCP

DAOP with 3 phr concentration of DCP used to initiate cure of DAOP was prepared in total of 1g weight. The sample are mixed in sample beaker and stirred well before pre-curing in the oven at 160^{o}C for 5 hours. The sample then testing using DSC. From the DSC result obtained, it shows the exorthermic peak for determination of T_g for DAOP.

3.3.2 Melt Blending of PS and DAOP without DCP

The sample was melt blended by using Haake Polydrive Internal Mixer at 190^{o}C with 50 rpm mixing speed and time period of 5 minutes. Table 3.3 shows the compositions for melt blending without DCP with their respective processing method and equipment.

Table 3.3: Wt% ratio of PS and DAOP blends and their processing method or equipment.

PS (wt%)	DAOP (wt%)	Processing Method
80	20	Internal Mixer
70	30	Internal Mixer
60	40	Internal Mixer
40	60	Oven
30	70	Oven
20	80	Oven
10	90	Oven

The blending of PS and DAOP in the beaker occurred by manually stirred the mixture of blend in the oven at 190℃ until it reach the melt condition. The processing method indicates that the processing can be obtain since there is no DAOP liquid phase flow out compared to internal mixer which might be not suitable for polymer that exhibit liquid state condition.

Different compositions of PS and DAOP were melt blended using oven and internal mixer at 190 °C. For PS and DAOP blends with 40wt% and less PS, the samples were prepared by melt blending in an oven at 190°C for 25 minute. Meanwhile, for blends with 60wt% and more PS, the blends were prepared using Haake Polydrive internal Mixer at 190°C and 50 rpm mixing speed for 5 minute. The total weight used for an internal mixer is 45 g.

Table 3.4: Weight distributions for PS and DAOP

PS (wt%)	DAOP (wt%)	Actual weight (g) PS	Actual weight (g) DAOP
80	20	36	9
70	30	31.5	13.5
60	40	27	18

3.3.3 Melt Blending of PS and DAOP with DCP

Blends of PS with DAOP and DCP were also prepared by melt blending using either internal mixer or oven. Table 3.5 shows the compositions of PS/DAOP-DCP blends that were prepared. For blends with 60 and more wt% PS samples were melt blended by using Haake Polydrive Internal Mixer at 190°C with 50 rpm speed and a total mixing time period of 5 minutes.

Half of the amount of PS was pre-melted with DAOP in the oven at 190°C and then DCP was added to prepare PS/DAOP-DCP. The mixing was initiated by firstly melted PS in the internal mixer for 4 minutes and subsequently added quantified PS/DAOP-DCP to the chamber. The mixing was then carried on for another 1 minute.

The obtained blended plastic was then compressed at 190ºC for 15 minutes (5 minutes to preheat the materials, 5 minutes for compression and 5 minutes to cooling the sample) and with the pressure of 1000 psi in a compression moulding machine (GOTECH) Figure 3.4 using tensile strip to obtain 1 mm thick plastic sheet for fractured surfaces shape sample preparation.

Table 3.5: Wt% ratio of PS, DAOP and DCP blends

PS (wt%)	**DAOP (wt%)**	**DCP (phr)**
90	10	3
80	20	3
70	30	3
30	70	3
20	80	3
10	90	3

In order to obtain the cured samples, a portion of tensile shape sample that prepared by compression moulding were used for curing the samples in an oven at 160℃ for 5 hours. After the curing process completed, these samples of approximately 10 mg for each composition were analysed using DSC machine by placing the samples in the aluminium pans. The test was done from -100ºC to 150ºC with heating rate of 10ºC/min for three segment which are heating, cooling and reheating.

Figure 3.4: Compression moulding machine (GOTECH)

3.4 Thermal Analysis

3.4.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. DSC can be 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) as shown in Figure 3.5 (Brydson, 1999).

Dynamic DSC studies were conducted using DSC machines which is the Mettler Toledo Star 1 DSC, Figure 3.6. The DSC was used to determine glass transition temperature of DAOP. The Tg was obtained by integrating the DSC exotherm peak area of the heat flow curve in Figure 3.7. The 100wt% DAOP with 3phr of DCP were prepared by mixing the DCP with DAOP in total of 1 g. The solution was stirred for about 5 minutes until DCP is completely dissolved with the DAOP. The mixture then pre-curing in an oven at 160ºC for 5 hours.10 mg of the sample was placed into the aluminium sample pan and then place in DSC sample holder. The test was done from -100ºC to 150ºC with heating rate of 10ºC/min.

Meanwhile the sample formed by the melt blending of PS/DAOP was used to measure the T_g of each sample which can be related with miscibility. Samples of approximately 10 mg for each composition were analysed using DSC machine by placing the samples in the aluminium pans. All samples were heated from -100ºC to 150ºC with heating rate of 10ºC/min to flatten the samples and to remove thermal history of PS/DAOP. Then the samples were cooled down from 150ºC to -100ºC at 10ºC/min by using liquid nitrogen at the rate of 50ml/min. The heating process was again repeated with the same heating rate and heating procedure to determine the Tg of blends as shown in Figure 3.6.

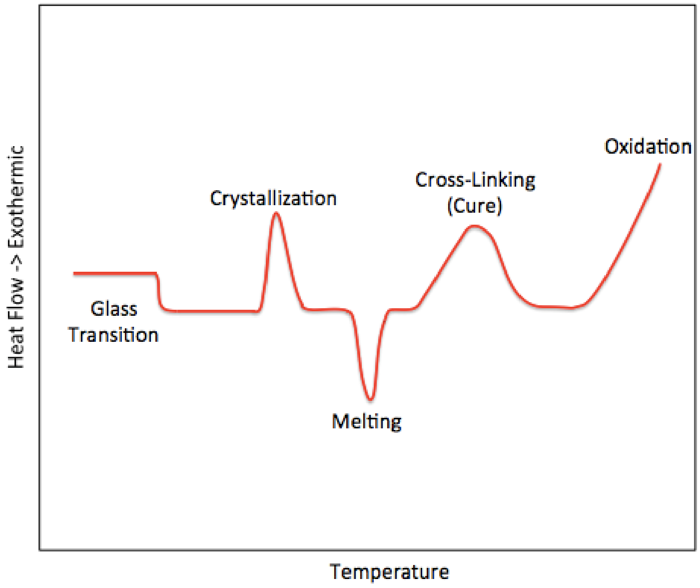


Figure 3.5: Variation of heat flow with different phase transition and chemical reactions in the polymers

The T_g of the PS/DAOP blends observe from DSC curve was compared with values of the T_g of the blends which were calculated using Fox equation (Cook et al., 2007):

$$1/Tg= w_1/ T_{g1} + w_2/ T_{g2} \tag{3.1}$$

Where w_1 and w_2 are the weight fractions of PS and DAOP and T_{g1} and T_{g2} are the glass transition of PS and DAOP, respectively. It should be noted that the Fox equation is applicable for miscible blends and also can be used to predict the T_g of polymer-plasticiser system (Koning et al., 1993).

T_g of cured PS/DAOP-DCP blends were measured using Mettler Toled Star 1 DSC. The samples were obtained from tensile strip that were compression moulded at 190°C for 15 minutes and cured at 160°C for 5 hours. Samples of approximately 10 mg for each composition were analysed using DSC machine by placing the samples in the aluminium pans. All samples were heated from -100°C to 150°C at heating rate of 10°C/min to flatten the sample and remove the thermal history of the sample. Then the sample was cooled down from 150°C to -100°C by using liquid nitrogen at the rate 50 ml/min. The heating process was again repeated with the same heating rate and heating procedure to determine the T_g of the cured blend. Figure 3.7 shows the practical determination of Tg from the DSC curve.

Figure 3.6: Mettler Toledo Star 1 DSC

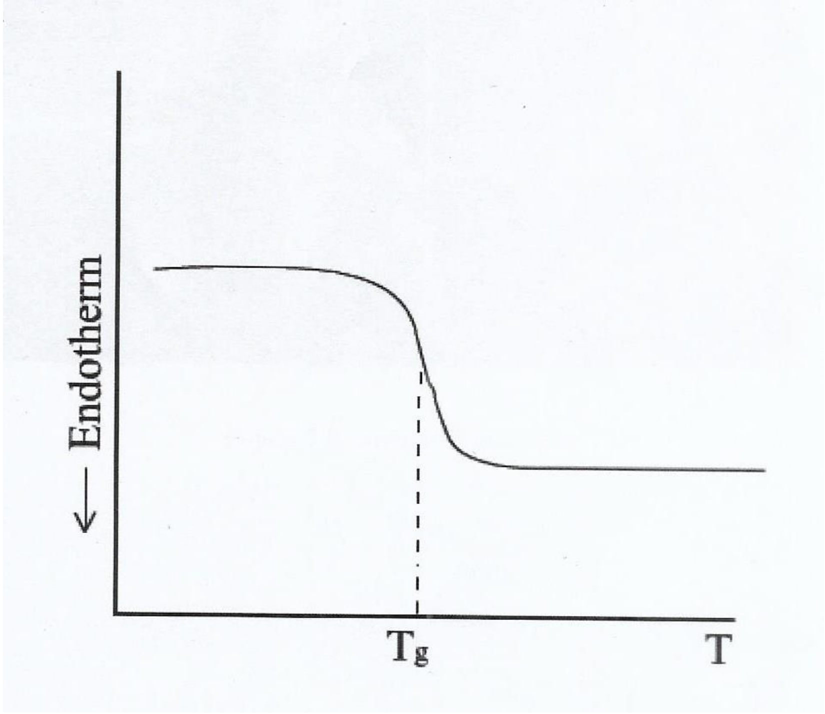


Figure 3.7: Practical determination of T_g in the DSC curve

3.5. Morphology of the Sample

3.5.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a useful imaging approach for the visualization of different polymers, because it provides a consistent picture of the polymer morphology. SEM is a microscope that uses a narrow beam of electrons that scans the surface of a sample to form an image from the backscattered or secondary electrons (Ward, 2008). Moreover, SEM has large depth of field compared to optical microscope, which allows the sample to be focused at one time. SEM produce images of high resolution ranging from 100x to 20,000x.

In this research SEM allows the illustration of the phase separation of the thermoplastic/thermoset blends. The samples were undergone fracture test after the samples freeze in the liquid nitrogen for 2 minutes. Etching was done on the blends in order to remove thermoplastic component of the blends. Fractured surfaces then etching in the toluene which is to dissolve PS.

The fractured surface morphology of the blends was then observed by Zeiss Supra 35vp (Germany) electron microscope with the acceleration voltage of 10kV as shown in Figure 3.8. The fractured samples were sputtered with thin gold before analysis to obtain the results.

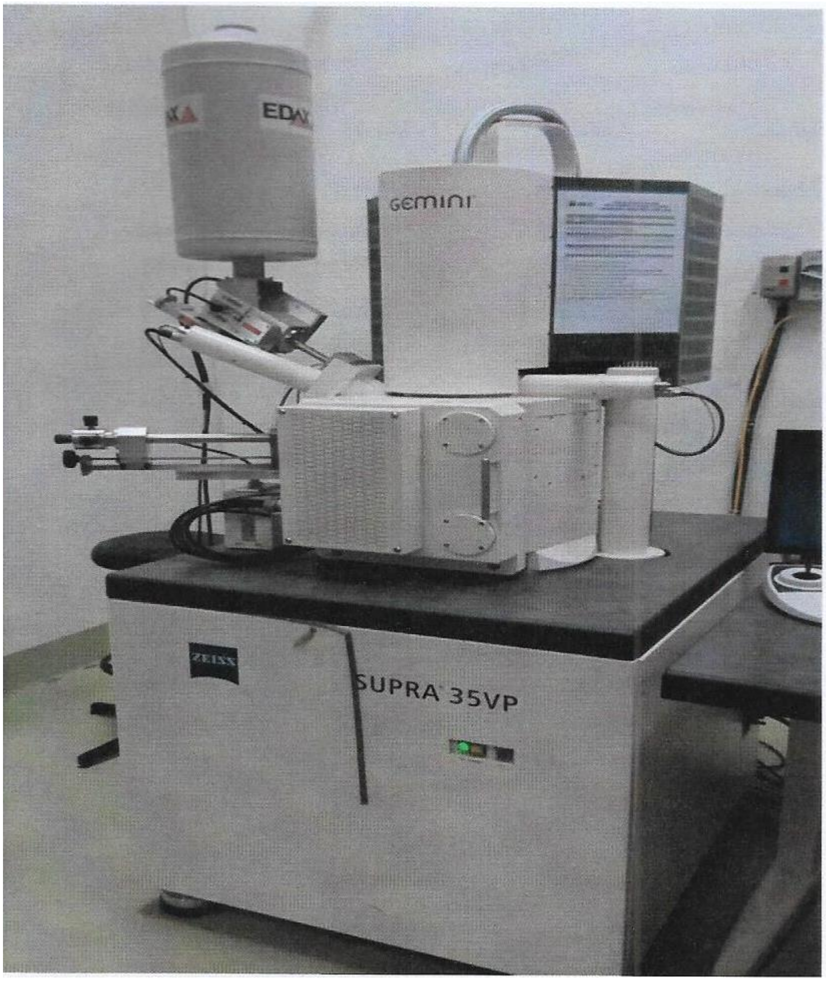


Figure 3.8: Zeiss Supra 35vp (Germany) electron microscope

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

All the results that were obtained throughout in this project are being discussed in this Chapter 4. Discussions consists of two parts, which are the solubility parameter of PS and DAOP suggesting their miscibility, the T_g of various compositions of PS/DAOP indicating the miscibility as reactive plasticizer in PS/DAOP blends and thermal, mechanical and morphological properties of PS/DAOP cured blends.

4.2 Solubility Parameter

To assess the likely solubility of DAOP with PS, the solubility parameters of the DAOP and PS were compared based on Hildebrand solubility parameter which was calculated using a few set of data available. The calculation was done by referring to the chemical structure of PS and DAOP. Meanwhile, Table 4.1 and 4.2 shows the calculation of solubility parameter of PS and DAOP based on the value of E_{coh} and V according to Fedor's Metho (Kreven & Nijenhius, 2009).

Table 4.1: Group contribution value of E_{coh} and V obtained for PS according to Fedor Method

Group	Ei		Vi	
	Each	**Total**	**Each**	**Total**
1 Phenyl	31940	31940	71.4	71.4
1 –CH	3430	3430	-1	-1
1 –CH_2	4940	4940	16.1	16.1
SUM		40310		86.5

$\delta^2 = E_{coh} / V$ (4.1)

Table 4.2: Group contribution value of E_{coh} and V obtained for DAOP according to Fedor Method

Group	**E_{coh}**		**V_c**	
	E_{coh}	**Total**	**E_{coh}**	**Total**
1 -Benzene	31940	31940	52.4	52.4
2 =CH	4310	8620	13.5	27
2 –CH_2	4940	9880	16.1	32.2
2 =CH_2	4310	8620	28.5	57
2 -O	3350	6700	3.8	7.6
2 –CO	17370	34740	10.8	21.6
Sum		100500		197.8

Table 4.3 and 4.4 shows the calculation of solubility parameter of PS and DAOP based on the value of F and V according to Small and Van Krevelan Method (Hildebrand, 1924). The calculation was based on the formula:

$E_{coh} = F^2 / V$ (4.2)

$E_{coh} = \delta^2 V$ (4.3)

Table 4.3: Group contribution value of F and V obtained for PS according to Small and Van Krevelan Method

Group	**F_{small}**	**$F_{van\ krevelan}$**	**V (cm^3/mol)**	**$E_{coh\ Fedor}$**
1 - phenyl	1504	1517	71.4	31940
1 - CH	57	140	-1	3430
1 – CH_2	272	280	16.1	4940
SUM	1833	1937	86.5	40310

Table 4.4: Group contribution value of F and V obtained for DAOP according to Small and Van Krevelan Method.

Group	**F_{small}**	**$F_{van\ krevelan}$**
2 –CH_2	544	560
2 –C=C	908	888
1 –Benzene	1346	1377
2 –C=O	1126	1370
2 –O-	286	512
SUM	4210	4707

Table 4.5: Solubility parameters obtained from Fedor's, Small and Van Krevelan Method.

Fedor's ($J^{1/2}/cm^{3/2}$)		**Small** ($J^{1/2}/cm^{3/2}$)		**Van Krevelan** ($J^{1/2}/cm^{3/2}$)	
PS	DAOP	PS	DAOP	PS	DAOP
21.587	22.541	21.191	22.393	22.393	23.797

For a polymer blend that tend to be miscible the value of solubility parameter obtained from two different materials or polymers should be almost similar. Since a mixture with solubility parameter difference of about 2 $MPa^{1/2}$ is considered to be miscible (Brydson, 1999), values of solubility parameters calculated from Fedor, Small, and Van Krevelan as tabulated in Table 4.5 suggested that PS should be miscible with DAOP. Meanwhile, PS is reported to has solubility of 17.4 $J^{1/2}/cm^{3/2}$ (Barton, 1983) which is different from the values obtained from calculation of solubility parameter. The variation in the solubility parameter values might be due to different measurement were used to obtain the data.

It should be noted that this approach is normally used as rough estimation on solubility and thus miscibility of a mixture, polymer-plasticizer and polymer blends system. The best approach in determining solubility parameter of a polymer is by dissolving/swelling of a polymer in a series of solvents with known solubility (Barton, 1983). The solubility parameter of the polymer is taken as the solubility parameter of the solvents in which the polymer indicates the highest degree of dissolution or swelling.

In addition, according with the theory of Hildebrand, polymer will be soluble in solvents whose solubility parameters are not too different from their own (Hildebrand, 1924). Based on that knowledge, the calculated solubility parameter of PS was compared with solubility parameter of solvents that known to be able to dissolve PS. PS is reported could dissolved in toluene and tetrahydrofuran (THF) (Buckley-Smith, 2006). Figure 4.3 and 4.4 shows the molecular structure of toluene and THF. The solubility parameter was calculated according to Fedor's method as shown in Table 4.6 and 4.7.

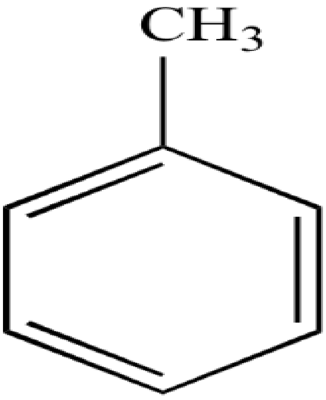


Figure 4.1: Chemical structure of Toluene

Table 4.6: Group contribution value of E_{coh} and V obtained for Toluene according to Fedor Method

Group	Ei		Vi	
	Each	**Total**	**Each**	**Total**
1 Phenyl	31940	31940	71.4	71.4
1 –CH_3	4710	4710	33.5	33.5
SUM		36650		104.9

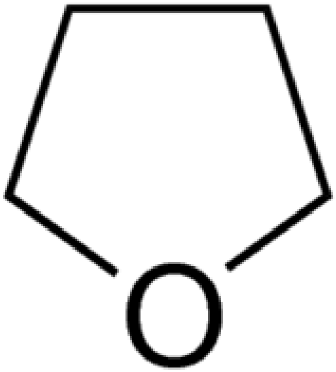


Figure 4.2: Chemical structure of tetrahydrofuran (THF).

Table 4.7: Group contribution value of E_{coh} and V obtained for tetrahydrofuran (THF) according to Fedor Method

Group	**Ei**		**Vi**	
	Each	**Total**	**Each**	**Total**
1 -O-	3350	3350	3.8	3.8
4 –CH_2	4940	19760	16.1	64.4
SUM		23110		68.2

From the calculated solubility parameters, it showed that toluene and THF merely able to dissolved PS because the values of solublility parameters of toluene and THF within the range of 2 $MPa^{1/2}$ from that of PS. The values support the ability of PS to be dissolved in both solvents due to small difference between solubility parameter of PS with the solvents.

The PS is reported could not be dissolved by solvents with parameters very different (1,3-butanediol and water) but is soluble in some of the solvents with similar parameters (benzene, toluene, xylene, THF, chloroform, eucalyptol, nitrobenzene, N.N-dimethylformamide). However, some of the solvents with similar Hildebrand parameters to PS do not dissolve polystyrene (2-butanol, linalool, terpineol). Finally, there are solvents which similar solubility parameters that nevertheless exhibit quite different solubility capacity (i.e. eucalyptol and limonene). Beside, this parameter alone is not entirely able to verify the trend behaviour of the PS in the different solvents (Miller et al., 1998).

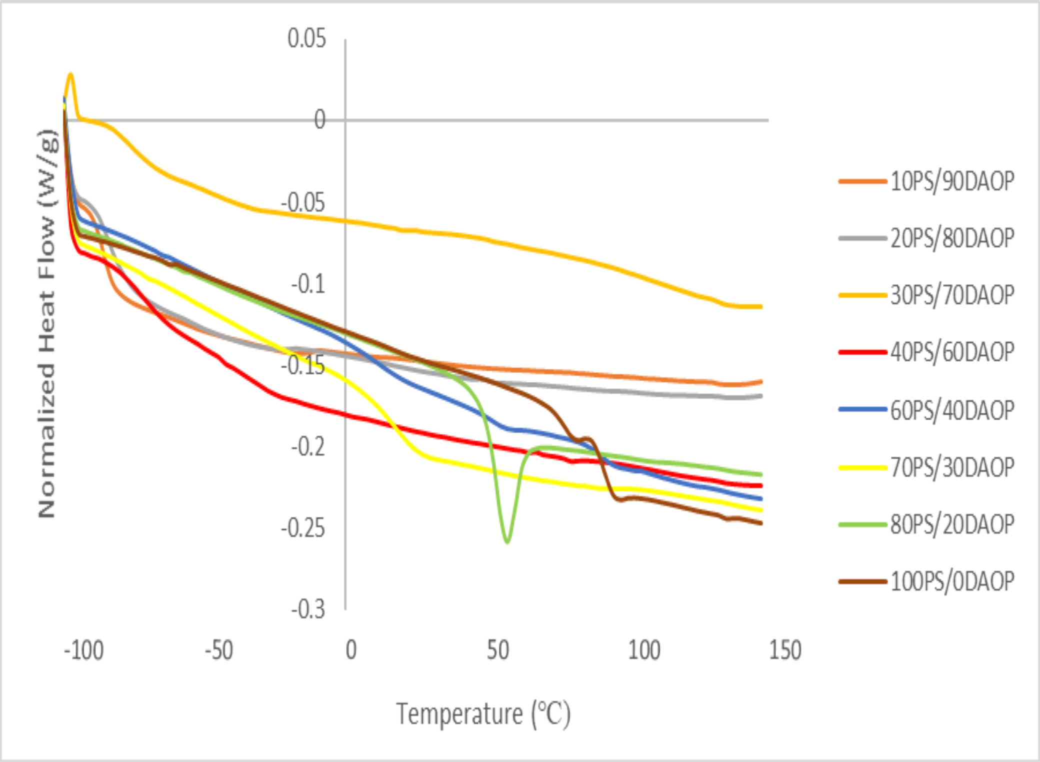
To explain this fact, it is needed to consider that the solubility parameter represents the total cohesive energy densities which result from additive effects of several types of contributions: non polar bonds, dipole–dipole bonds and hydrogen bonds. Therefore, some solvents with similar total solubility parameter exhibit different behaviour since they have different individual contributions (Hoernschemeyer, 1974).

4.3 The Efficiency of DAOP as Reactive Plasticizer on PS/DAOP Blends

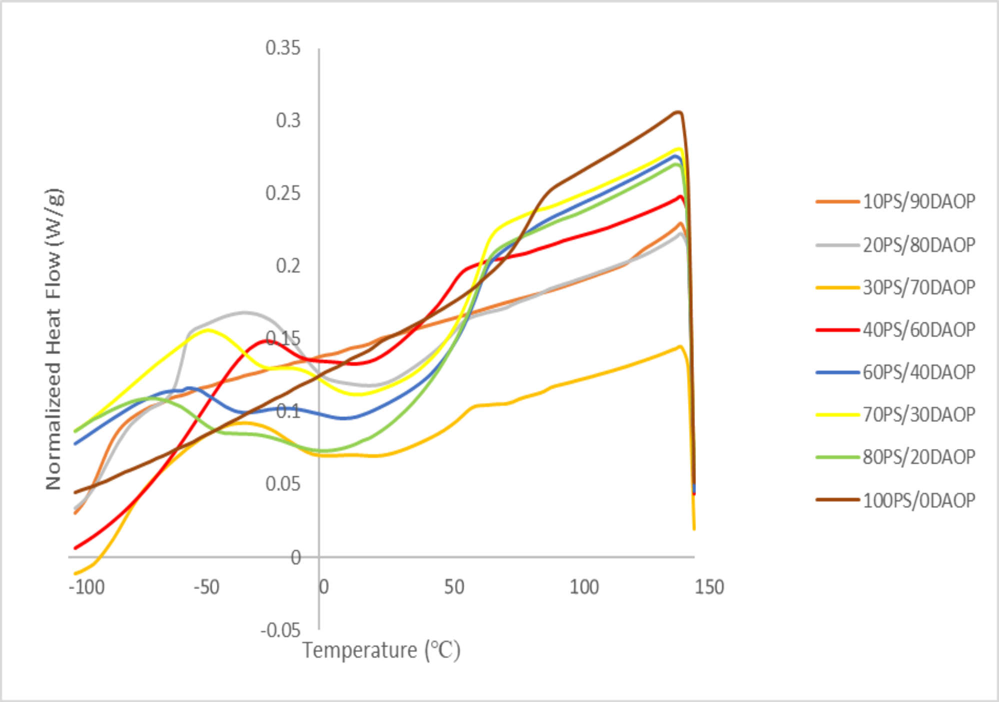
4.3.1 DSC study of various concentrations of PS/DAOP blends without DCP

Since solubility parameter calculations estimated that PS miscible with DAOP, it suggested that DAOP act as reactive plasticizers in PS. In addition, the T_g's of the various concentrations of PS and DAOP blends which can give indication of miscibility of the blends were also examined. Temperature-ramping DSC studies were conducted on the samples of various ratios of PS/DAOP blends and the DSC curves during re-heating were analysed in order to determine of Tg of the blends.

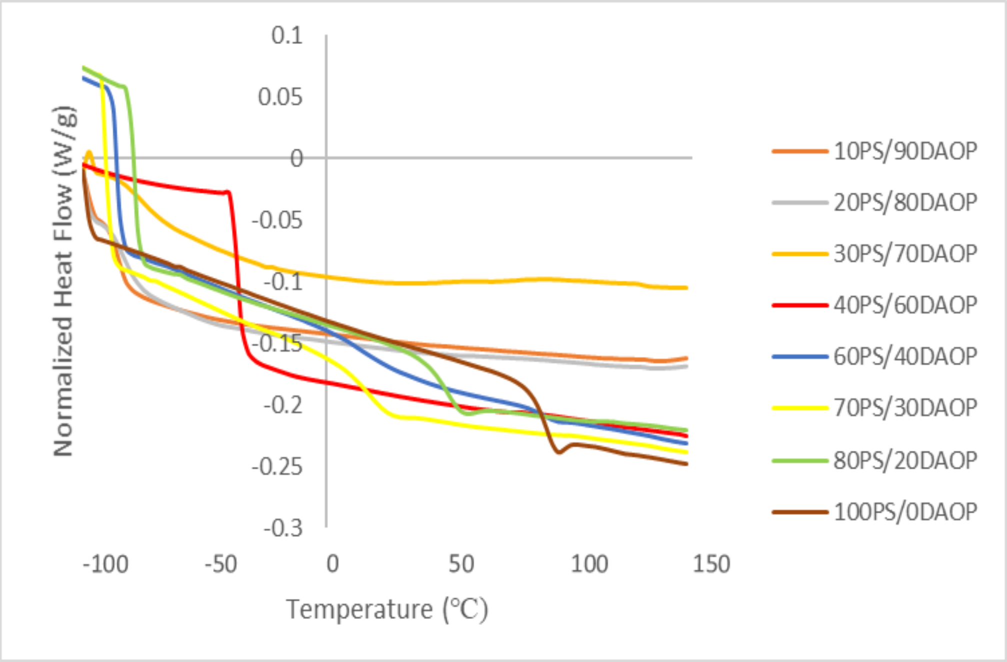
DSC test was done in order to determine the effect of different compositions of PS/DAOP blends on the thermal characteristics. The DSC curves for all samples during heating, cooling and reheating are shown in Figure 4.3 (a), (b) and (c), respectively. All the obtained results are summarized in the Table 4.8.


0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
Normalized Heat Flow (W/g)
-100
-50
0
50
100
150
Temperature (℃)
10PS/90DAOP
20PS/80DAOP
30PS/70DAOP
40PS/60DAOP
60PS/40DAOP
70PS/30DAOP
80PS/20DAOP
100PS/0DAOP

(a)


0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
Normalized Heat Flow (W/g)
-100
-50
0
50
100
150
Temperature (℃)
10PS/90DAOP
20PS/80DAOP
30PS/70DAOP
40PS/60DAOP
60PS/40DAOP
70PS/30DAOP
80PS/20DAOP
100PS/0DAOP

(b)



(c)

Figure 4.3: DSC plots of PS/DAOP blends (a) first heating scan (b) cooling scan (c) second heating scan.

Figure 4.3 (a), (b) and (c), each shows the DSC curves of various ratios of PS/DAOP blends in first heating scan, cooling scan and second heating scan, respectively. For a polymer or blends, normally there are T_g and T_m during heating scan. T_g is defined as the onset or midpoint of the steep change in energy, depending on certain circumstances. When obtained (semi)crystalline polymer is heated further in the DSC pan, its melting temperature, T_m can be reached (Harald Cherdron, 2013). On the other hand, during cooling scan the temperature at the highest point is usually taken as the crystallization temperature, T_c. The area of the peak corresponds to the latent heat energy of crystallization. For blends that contain PS and DAOP without initiator, T_g of the blends can be obtained from both heating and re-heating curves. However, first heating curve is normally affected by thermal history of the sample thus reheating curve is considered as more reliable in determining T_g of the blends. Meanwhile, the cooling scan of various compositions of PS/DAOP blends did not show obvious crystallization heat step occur.

For 100wt% PS, a heat step suggesting T_g of PS was found at 90^{o}C. For the blends of PS/DAOP which have high PS contents (60wt% and more PS), the curves indicated the presence of one heat step at temperature higher than room temperature in which the heat step could represent the T_g of the blends. The presence of only one heat step for the blend could be miscible at high PS content. In addition, it could be observed the heat step occurred at lower temperature with reducing amount of PS. However, with high content of DAOP (70wt% and more), it seems that a small heat transition occurred at beginning of the DSC test (around -80^{0}C) which might be due to the T_g of the DAOP. It is reported that DAOP has T_g of -91^{o}C (Dodiuk & Goodman, 1998). Table 4.8 tabulate the T_g's of all the compositions that obtained from DSC curve.

Table 4.8: T_g of various compositions of PS/DAOP blends obtained from heating and re-heating curve of DSC

Compositions	**T_g obtained from heating curve (^{o}C)**	**T_g obtained from re-heating curve (^{o}C)**
10PS/90DAOP	-86.0	-85.0
20PS/80DAOP	-82.5	-82.3
30PS/70DAOP	-74.5	-70.0
60PS/40DAOP	48.6	48.1
70PS/30DAOP	49.7	49.2
80PS/20DAOP	51.2	50.0
100PS/0DAOP	92.0	90.0

Table 4.8 tabulates the T_g value for each composition of PS/DAOP blends which are taken from the first heating scan and second heating scan. It can be seen that there are slight changes in the T_g of the PS component in each blend compositions. With the addition of DAOP, the T_g's of the PS were gradually decreased as the amount of DAOP content increased. It was reported by George Wypych (2012) that the T_g of the PS is around 100^{o}C. From the DSC curve above, it can be observed that the experimental T_g for PS obtained is 90.0^{o}C.

However, it shows the decreasing trend of T_g for the other compositions for PS/DAOP blends where T_g reduced from 90^{o}C for pure PS to about 50^{o}C in the presence of 20wt% DAOP. The results were expected since the addition of the DAOP which can acts as plasticizer before curing caused reduction T_g to ease the processing. A similar observation was reported in polyphenyelene oxide (PPO) and DAOP blends (Rusli et al., 2011) at high content of the thermoplastic (PPO).

Meanwhile at low PS content (30wt% and less PS), the presence of one T_g around -80^{o}C might be represents T_g of DAOP since DAOP is the major component of the blends.

Since there is a single phase transition T_g, it is suggested that the PS is miscible with DAOP. A single T_g of a blend implies complete miscibility between the polymer pairs in their amorphous fractions, whose value is an average of the individual component's T_g depending on each composition. However, the T_g obtained from DSC was slightly different form that calculated Fox equation (Fox,1956) assuming no interaction occurs between both PS and DAOP component. According to Brostow et al. (2008), the Fox equation can only serve for miscible blends and as well as for copolymers.

$$1/Tg = w(PS)/Tg(PS) + w(DAOP)/Tg(DAOP) \qquad (4.4)$$

Where w is the weight fraction of the component and T_g is the T_g of each of the component.

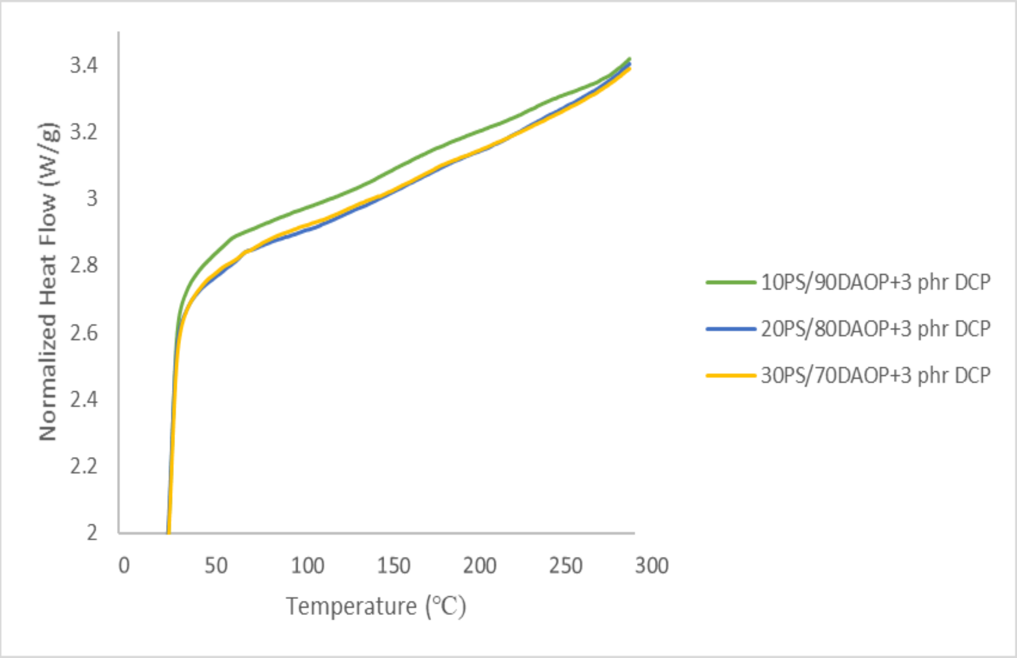
The theoretical value of T_g for 80PS/20DAOP blend obtained from Fox equation is 35.3°C. In the presence of higher amount of DAOP, the Tg of PS/DAOP blends at different compositions of the blends reduce from 50.0°C to -70.0°C and constant or still reduce to -85.0℃ as the wt% of DAOP increased to 90wt%.

4.3.2 DSC test of PS/DAOP with DCP after melt blending

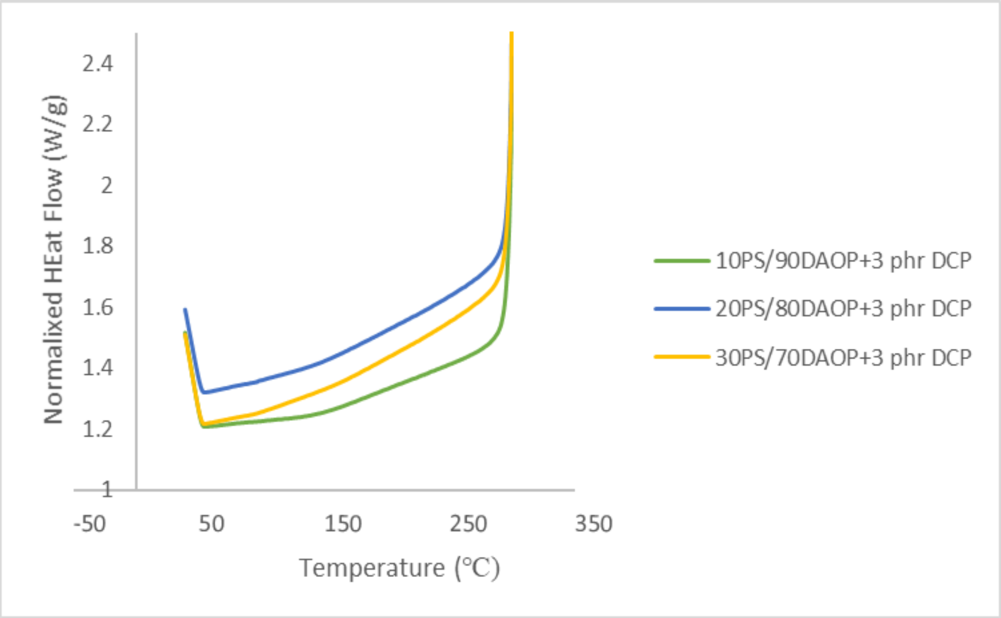
DSC test was done in order to determine the effect of different compositions of PS/DAOP blends for low PS content (less than 30wt%PS) on the thermal characteristics using Perkin Elmer Pyris 1 DSC. The samples which are 10wt% PS 90wt% DAOP+3 phr DCP, 20wt% PS 80wt% DAOP+3 phr DCP and 30wt% PS 70wt% DAOP+3 phr DCP were blended at 190°C in an oven before hot pressing done at 160°C for 15 minutes. For these samples, partial cure or pre-curing is presumably happening during blending and hot pressing and the effect of pre-curing on the heat of reaction and T_g of the blends were examined. The test was done from 30°C to 300℃ with heating rate of 10°C/min for three thermal conditions which are heating, cooling and reheating.

For a monomer to be used as an effective reactive plasticiser for thermoplastic, it must have relatively low reactivity during the processing but capable of undergoing high level reactions at higher temperature. This information could be obtained by examining exotherm peak temperature of the blends that undergo scanning temperature-ramping DSC (Rusli et al, 2011) on first heating. Meanwhile, second heating/reheating of the sample could provide information on the T_g of pre-curing sample during first heating scan.

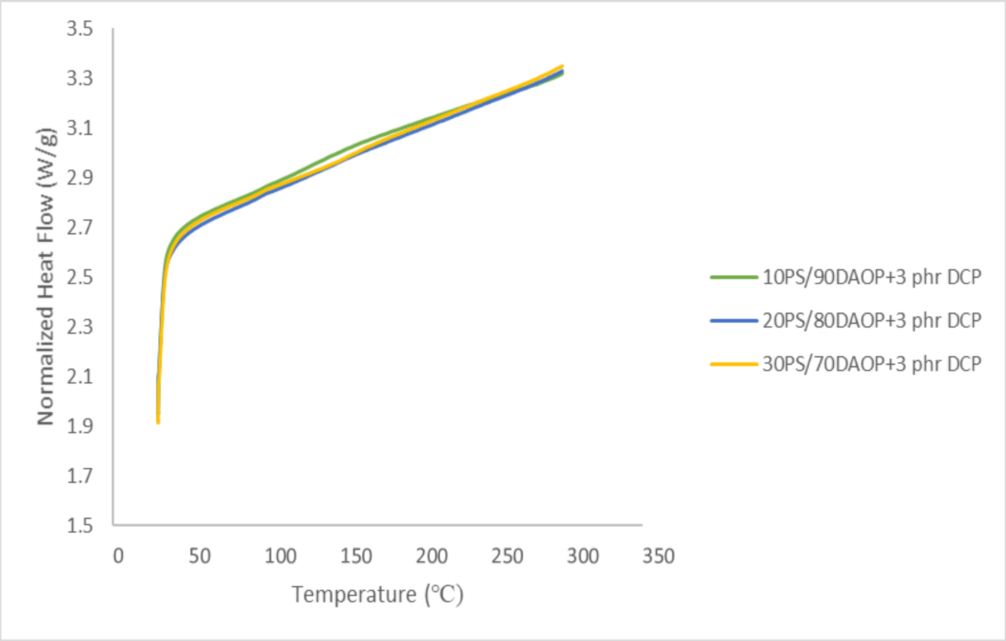
Figure 4.4 (a), (b) and (c), each showed the DSC graphs of PS/DAOP blends with DCP for low PS content in first heating scan, cooling scan and second heating scan, respectively.


Normalized Heat Flow (W/g)
3.4
3.2
3
2.8
2.6
2.4
2.2
2
0
50
100
150
200
250
300
Temperature (℃)
10PS/90DAOP+3 phr DCP
20PS/80DAOP+3 phr DCP
30PS/70DAOP+3 phr DCP

(a)


Normalized HEat Flow (W/g)
2.4
2.2
2
1.8
1.6
1.4
1.2
1
-50
50
150
250
350
Temperature (℃)
10PS/90DAOP+3 phr DCP
20PS/80DAOP+3 phr DCP
30PS/70DAOP+3 phr DCP

(b)



(c)

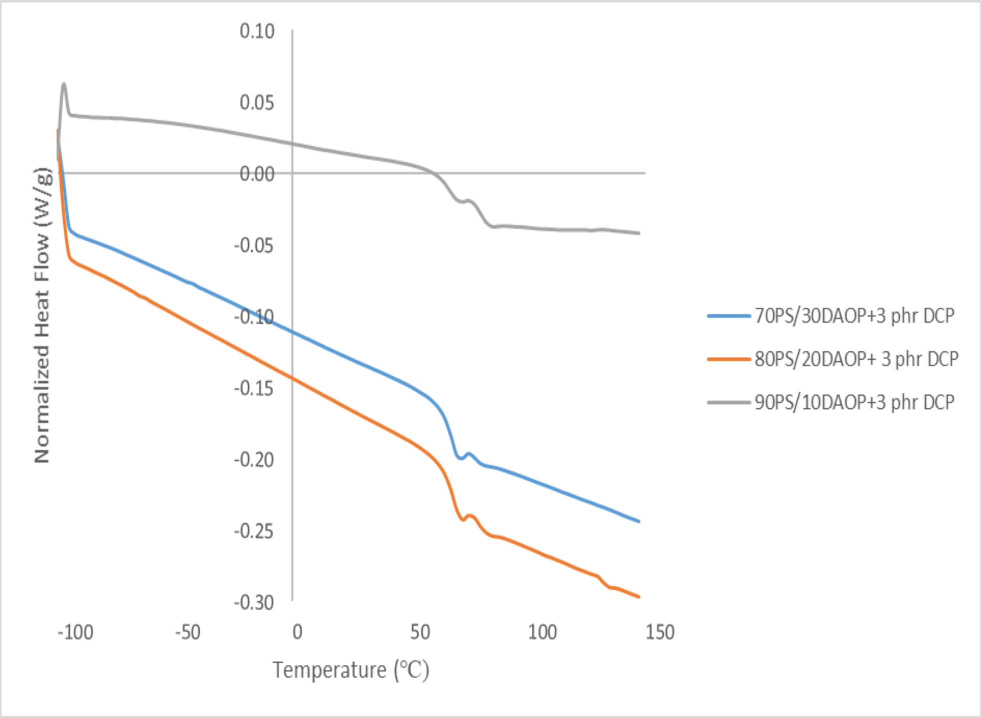
Figure 4.4: DSC plots of PS/DAOP-DCP blends for low PS content

(a) first heating scan (b) cooling scan (c) second heating scan

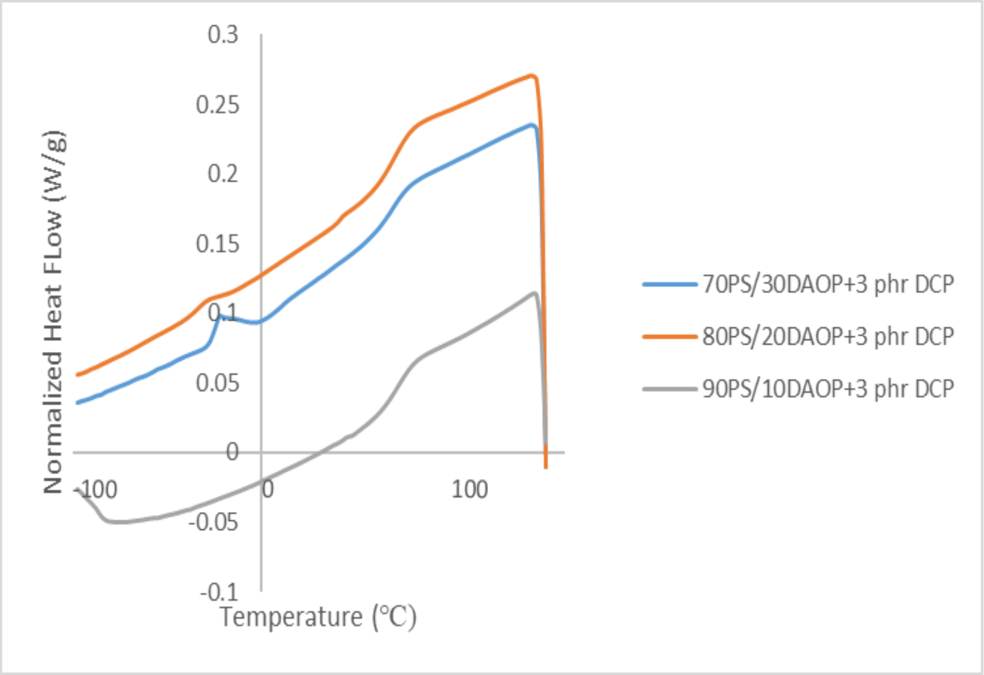
Brydson, (1999) stated that, DSC is used to observe the fusion and crystallization events as well as the glass transition (T_g) temperature of a polymer. It also can be used to monitor curing reaction of a thermoset. So, the DSC curve obtained could be used to examine polymerization of DAOP and T_g of the blends. It is believed that the DAOP component in PS/DAOP blends with DCP after blending and hot pressing is partially cured thus should indicate polymerization curve during heating and T_g of the blends after partially cured during reheating. However, the result obtained did not reveal any exothermic heat curve or heat steps representing Tg of blend samples either during heating or reheating. This might be due to less sensitivity of the Perkin Elmer Pyris 1 DSC in detecting T_g of thermoset and exothermic heat curve of partially cured thermoset.

A similar test was conducted for the blends with high PS content but using Mettler Toledo Star 1 DSC. The samples were prepared by Haake Polydrive Internal Mixer at

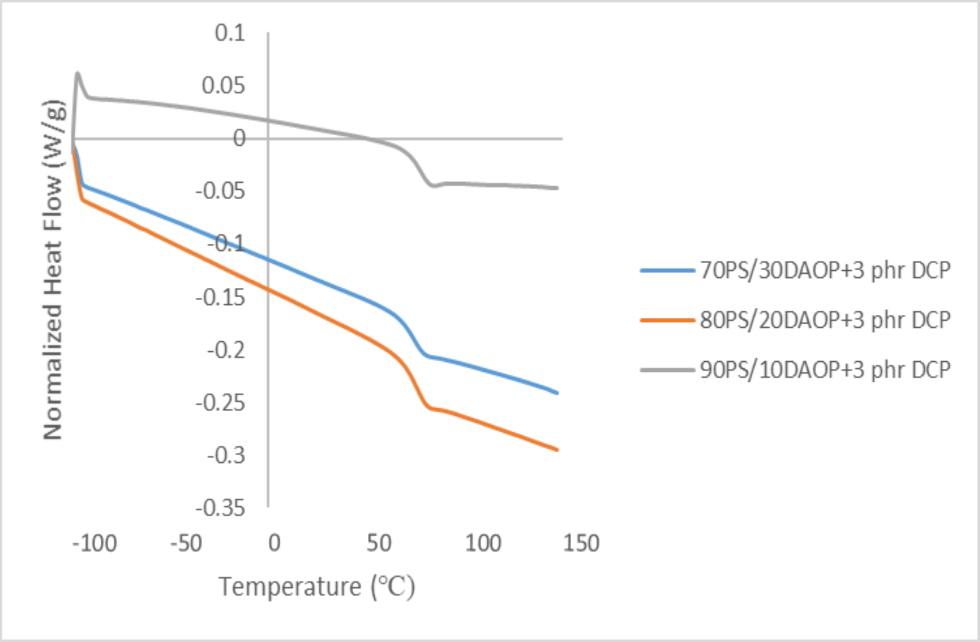
190℃ for 5 minutes and hot pressed at 190ºC for 15 minutes (5 minute pre-heat, 5 minute compress and 5 minute cooling). The DSC curves of PS/DAOP-DCP blends for high PS content (70wt% PS to 90wt% PS) are presented in Figure 4.5. Interestingly, heat steps representing T_g could be observed from Figure 4.5 and Table 4.9 shows the tabulates data from the DSC curves. However, heat of polymerization curve could not be observed suggesting that the sample might fully polymerized during processing and hot pressed.



(a)



(b)



(c)

Figure 4.5: DSC plots of PS/DAOP-DCP blends for high contents PS at

(a) first heating scan (b) cooling scan (c) second heating scan.

Table 4.9: T_g of the PS/DAOP-DCP blends of high PS content for uncured blend according to different compositions

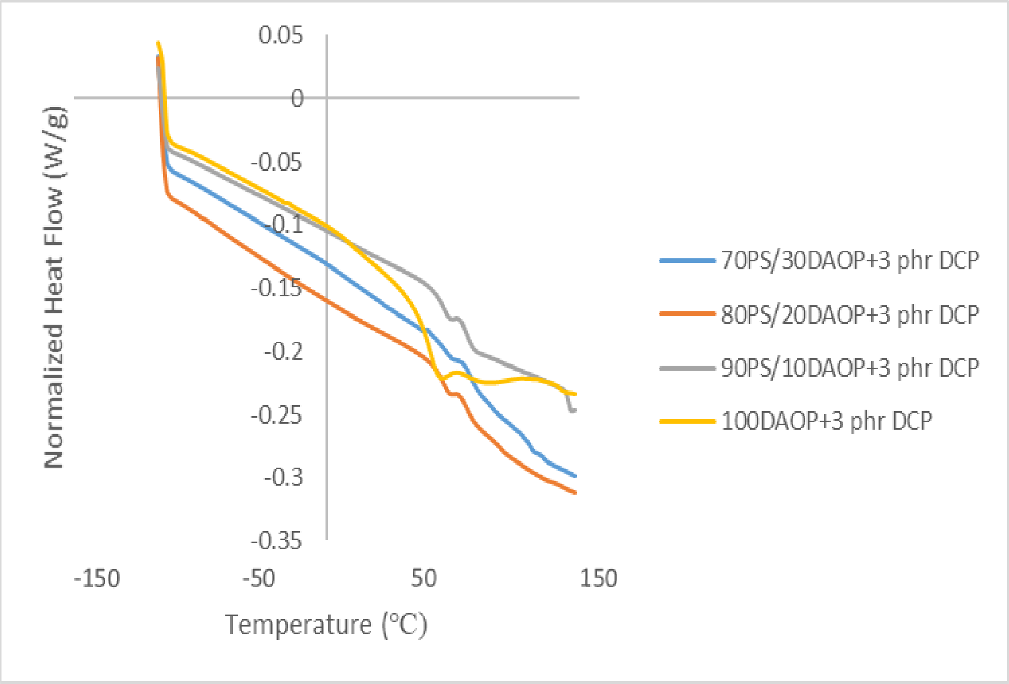
Compositions	T_g obtained from heating curve (°C)	T_g obtained from re-heating curve (°C)
70PS/30DAOP-DCP	$Tg_1 = 68.0$ $Tg_2 = 78.1$	74.4
80PS/20DAOP-DCP	$Tg_1 = 69.8$ $Tg_2 = 79.2$	76.1
90PS/10DAOP-DCP	$Tg_1 = 66.5$ $Tg_2 = 80.0$	76.5

As shown in Table 4.9, at the first heating scan DSC curves exhibited one significant heat step and an additional small heat steps at slightly higher temperature. These heat steps might represent two T_g's (one Tg represents PS component and another Tg represents DAOP) or might be due to thermal history of the sample since the two steps could not be observed in the second heating scan (re-heating).

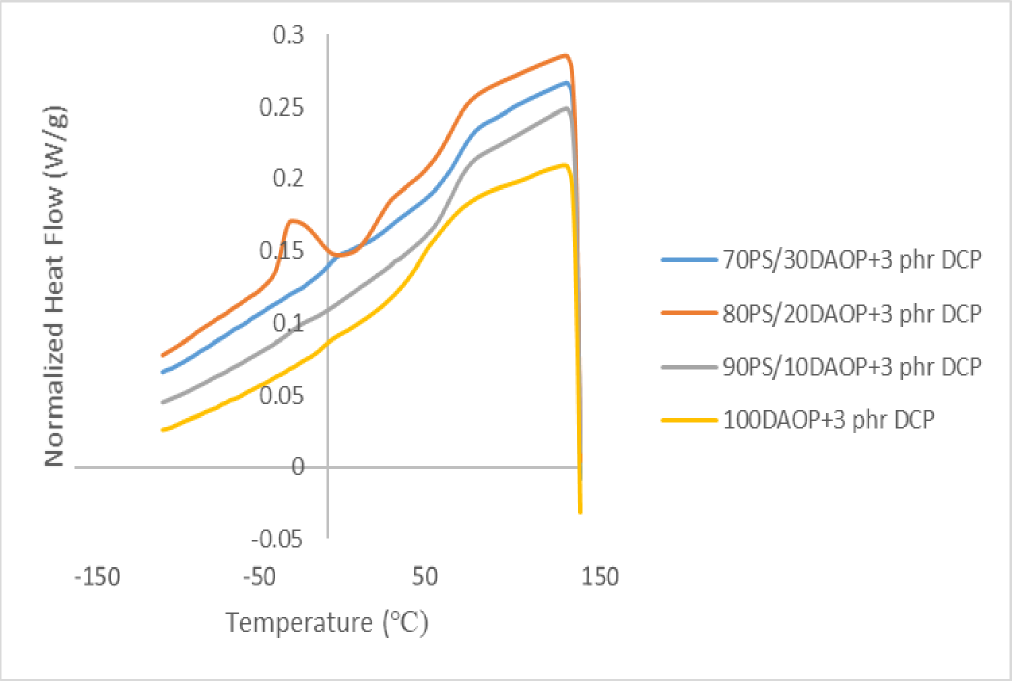
However, at the second heating scan the DSC curves in Figure 4.5 (c) indicated that all compositions tend to exhibit a single heat step T_g suggesting miscibility of the components in the blends. This result is unexpected since in thermoplastic-thermosets blends, phase separation always occurred in cured blends. It is believed that this observation might be due to the small differences between the T_g of cured DAOP which is around 68°C with the T_g of PS thus illustrating one single T_g around 75°C. Meanwhile, the reduction of T_g of the blends compared with T_g of pure PS might be due to the presence of uncured DAOP in PS matrix thus reducing the T_g of the PS component. Rusli et al. (2011) studied cure kinetics and conducted DMTA test on PPO/DAOP blends in the presence of dicumyl peroxide (DCP) or tert-butyl hydroperoxide (TBHP) as initator. They observed one T_g even though morphological studies indicated phase separation.

4.3.3 DSC of PS/DAOP with DCP after post curing

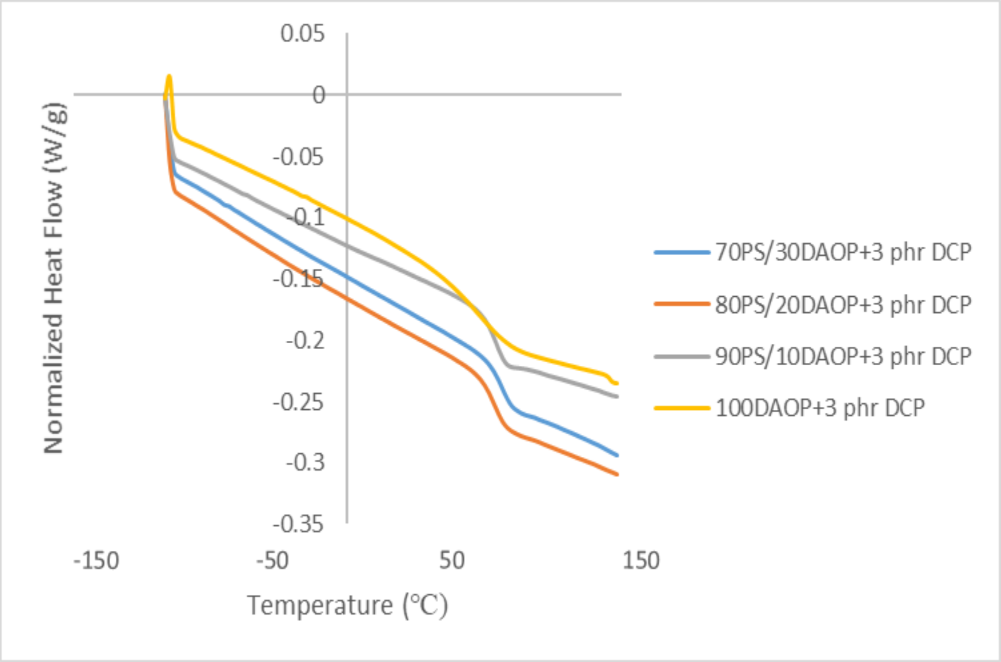
For the application of thermoset as reactive plasticizer in thermoplastic, the T_g thus thermomechanical properties of the thermoplastic should be retain. It is also important that the thermoset is fully cured after processing. The effect of corporation of thermosetting component (DAOP-DCP) at high PS content after processing in Haake internal mixer, hot pressing at 160°C for 15 minutes and finally curing at 160°C for 5 hours on the T_g were examined. Figure 4.6 and Table 4.10 show the DSC curves and the T_g of various PS/DAOP blends, respectively after subjected to that conditions.



(a)



(b)



(c)

Figure 4.6: DSC plots of PS/DAOP-DCP blends for high contents PS at

(a) first heating scan (b) cooling scan (c) second heating scan.

Table 4.10: T_g various cured blends of PS/DAOP-DCP of high PS content

Compositions	**T_g obtained from heating curve (°C)**	**T_g obtained from re-heating curve (°C)**
70PS/30DAOP-DCP	Tg = 90.0	84.0
80PS/20DAOP-DCP	Tg_1 = 70.0 Tg_2 = 84.2	80.3
90PS/10DAOP-DCP	Tg_1 = 69.9 Tg_2 = 82.0	81.4
100DAOP-DCP	62.42	69.0

Figure 4.6 (a), (b) and (c), each shows the DSC graphs of cured PS/DAOP blends for high PS content in first heating scan, cooling scan and second heating scan, respectively. The cured blends of PS/DAOP with DCP, indicate two heat steps suggesting immiscibility of the blend at the first heating scan. However, it is believed that this observation might be affected by thermal history of the blends. On second heating scan, Figure 4.6 (c) shows a single heat step T_g for all composition suggesting miscible blend.

Table 4.11: Comparison between T_g partially cured and cured blends according to all compositions

Compositions	**T_g obtained from partially cured blend (°C)**	**T_g obtained from cured blend (°C)**
70PS/30DAOP-DCP	71.4	84.0
80PS/20DAOP-DCP	76.1	80.3
90PS/10DAOP-DCP	76.5	81.4

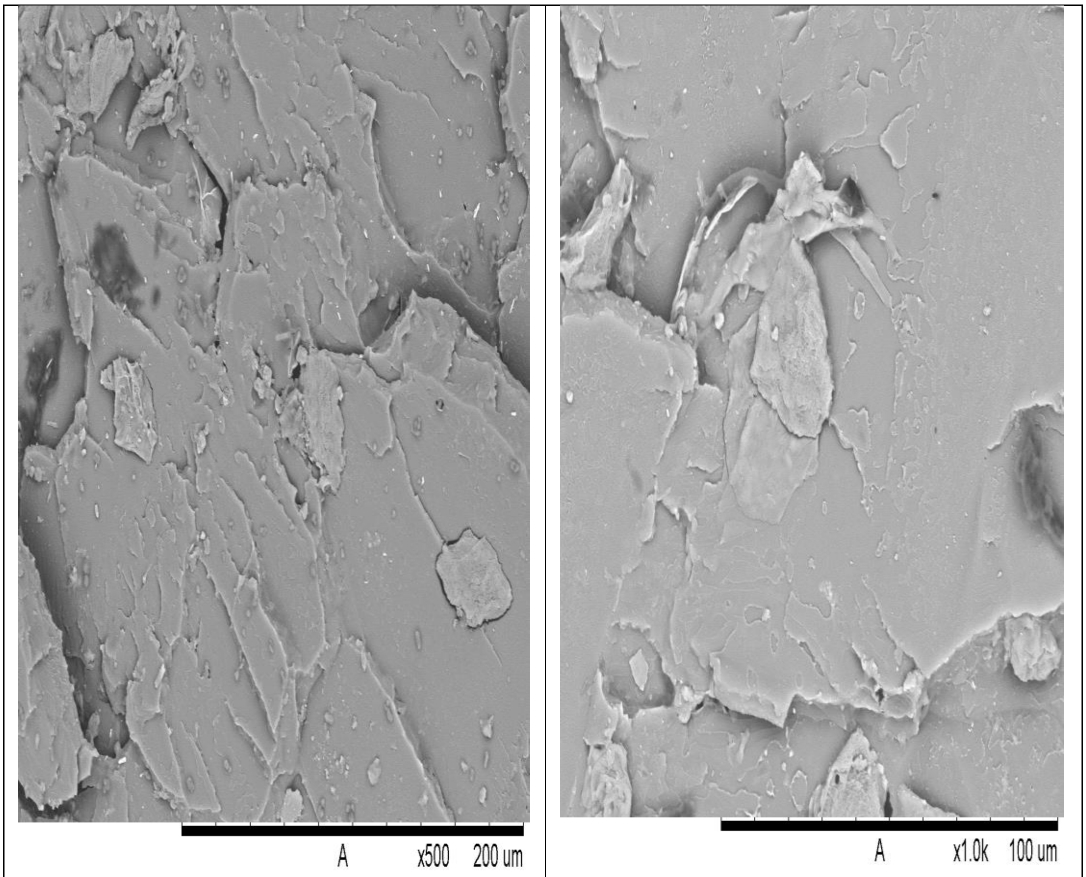
As shown in Table 4.11, the T_g's of the postcured cured blends are about 5℃ higher than that of the partially cured blends. This is due to the higher crosslinking occurred during cured process at 160°C for 5 hours compared with blends without postcuring process thus higher T_g of cured DAOP and less remaining uncrosslinked DAOP in PS phases (so that T_g of PS increase). The T_g PS/DAOP-DCP blends increased because of the rise of the thermoplastic concentration in the PS phase (the continuous phase) until it reached the curing temperature T=160°C.

4.4 Morphology of fracture surface

In thermoplastic and thermoset blend systems, the miscibility and composition of different thermoplastics with thermoset has deep effect on the morphology of modified blends, which in turn influences the processing, mechanical, thermal and other properties of blends greatly (Liu et al., 2010). In this research, thermoplastic which is PS was blended with different compositions of DAOP-DCP as reactive plasticizer. The fracture surfaces of the blends were observed using SEM to examine the phase morphology of the blends after cured.

SEM was conducted in order to determine the effect of different compositions of blends on the morphology characteristics of the PS/DAOP blends. Kang et al., (1999) stated that morphology is a major factor that determine the mechanical properties of the immiscible blends. In addition, the main point that determine the final morphology of a blend is the component composition. In past studies, Nielson (1974) stated that morphology of the blends that was prepared by melt mixing, changes with the composition.

Evidence of phase separation and changes in the morphology with decreasing DAOP content in cured PS/DAOP-DCP blends, as revealed by SEM, are illustrated in Figure 4.14. For the blends of 100PS/0DAOP without DCP, fractured surfaces was rough. Etching was done on blends in order to remove thermoplastic component of the blends.



100PS/0DAOP

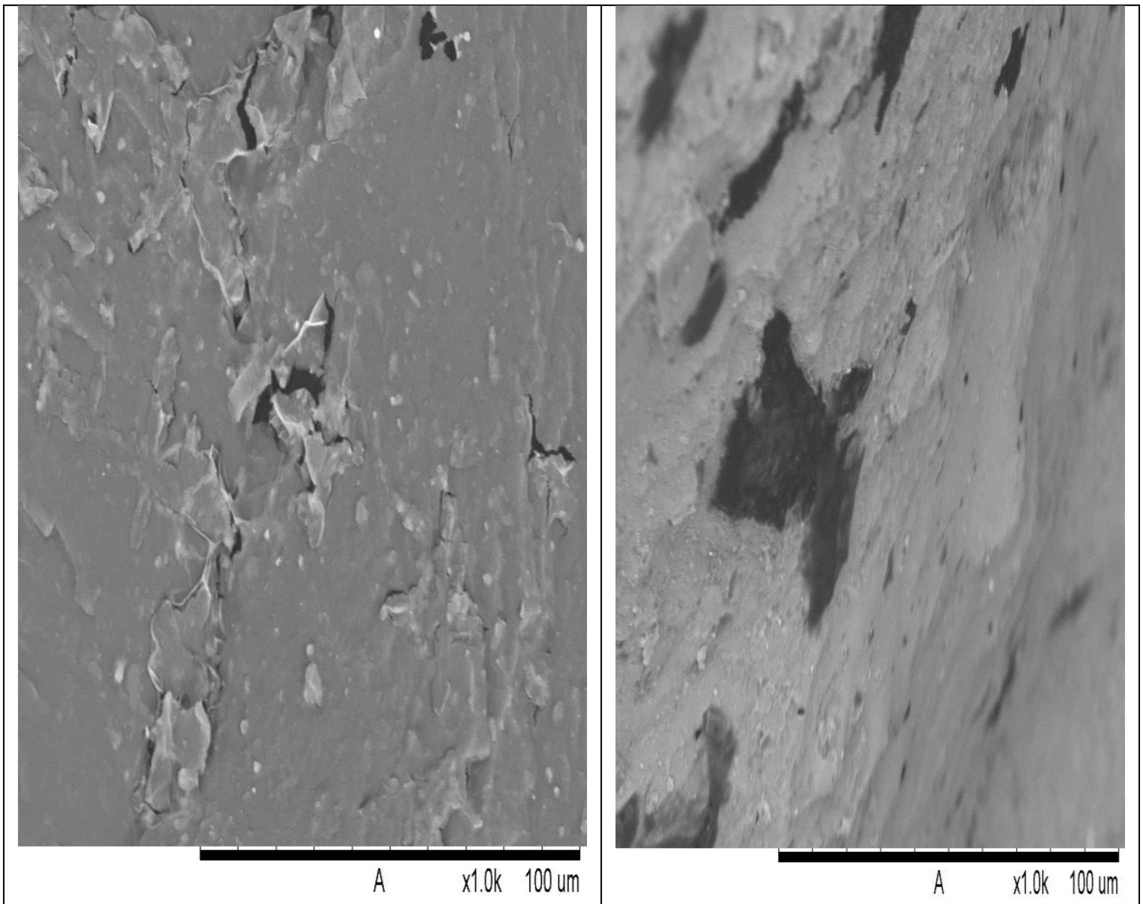
Magnification x 500

100PS/0DAOP

Magnification x 1000

Figure 4.7: SEM image of fractured surface of 100PS/0DAOP blend

The unetched fractured surface of 70PS/30DAOP-DCP also showed a rough surface with some indication of the presence of small dispersed particles which is believed of poly (DAOP) phases. After etching, the 30wt% DAOP sample exhibit a smooth surface with wide distribution of holes (big and small holes). Such morphology could result from fact that PS is the primary component of the continuous phase and cured DAOP constitutes the major component of the dispersed phase. For this blend, the holes in the etched surface could be caused by the partial dissolution of the PS-rich matrix surrounding the DAOP-rich particles.

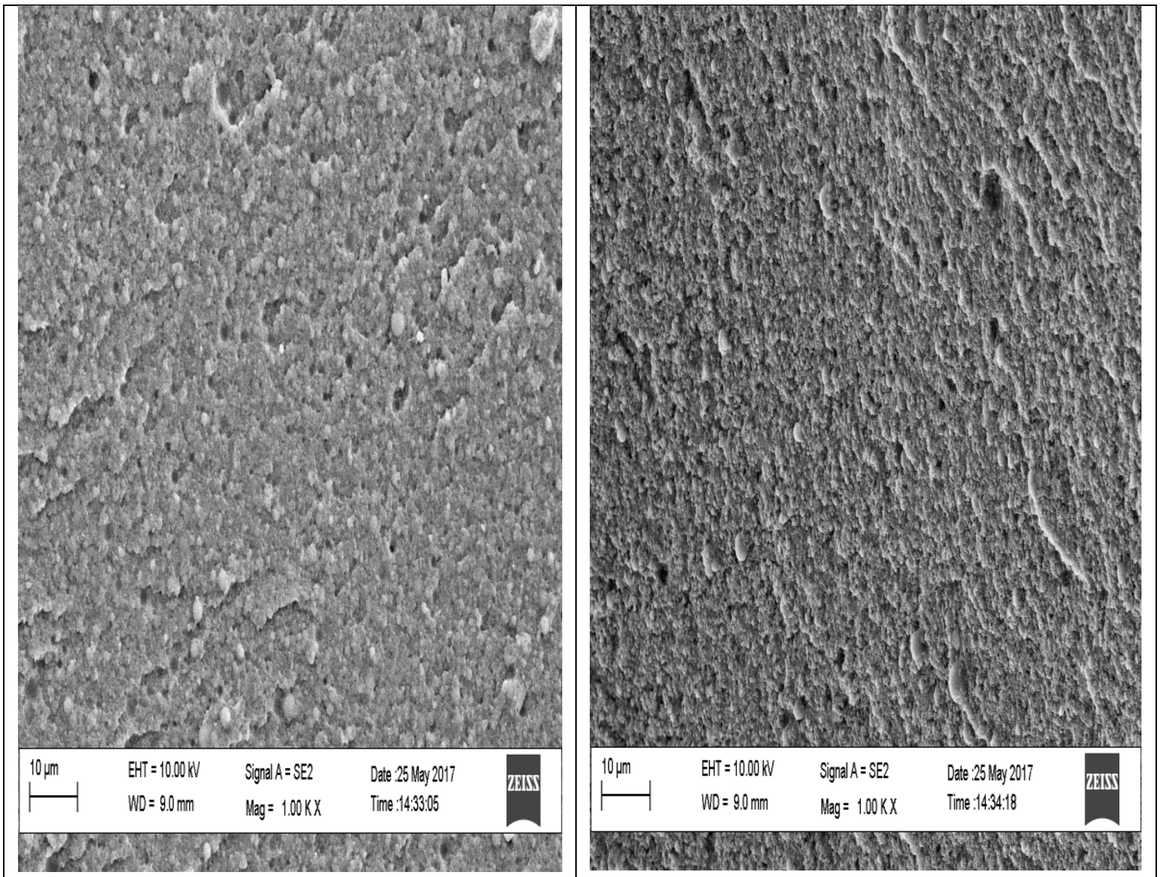


70PS/30DAOP-DCP unetched
Magnification x 1000

70PS/30DAOP-DCP etched
Magnification x 1000

Figure 4.8: SEM images of fractured surface of 70PS/30DAOP-DCP blend (unetched and etched in toluene for 10 minutes)

With a further decreased of PS level to 40wt% and increased of reactive plasticizer content to 60wt%, rougher surface was observed. Also, it showed smoother surface after etching might be due to the dissolution of PS in DAOP continuous phase. The holes formed were smaller compared with 70PS/30DAOP-DCP blends due to the less PS content in the blend with 40wt% PS that present in DAOP rich particles.



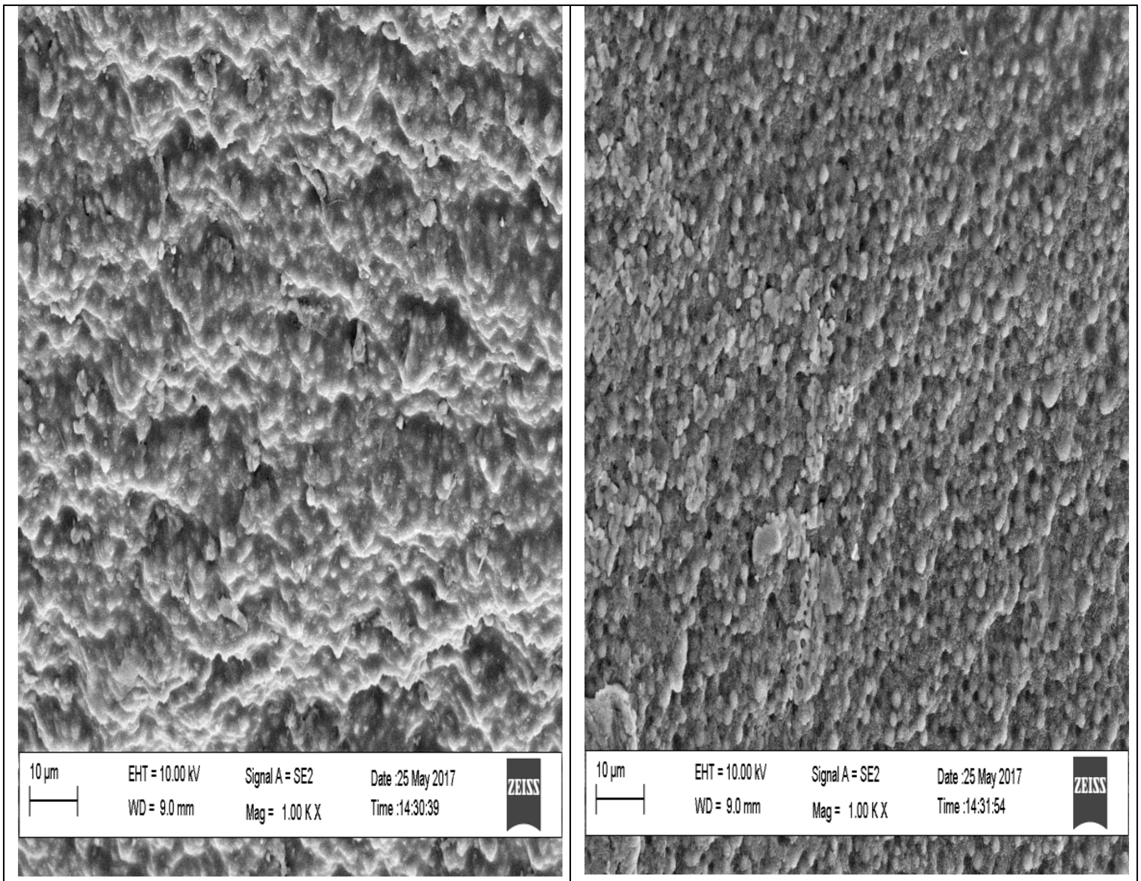
40PS/60DAOP-DCP unetched
Magnification x 1000

40PS/60DAOP-DCP etched
Magnification x 1000

Figure 4.9: SEM images of fractured surface of 40PS/60DAOP-DCP blend

(unetched and etched in toluene for 10 minutes)

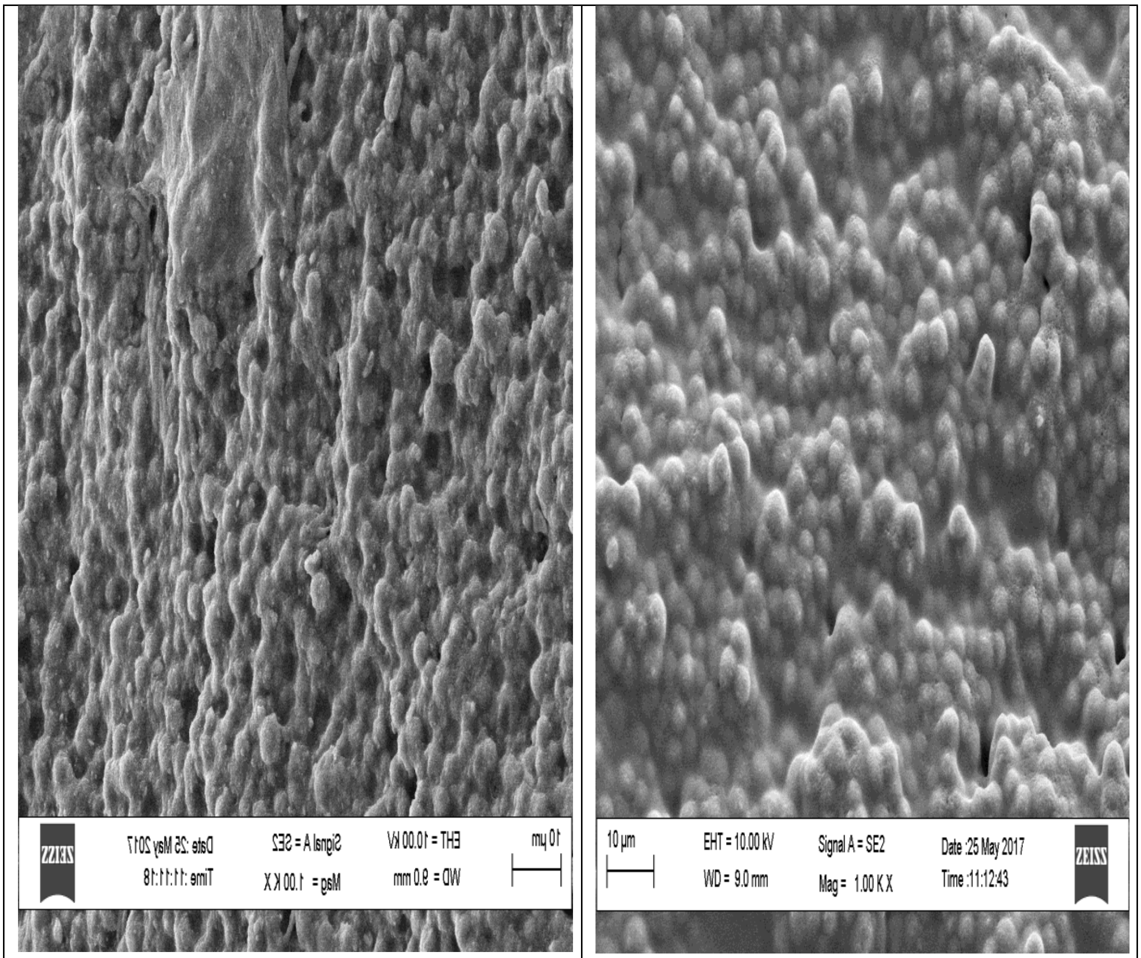
The morphology of PS/DAOP-DCP blends were examine using SEM micrographs shown in Figure 4.10, 4.11 and 4.112, of various PS/DAOP-DCP blends indicated two phase morphology with dispersed particles in a continuous matrix. It can be observed when PS content increase from 10 to 30wt% the size of the dispersed particles formed become smaller with further increased of PS in the blends. The in trends might be due to phase inversion which normally found in thermoset-thermoplastic blends. It is believed that PS phase are dispersed in continuous DAOP matrix in the blends with low PS contents (10, 20 and 30 wt% PS), while in the blends with 40 wt% PS and more, DAOP formed dispersed phase in a continuous PS matrix. The changes also might contribute to the significant different of Tg's of DAOP in the curing blends at low PS content (10, 20 and 30 wt% PS) compared with high PS content.



30PS/70DAOP-DCP unetched
Magnification x 1000

30PS/70DAOP-DCP etched
Magnification x 1000

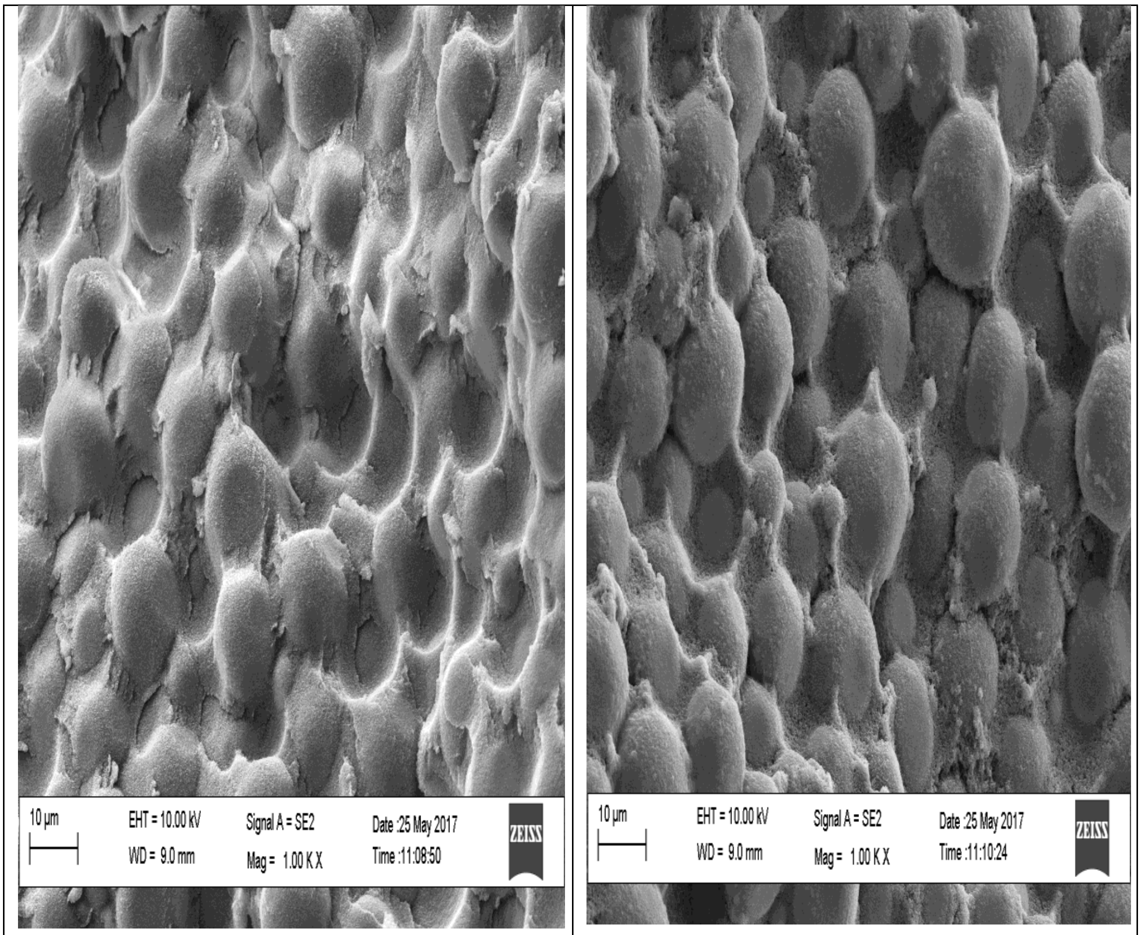
Figure 4.10: SEM images of fractured surface of 30PS/70DAOP-DCP blend (unetched and etched in toluene for 10 minutes)



20PS/80DAOP-DCP unetched
Magnification x 1000

20PS/80DAOP-DCP etched
Magnification x 1000

Figure 4.11: SEM images of fractured surface of 20PS/80DAOP-DCP blend (unetched and etched in toluene for 10 minutes)



10PS/90DAOP-DCP unetched
Magnification x 500

10PS/90DAOP-DCP etched
Magnification x 500

Figure 4.12: SEM images of fractured surface of 10PS/90DAOP-DCP blend (unetched and etched in toluene for 10 minutes)

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The applicability and efficiency of DAOP as reactive plasticizer in PS were studied by calculating solubility parameter of the component and examining the T_g and morphology of the blends with and without DCP as initiator. Solubility parameter of PS and DAOP calculated from group additivity approach suggested that the blend should be miscible.

Meanwhile, the various concentration of PS/DAOP without DCP samples showed the presence of the single heat step T_g suggesting the miscibility of the blends at all compositions. The T_g observed from DSC curve slightly different from T_g calculated from the Fox Equation assuming no interaction occurs between both PS and DAOP component. It is expected since the presence of reactive plasticizer will reduce the T_g of the blends.

In PS/DAOP cured with DCP blends, all compositions tend to exhibit a single heat step T_g suggesting miscibility of the components in the blends which is unexpected since in thermoplastic-thermosets blends, phase separation always occurred in cured blends that might be due to small differences between T_g PS and cured DAOP. While PS/DAOP postcured cured DCP blend, the T_g slightly higher than the cured blends. This is might be due to the higher crosslinking occurred during cured process compared with blends without postcuring process thus higher T_g of cured DAOP and less remaining uncrosslinked DAOP in PS phases (so that T_g of PS increase).

The morphological behaviour of various compositions of postcured PS/DAOP-DCP indicated the formation of two phases system. As the PS contents decreased, the dispersed particles of poly (DAOP) become bigger and the surface fracture of the blends become smoother. While, the blends indicated two phase morphology with dispersed particles in a continuous matrix.

5.2 Recommendation for Future Works

There are some recommendations for future research on this topic such as:

1) Other melt blending method such as extrusion instead of internal mixer could be used to obtain a homogeneous blend.

2) Dynamic Mechanical Thermal Analysis (DMTA) can be performed to obtain the T_g of the blends. DMTA has an advantage over DSC since DMTA can indicate not only glass transition temperature but also other transition. Immiscibility can be observed using DMTA by the presence of more than one glass transition.

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APPENDICES

APPENDIX A

Solubility parameters calculation according to Fedor's method:

Polystyrene (PS)

$\delta^2 = E_{coh} / V$

$\delta^2 = E_{coh} / V = 40310 / 86.5 = 466.012$ J/cm^3

$\delta = 21.587$ (J/cm^3)$^{1/2}$

Diallyl Ortho-phthalate (DAOP)

$\delta^2 = E_{coh} / V = 100500 / 197.8 = 508.089$ J/cm^3

$\delta = 22.541$(J/cm^3)$^{1/2}$

Toluene

$\delta^2 = E_{coh} / V = 36650 / 104.9 = 349.380$J/cm^3

$\delta = 18.691$ (J/cm^3)$^{1/2}$

Tetrahydrofuran (THF)

$\delta^2 = E_{coh} / V = 23110 / 68.2 = 338.856$ J/cm^3

$\delta = 18.408$(J/cm^3)$^{1/2}$

APPENDIX B

Solubility parameters calculation according to Small method:

Polystyrene (PS)

$F = 1833$

$V = 86.5\ cm^3/mol$

$E_{coh} = F^2 / V$

$E_{coh} = \delta^2\ V$

$E_{coh} = 1833^2 / 86.5 = 38842\ J/mol$

$38842\ J/mol = \delta^2\ (86.5\ cm^3/mol)$

$\delta = \sqrt{449.040}$

$\delta = 21.191\ J^{1/2}/cm^{3/2}$

Diallyl Ortho-phthalate (DAOP)

$E_{coh} = F^2 / V$

$E_{coh} = \delta^2\ V$

E_{coh} and V obtained from Fedor’s method

$E_{coh} = 100500$

$V = 197.8\ cm^3/mol$

$E_{coh} = 4210^2 / 197.8 = 89606\ J/mol$

$89606\ J/mol = \delta^2\ (197.8\ cm^3/mol)$

$\delta = \sqrt{453.013}$

$\delta = 21.284\ J^{1/2}/cm^{3/2}$

APPENDIX C

Solubility parameters calculation according to Van Krevelan method:

Polystyrene (PS)

$F = 1833$

$V = 86.5\ \text{cm}^3/\text{mol}$

$E_{coh} = 1937^2 / 86.5 = 43375\ \text{J/mol}$

$43375\ \text{J/mol} = \delta^2\ (86.5\ \text{cm}^3/\text{mol})$

$\delta = \sqrt{501.449}$

$\delta = 22.393\ \text{J}^{1/2}/\text{cm}^{3/2}$

Diallyl Ortho-phthalate (DAOP)

$E_{coh} = 4707^2 / 197.8 = 112011\ \text{J/mol}$

$112011\ \text{J/mol} = \delta^2\ (197.8\ \text{cm}^3/\text{mol})$

$\delta = \sqrt{566.286}$

$\delta = 23.797\ \text{J}^{1/2}/\text{cm}^{3/2}$