SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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EFFECT OF POLY (ETHYLENE -CO- METHYL ACRYLATE -CO- GLYCIDYL METHACRYLATE) AND POLYETHYLENE GRAFTED MALEIC ANHYDRIDE AS COMPATIBILIZERS ON THE PROPERTIES OF POLYBUTYLENE TEREPHTHALATE/LOW DENSITY POLYETHYLENE BLENDS

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"Effect of Poly (ethylene -co- methyl acrylate -co- glycidyl methacrylate) and Polyethylene grafted Maleic Anhydride as Compatibilizers on the properties of Polybutylene Terephthalate/Low Density Polyethylene Blends"**. 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
ASTM	American Society for Testing and Materials
DMA	Dynamic Mechanical Analysis
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
EBAGMA	Poly (Ethylene-Butyl Acrylate-Glycidyl Methylacrylate)
Eb	Elongation at break
EEAGMA	Ethylene/Ethyl Acrylate Glycidyl Methacrylate terpolymer
EGMA	Ethylene-co-glycidyl methacrylate copolymers
EMAGMA	Poly (Ethylene-co-methyl acrylate-co-glycidyl methacrylate)
EPDM	Ethylene Propylene-Diene copolymers
EPDM-g-SAN	Ethylene propylene diene rubber grafted styrene acrylonitrile
EPM	Ethylene-Propylene copolymer
EPR	Ethylene Propylene Rubber
EVA	Ethylene-co-Vinyl Acetate
EVA-g-MA	Ethylene-co-Vinyl Acetate grafted Maleic Anhydride
FESEM	Field Emission Scanning Electron Microscopy
GMA	Glycidyl Methacrylate
HDPE	High Density Polyethylene
HDPE-g-MA	High Density Polyethylene grafted With Maleic Anhydride
IIR	Butyl Rubber
LCP	Liquid Crystalline Polymer
LDPE	Low Density Polyethylene

LLDPE	Low Linear Density Polyethylene
MA	Maleic Anhydride
NR	Natural Rubber
PA	Polyamide
PBT	Polybutylene Terephthalate
PE	Polyethylene
PE-g-MA	Polyethylene grafted Maleic Anhydride
PEEK	Polyether ether ketone
PEI	Polyetherimide
PET	Polyethylene Terephthalate
PP	Polypropylene
PPO	Polyphenylene Oxide
PS	Polystyrene
rHDPE	Recycled High Density Polyethylene
SAN	Styrene Acrylonitrile
SBS	Styrene-Butadiene-Styrene block copolymer
SEBS-g-MA	Maleic Anhydride grafted Styrene-Ethylene Butylene-Styrene
TGA	Thermal Gravity Analysis

LIST OF SYMBOLS

$wt\%$	Weight percent
%	Percent
°C	Degree Celcius
T_g	Glass transition temperature
T_c	Crystallization temperature
T_m	Melting temperature
ΔH_c	Heat of crystallization
ΔH_m	Heat of fusion
MPa	Mega Pascal
J	Joule
mm	Milimetre
mg	Miligram
min	Minutes
h	Hours
rpm	Revolution per minute
mm/min	Milimetre per minute
J/mm	Joule per millimeter
g/mol	Gram per mol
W/g	Watt per gram
J/g	Joule per gram
g/cm^3	Gram per centimetre cube
°C/min	Degree Celcius per minute

KESAN POLI (ETILENA-KO-METIL AKRILAT-KO-GLICIDIL METAKRILAT) DAN POLIETILENA DICANTUMKAN DENGAN MALEIK ANHIDRIDA SEBAGAI BAHAN PENSERASI TERHADAP SIFAT-SIFAT CAMPURAN POLIBUTILENA TEREPHTHALATE/POLIETILENA BERKETUMPATAN RENDAH

ABSTRAK

Kesan komposisi yang berbeza bagi adunan polibutilena terephthalate (PBT) dan polietilena berketumpatan rendah (LDPE) (20/80, 50/50, 80/20 PBT/LDPE) dan kesan kuantiti yang berbeza (5, 10 dan 15 wt%) poli (etilena-ko-metil akrilat-ko-glicidil metakrilat) (EMAGMA) terpolimer dan polietilena dicantumkan dengan maleik anhidrida (PE-g-MA) sebagai bahan penserasi terhadap sifat-sifat mekanikal dan morfologi adunan PBT/LDPE telah dikaji. Analisis imbasan mikroskop elektron medan pancaran (FESEM) menunjukkan dua fasa morfologi dengan interaksi yang lemah antara fasa. Berdasarkan sifat-sifat mekanikal, 80PBT/20LDPE menunjukkan kekuatan tegangan dan modulus yang tinggi dan ia dianggap sebagai sistem campuran yang terbaik. Penggabungan EMAGMA atau PE-g-MA sebagai bahan penserasi di dalam 80PBT/20LDPE campuran menunjukkan peningkatan dalam kekuatan impak tetapi penurunan dalam kekuatan tegangan. Walau bagaimanapun, sifat-sifat mekanikal campuran 80PBT/20LDPE dengan bahan penserasi lebih ketara dengan kehadiran EMAGMA berbanding PE-g-MA, walaupun sifat-sifat mekanikal masih lebih rendah daripada 80PBT/20LDPE campuran tanpa bahan penserasi. Analisis FESEM menunjukkan kurang pemisahan fasa, mencadangkan interaksi yang lebih baik antara komponen dalam PBT/LDPE/EMAGMA campuran berbanding dengan PBT/LDPE/PE-g-MA. Kesimpulannya, bahan penserasi EMAGMA dianggap sebagai bahan penserasi

yang lebih baik berbanding dengan PE-g-MA, tetapi ia tidak boleh bertindak sebagai bahan penserasi yang berkesan untuk sistem PBT/LDPE campuran pada kandungan yang rendah.

EFFECT OF POLY (ETHYLENE -CO- METHYL ACRYLATE -CO- GLYCIDYL METHACRYLATE) AND POLYETHYLENE GRAFTED MALEIC ANHYDRIDE AS COMPATIBILIZERS ON THE PROPERTIES OF POLYBUTYLENE TEREPHTHALATE/LOW DENSITY POLYETHYLENE BLENDS

ABSTRACT

The effect of different compositions of polybutylene terephthalate (PBT) and low density polyethylene (LDPE) blends (20/80, 50/50, 80/20 of PBT/LDPE) and the effect of different amounts (5, 10 and 15 wt%) of poly (ethylene -co- methyl acrylate -co- glycidyl methacrylate) (EMAGMA) terpolymer and polyethylene grafted maleic anhydride (PE-g-MA) as compatibilizers on the mechanical and morphological properties of PBT/LDPE blends were investigated. Field emission scanning electron microscope (FESEM) showed two phase morphology with poor interaction between the phases. Based on mechanical properties, 80PBT/20LDPE exhibited the highest tensile strength and modulus and it was considered as the optimum blend system. Incorporation of EMAGMA or PE-g-MA as compatibilizer in the 80PBT/20LDPE blend showed improvement in impact strength but reduction in tensile strength. However, 80PBT/20LDPE blend with EMAGMA have better mechanical properties compared with the blend with PE-g-MA, even though the mechanical properties lowered than uncompatibilized 80PBT/20LDPE blend. FESEM study indicated less phase separation suggesting better interaction between the components in PBT/LDPE/EMAGMA blends compared with the PBT/LDPE/PE-g-MA blends. In conclusion, EMAGMA is considered as a better compatibilizer compared with PE-g-MA, but it could not act as an effective compatibilizer for the PBT/LDPE blend system at low content.

CHAPTER 1

INTRODUCTION

1.1 Background Study

Polymer polyesters such as Polybutylene terephthalate (PBT) and Polyethylene terephthalate (PET) are considered as engineering thermoplastics since these polymers exhibit higher performance properties, environmental resistance as well as thermal stability than commodity thermoplastics. Polyester polymers combine excellent mechanical, electrical and thermal properties with very good chemical resistance and dimensional stability. They also offer low moisture absorption and have good flow properties (Rosalind, 1990).

PBT, which is one of the polyesters, is a conventional semi-crystalline engineering polymer having high degree and rate of crystallization, good chemical resistance, thermal stability and excellent flow properties. PBT was introduced in 1970 and grew rapidly, since it possesses good tensile strength, flexural modulus and dimensional stability, especially in water, and high resistance to hydrocarbons. Because of these characteristics, it was found utility in various high-volume automotive, electrical, and other engineering applications (Kang et al., 1997).

However, PBT suffers from low impact strength, and there have been many experimental studies on the improvement of this property by blending of PBT with other rubber-like polymers such as styrene-acrylonitrile (SAN) grafted ethylene propylene diene rubber (EPDM-g-SAN) (Wefer, 1984), low linear density polyethylene (LLDPE) (Kang, 1999) and ethylene propylene rubber (EPR) (Laurienzo et al., 1989) which possess high impact strength properties. Polymer blends is a mixture of two or more polymers that have been blended together to create a new material with properties (physical or mechanical) which are different from pure components (Paul, 1989).

Blending of PBT with other thermoplastics for example, low density polyethylene (LDPE) is very interesting. This might act as a way to meet new market applications with minimum development cost. Blends of thermoplastic polyesters and polyolefins are considered as one of important groups of polymer blends. There are a few of commercially available applications of polyester/polyolefins blends such as PET/HDPE blends in food packaging film (Bower et al., 1993) and PET/PP blends in carpet manufacturing (Heino et al., 1997).

Polymer blend systems in the presence of polyalkyl terephthalates and polyolefins without compatibilizer are considered to be immiscible and incompatible (Tsai & Chai, 1996). Because of that, PBT/LDPE blend system is characterized to have poor mechanical properties due to the formation of gross phase separation between components. Therefore, compatibilization is needed in order to improve the compatibility and miscibility of the PBT/LDPE blend system. Various compatibilization methods have been used to achieve the objective such as by using reactive compatibilizer and non-reactive compatibilizer. It should be noted that a compatibilization method might be good in one system and could be ineffective in another system.

As polyolefins do not contain reactive functionality, adding functionalized copolymers that are miscible with polyolefins is an effective approach for reactive compatibilization of polyolefin blends with other polymers. A few studies reported the use of reactive compatibilizer in the polymer blends. Tsai and Chang (1996) studied on the polymer blends of PBT/PP compatibilized by ethylene-co-glycidyl methacrylate (EGMA) copolymers. They reported on the improvement in the mechanical properties. In other study, Pawlak et al (2002) studied the compatibilization of recycled HDPE/PET blends. They reported that the elongation at break and impact strength of recycled HDPE/PET blends increased with addition of EGMA or maleic anhydride grafted styrene-ethylene butylene-styrene (SEBS-g-MA).

1.2 Problem Statement

Blending two or more polymers to obtain polymer alloys has become one of the main methods for tailoring mechanical properties and other properties of polymeric materials. Because of thermodynamic immiscibility, polymer blends often represent a two-phase morphology that depends on the compositions, process parameters, intrinsic properties and interfacial properties of the component polymers. For a fine and stable morphology for immiscible polymer blends, compatibilization is usually needed.

PBT/LDPE blends might offers advantages in term of improving impact toughness of PBT. However, blending of these polymers is quite challenging since the blends are characterized to have weak interfacial adhesion as both of the polymer components are immiscible and usually resulted in poor mechanical properties. So, in order to improve the miscibility of PBT/LDPE blend system, usually a compatibilizer is added. The most promising way to achieve PBT/LDPE blends with good properties is by the addition of a compatibilizer with reactive groups for example an epoxy, maleic anhydride (MA), or acrylic acid functional group.

In this work, the effects of polyethylene grafted maleic anyhydride (PE-g-MA) and poly (ethylene-co-methyl acrylate-co-glycidyl methacrylate) EMAGMA as compatibilizers on the morphology, thermal and mechanical properties of PBT/LDPE blends are investigated. The properties of different compositions of PBT/LDPE blends and different amount of the two compatibilizers on the morphological and mechanical properties of PBT/LDPE blend also are determined.

1.3 Research Objective

The main aim of this study is to investigate the effects of two different types of compatibilizers on the properties of PBT/LDPE blends system. The objectives of the research are as follow:

1. To investigate the effect of various compositions of PBT/LDPE blends on the morphology, thermal and mechanical properties of PBT/LDPE blends.
2. To study the effect of different amounts of EMAGMA as compatibilizer on the morphology, thermal and mechanical properties of PBT/LDPE blends.
3. To determine the effect of different amounts of PE-g-MA as compatibilizer on the morphology, thermal and mechanical properties of PBT/LDPE blends.

In order to achieve the objectives, the effect of various composition of PBT/LDPE blends on the morphology, thermal and mechanical properties of PBT/LDPE blends was investigated. The blends were prepared by using single screw extruder. Then, tensile testing, impact test, thermal and morphology analysis were done in order to determine the best PBT/LDPE blend composition for further study in incorporated with compatibilizer which are poly (ethylene-co-methyl acrylate-co-glycidyl methacrylate) (EMAGMA) and polyethylene grafted with maleic anhydride (PE-g-MA) compatibilizer. The compatibilized blend samples were again prepared by using the same equipment and methods. Also, the same testing were done in order to determine the effect of different amounts of both compatibilizers on the morphology, thermal and mechanical properties of PBT/LDPE blends.

1.4 Scope of Research Study

Chapter 1 consists of a brief introduction of the whole research project. It covers the background study, problem statements, research objectives and scope of this research study.

Chapter 2 gives out on the literature review of this research study. It discusses on the general point of the polymer blend, miscible/immiscible blend, polyolefin/polyester blend system and compatibilization of the polymer blend.

Chapter 3 provides information about the materials and the experimental methods that were used during this project. It also describes testing methods conducted on the samples namely tensile, impact, thermal analysis and morphological analysis.

Chapter 4 presents the experimental result and discussion. It describes the effect of variation in the composition of the blends and also the effect of different amount of EMAGMA and PE-g-MA compatibilizers on the mechanical, thermal and morphology properties of the PBT/LDPE blends.

Chapter 5 covers the conclusion of this research work and also recommendation for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Polymers

The usage of the polymers has completely revolutionized the daily life and the industrial scenario in the plastic buckets, cups and saucers, children's toys, packaging bags, synthetic clothing materials, electrical insulating materials and machine parts manufacturing. Indeed, the polymers are the backbone of some major industries. The word 'polymer' comes from two Greek words which are, *poly* means many and *mer* means unit or part. Polymer can be defined as very large molecules having high molecular mass and also referred as macromolecules, which are forms by joining of repeating structural unit, known as monomers, and are linked to each other by covalent bonds on a large scale (Ibn Kaseer, 2005).

Polymer, depending on their response to thermal treatment, can be classified as elastomer, thermoset and thermoplastic polymers. Elastomers are rubberlike elastic materials where the polymer chains are random coiled structure, held together by weak intermolecular forces. So, they are highly amorphous polymer. This weak binding force permit the polymer to be stretched. In between the chains, a few 'crosslinks' are introduced, in which, it help the polymer to retract to its original position after the force is released as in vulcanized rubber. Usually, they cannot be melted without degradation of the molecule structure (Bhowmick & Stephen, 2000). Examples of the elastomers are natural rubber (NR) elastomer, butyl rubber (IIR) elastomer and silicon elastomer. Their main applications are, for NR in the large tires and bearings, for IIR in gas retention application such as vacuum seals and membrane, and for silicon elastomer, its application is in electrical insulator.

Meanwhile, thermoset polymers assume a permanent shape or set once cured and cannot be reshaped (Philip, 2006). In thermosetting polymers, the chains are cross-linked. The neighbouring chains are linked together instead of each chain being separate. Thus making it difficult for polymer chains to move past each other, results in hard and rigid polymer. The polymer does not melt or soften upon heating (John & Phil, 2001). Examples of thermoset polymer is epoxy resin and its main application is in the coating and adhesives.

On the other hand, thermoplastic resins consist of macromolecular chains with no crosslinks between the chains. Klein (2011) stated that, macromolecular chains themselves can have statistical oriented side chains or can build statistical distributed crystalline phases. They have the simplest molecular structure, with chemically independent macromolecules. Upon heating, they are softened or melted, then solidified, shaped, welded, and formed when cooled. The heating and cooling of thermoplastics can be repeated without affecting the physical properties, thus allowing reprocessing and recycling (Biron, 2007). Examples of thermoplastics are polyethylene (PE) and polystyrene (PS) which are used in packaging films and food container.

2.2 Polymer Blend

As mentioned earlier, different polymers have different properties and if in polymer blending, the properties might slightly increase. Polymer blending can be defined as a mixture of two or more polymers that have been blended together to create a new material with different physical and mechanical properties. Polymer blend has attracted much attention due to its cost-effective method of developing polymeric materials that have versatility for commercial applications. Besides, the properties of the blends can be employed based on their end use by correct selection of the component polymers (Paul, 1989).

The interest in polymer blend systems as a way to meet new market applications with minimum development cost has rapidly increased particularly over the last decade (Paul & Barlow, 2007) and for the same reasons, the coatings and rubber industries have long blended together different polymers. Usually, the development and commercialization of new polymer needs many years and is also extremely costly. However, by utilizing a polymer blending process, the time to commercialization is often possible to reduce to perhaps two to three years and is also very cheap to operate (Utracki, 2003).

At the same time, the performance capabilities of polymer blends also can be greatly extended by this modern blending technology, increasing market pressure now determines that, polymer blends must perform under some specific conditions, for specific applications. Many plastic manufacturers and compounders are developing new blended products due to they offer a convenient, less expensive alternative to develop a new product (Mark, 1988).

In addition, blending technology also provides opportunities for reuse and recycling of polymer wastes, such as mechanical recycling of carpet results in blends of poly (ethylene terephthalate) (PET) and poly (propylene) (PP) (Heino et al., 1997). There are many advantages from blending technology which are: the opportunity to improve on properties to meet specific customer needs, the capability to reduce material cost with or without little sacrifice in properties, extended service temperature range, light weight, the ability to improve the processability of materials which are otherwise limited in their ability to be transformed into finished products, increased toughening, and also improved barrier property, flame retardant property, impact and environmental stress cracking resistance (Walsh & Rostami, 1985). The biggest advantage of the polymer blend is its significantly improved performance compared to the individual components of the blends.

2.2.1 Miscible and Immiscible Blends

Typically, polymer blends are normally classified into two types which are either homogeneous (miscible) or heterogeneous (immiscible) blends. For example, polystyrene (PS)/poly (phenylene oxide) (PPO) is miscible blends (Paul, 2012), while polypropylene (PP)/poly (ethylene terephthalate) (PET) (Heino, 1997) and polypropylene (PP)/polyamide (PA) are immiscible blends (Thomas et al., 2015).

Miscible blends are usually optically transparent and are homogeneous to the polymer segmental level. These blends are represented by the presence of single phase and single glass transition temperature with value in between the individual component (Flory, 1953). Miscible blends results in good properties where their properties are a combination of the properties of pure components. Example of miscible blends is polystyrene (PS)/poly (phenylene oxide) (PPO). This blends had a very good dielectric properties over a wide range of temperature, good dimensional stability and low water absorption (Kramer, 1970).

Conversely, the immiscibility in polymer blends revealed itself as opacity, delamination, double glass transition temperature (Olabis, 2012). The presence of coarse morphology, sharp interface and poor adhesion between the blend phases indicate fully immiscible blends. So, without compatibilization, these blends are of no use. These blends will exhibit different T_g corresponding to the T_g of the component polymers. Example of fully immiscible blends is polyamide (PA)/acrylonitrile butadiene styrene (ABS). After being efficiently compatibilized using suitable compatibilizers, this blend now has become commercially successful (Andrew, 2015).

Most of the polymer pairs are immiscible and have two phase system with large, irregular and unstable domain size, interface is weak and sharp, giving poor properties and practically incompatible. Meanwhile, the partial miscible blends is defined when the two phase system have naturally good properties with practically compatible (Shonaike & Simon, 1999). Example of the partially miscible blends is polyether ether ketone (PEEK) /polyetherimide (PEI) (Yu et al., 1990).

Miscibility or immiscibility of polymer blends are dependent on a number of specific features. These may be listed in order of commercial importance: (Utracki, 1990)

- Polarity

In term of polarity, the polymers that are similar in polarity are less likely to repel each other and more likely to form miscible blends (Gaylord, 1976; Paul, 1978). Meanwhile, diverging polarities generally produce immiscible blends. For example, poly (butylene terephthalate)/low linear density polyethylene blend was classified as an immiscible blend due to difference in polarity between these two polymers, and is characterized by having poor impact properties (Kaci et al., 1999).

- Specific Group Attraction

Polymers that are drawn to each other by hydrogen bonding, acid-base, charge-transfer, ion-dipole, donor-acceptor adducts, or transition metal complexes are less common. They tend to produce miscibility when such attractions occur (Utracki, 1990; Deanin, 1999).

- Molecular weight

Lower molecular weight normally permits greater randomization on mixing and thus greater gain of entropy, which favors miscibility (Markham, 1991). Polymers with similar molecular weight are more miscible, while polymers with different molecular weights may be immiscible, even if both of them have the same composition (Utracki, 1990).

- Ratio

Two polymers appear immiscible at high ratio of both components. However, it is quite possible that a small amount of one polymer may be soluble in a large amount of another polymer, as understood in conventional phase rule. This consideration is extremely important in natural compatibility (Bonner & Hope, 1993).

- Crystallinity

Polymer already forms a two-phase system, with important consequences for practical compatibility when it crystallizes. In a polymer blend, when a polymer crystallizes, this adds another phase to the system whereas if both polymers crystallize, they will usually form two separate crystalline phases. It is quite rare for the two polymers to co-crystallize in a single crystalline phase (Chen & White, 1993).

2.3 Method of Blending

There are various methods to make the polymer blends (Anastasiadis, 1989) such as melt blending, solution blending and etc. Each method has its own advantages and disadvantages:

- Melt blending

Melt blending normally done in an internal mixer or an extruder where the blends can be prepared by melt mixing the ingredients. This method is free from contamination and presence of solvent. The primary disadvantage of melt mixing is the possibility for degradation if the processing temperature is too high and high cost of equipment.

- Solution blending

The simplest mixing method available and widely practiced is the casting blend from a common solvent, in which the component polymers are dissolved in common solvent in this method. In solution blending, there is no chance of degradation like in the melt blending method. However, the incompatible nature of polymers in many of the commonly used solvents is the main limitation of this method. In addition, the analysis result can be affected by the residual solvents and is very difficult to make thick films using this method. Moreover, the waste solvents can cause environmental problems.

- Mill mixing technique

In mill mixing techniques, very small amount of polymer can be mixed in electrically heated two-roll mixing mill. The rheology of the components and the skill of the operator affect the efficiency of a two-roll mixing method which it can vary from good to very poor.

Das and Banerjee (1996) reported that melt blending is the common method, widely practiced in industries and many laboratories and it is also the most widely practiced method in preparation of polymer blend. This is because this method is easy in blending different types of polymers. The polymer blends can be prepared by melt mixing the ingredients in an internal mixer or an extruder either single or twin screw extruder.

Melt blending is normally applied when there are solid pellets or powders with millimeter size range. They are sheared inside using an intensive mixing device such as an extruder or batch mixer. During the initial softening stages, these millimeter size domains melt and break up into micrometer or nano meter sized domains (Macosko et al., 1996).

2.4 Polyolefin/Polyester Blend

Polymer blending of thermoplastic polyesters and polyolefin are considered as one of the important groups of polymer blends. The primary reason for blending polyolefins with polyesters is to combine the high impact strength of the former at low temperature with the solvent resistance and good mechanical properties of the later. Another benefits of polyester/polyolefin blending include good processability and cost reduction (Hwang, 2006; Paul, 2001).

Blends without compatibilizer between polyalkyl terephthalates and polyolefins are considered to be immiscible (Tsai & Chang, 1996). As mentioned earlier, immiscible blends are characterized to have a coarse morphology and poor interfacial adhesion between the blend phases. Therefore, this blend need to be efficiently compatibilized by using suitable compatibilizers in order to improve their properties (Andrew, 2015).

There are a few examples on the polyester/polyolefin blends such as polypropylene (PP)/poly (butylene terephthalate) (PBT) (Tsai & Chang, 1996), and recycled high density polyethylene (rHDPE)/polyethylene terephthalate (PET) (Jarukumjorn & Chareunkvun, 2006).

Tsai and Chang (1996) studied the polymer blends of PBT and PP compatibilized by ethylene-co-glycidyl methacrylate copolymers. They reported that the EG copolymer was an effective in situ reactive compatibilizer for the immiscible and incompatible PBT/PP blends. They also reported that in the morphology study, the interfacial adhesion increased with finer phase domain, thus resulting in better mechanical properties. Meanwhile, Jarukumjorn and Chareunkvun (2006) investigated the compatibilization of rHDPE/PET blends with PE-g-MA. They reported that the mechanical properties of the compatibilized blends improved with an increased in compatibilizer content and the addition of the compatibilizers to the blends reduced the dispersed phase size in the morphology. Therefore, interaction between the matrix and dispersed phase was enhanced.

The issue of compatibilization is critical for polyester/polyolefin blend system for example polybutylene terephthalate (PBT)/polyethylene (PE) blends, since PBT and LDPE are immiscible because of great differences in polarity and chemical structure (Nadkarni & Rath, 2002). This is the case for PBT and LDPE blend that are being characterized to have weak interfacial adhesion due to this polymer blend system are immiscible and have extremely poor mechanical properties. The chemical structure for both PBT and LDPE are shown in Figure 3.1 and Figure 3.2.

2.5 Compatibilization of Polymer Blend

Most of the polymer blends are immiscible, having poor properties and coarse morphology. The driving forces for the phase segregation of blend components are gravity and interfacial tension. The rate of demixing depends on interfacial tension, viscosity and density differences (Utracki, 1997; Thomas, 1998). In order to solve the problems of coarse morphology is, the interfacial tension in the melt need to be reduced and adhesion between the immiscible phases in the solid state need to be enhanced. Therefore, compatibilizers are used to enhance the adhesion between the immiscible blends.

Without compatibilizers, the physical, thermal and mechanical properties of the immiscible blend are poor than the parent polymers in most cases. The immiscible blends are characterized by two phase morphology, narrow interface and poor physical and chemical interactions across the phase boundaries (George, 1995).

Koning (1998) stated that compatibilizers are the macromolecular species exhibiting interfacial activities in heterogenous polymer blends. The chains of a compatibilizer normally have a blocky structure, with one block miscible with one blend component and a second block miscible with another blend component. These blocky structures can be pre-made and added to the immiscible polymer blend, but they also can be generated in-situ during the blending process. The compatibilization process aim to: (i) improve the interfacial tension; (ii) stabilize the morphology against high stresses during forming; and (iii) enhance the adhesion between the phases in the solid state (Utracki, 2002).

Compatibilization process is also very useful in enhancing the dispersity in the polymer blends. It reduces the interfacial tension, enhance adhesion between phases, facilitate dispersion, stabilize the morphology against abusive stresses and strains, and improve the overall mechanical properties of the products (Paul & Vinson, 1972). Hence, Yang (2002) stated that, for a fine and stable morphology for immiscible polymer blends, compatibilization is normally needed.

There are two methods of compatibilization that have found practically application, which are (i) incorporation of a separate chemical compatibilizer into an immiscible polymer blend during melt compounding, such as non-reactive graft or block copolymers (Dhairaya, 2005) and (ii) reactive compounding to form in situ a compatibilizer (Manas, 2008).

2.5.1 Non-reactive Compatibilizer

Non-reactive compatibilizers are normally graft or block copolymers, in which the blocks are chemically similar or even identical to the blend components, therefore, the interfacial adhesion improved by the physical miscibility of the copolymer segments in different blend phases. Then, the interfacial tension will be lower and better in interfacial adhesion and dispersion. The most common type of non-reactive compatibilizers is a copolymer of A and B for a mixture of polyA and polyB. However, other copolymers may be effective if they have specific interactions for example miscible with one or both of the blend components (Cheremisinoff, 1993).

Graft or block copolymers, act as compatibilizers for immiscible blends, can be formed in situ through the chemical bonding either ionic or covalent, during melting processes. There are several examples of non-reactive compatibilizers, which are, ethylene-propylene elastomers (EPR), ethylene-propylene copolymer (EPM), ethylene propylene-diene copolymers (EPDM) and styrene-butadiene-styrene (SBS) block copolymer (Ignazack et al., 2015).

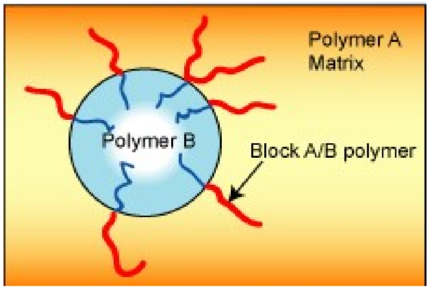


Figure 2.1: Block copolymer (Khorasani et al., 2013)

2.5.2 Reactive Compatibilizer

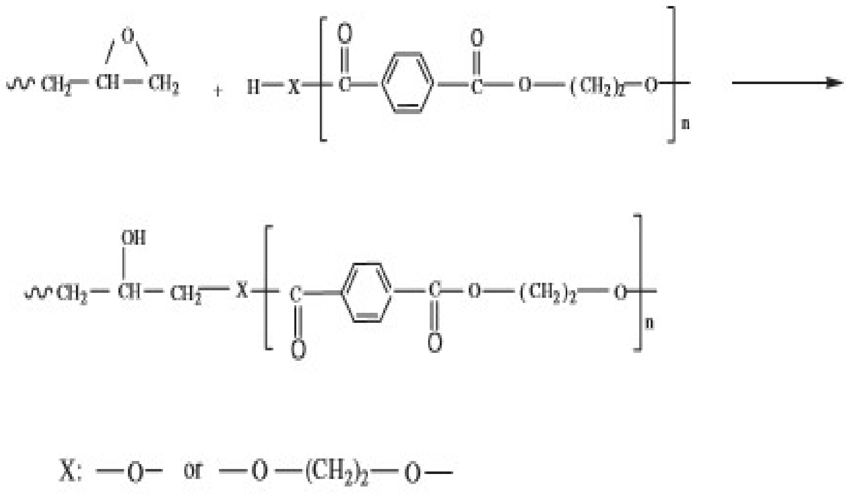
Reactive compatibilizers usually employ a copolymer containing some functional groups that can react with one or more of the blend components, such as anhydrides, methacrylate or acrylic acid. These in situ formed compatibilizers are believed to have an interaction with the blend components and thus reducing the interfacial tension, enhancing the interfacial adhesion, and stabilizing the domain structure.

It is well known that polyesters and polyolefins are immiscible. Since the polyolefins do not have reactive functionality, adding functionalized copolymers that are miscible with polyolefins is such an effective approach for reactive compatibilization process. The commonly used reactive compatibilizers are copolymers functionalized with maleic anhydride (MAH) or glycidyl methacrylate (GMA) (Zhang, 2003; Liu, 1993; Chen, 2008).

Kang et al. (1999) suggested that the addition of ethylene-co-vinyl acetate (EVA) or ethylene-co-vinyl acetate grafted maleic anhydride (EVA-g-MAH) as a compatibilizer to PBT/LLDPE blending systems considerably improved the impact properties. However, more improvement in the mechanical properties in the case of EVA-g-MAH system was observed than in EVA system.

Tsai and Chang (1996) studied the polymer blends of PBT and PP compatibilized by ethylene-co-glycidyl methacrylate copolymers and they reported that the EG copolymer appeared to be an effective in situ reactive compatibilizer for immiscible PBT/PP blends. These in situ formed grafted copolymers reduce the interfacial tension in the melt and result in finer domains. Additionally, higher quantity of EG compatibilizer in the blends contributes in finer phase domains and better mechanical properties.

Other than that, Kaci et al., (2005) investigated the waste and virgin PET/LDPE blends compatibilized with an ethylene-butyl acrylate-co-glycidyl methacrylate (EBAGMA) terpolymer and they reported that the mechanical and morphological properties was improved with addition of EBAGMA compatibilizer. The morphological properties improved with the presence of an improvement in the interfacial adhesion between the PET and LDPE which was probably from the strong chemical interaction between the components, presumably arise from the reaction of the alcohol and ester groups of PET with the epoxy group of glycidyl methacrylate (GMA) of the EBAGMA as shown in scheme 2.1.



Scheme 2.1: Chemical reaction of the glycidyl epoxy groups of the GMA in the EMAGMA terpolymer with PET (Kaci et al., 2005).

In the above-mentioned literature on polyester/polyolefin blends, they were compatibilized by copolymers containing an epoxy or MAH functional group. The best candidates of reactive compatibilizers for polyester-related blends most probably the epoxy-containing copolymers, because the reactions between epoxy and carboxylic acid or hydroxyl groups are well-known chemistry.

Reactive compatibilization is not specifically applicable to all polymer blends, only to those blends having at least one of the blend components contain functional groups that can react with the reactive compatibilizer. Most polyesters essentially contain carboxylic acid and/or hydroxyl terminal groups, making them particularly suitable as one blend component for reactive compatibilization. Based on previous research the most promising way to achieve polyester/polyolefin blends is by the incorporation of a compatibilizer with the reactive groups, e.g., maleic anhydride (MA) or glycidyl methacrylate (GMA).

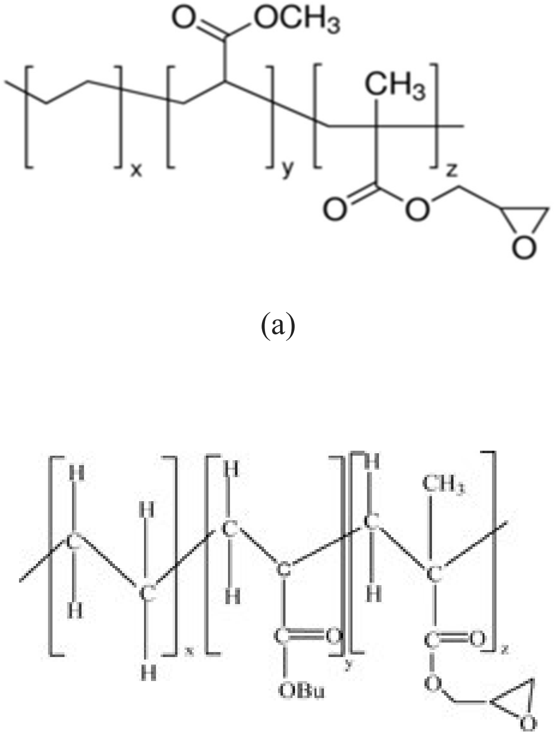
2.6 Type of Compatibilizer Used

2.6.1 Poly (ethylene- co- methyl acrylate-co- glycidyl methacrylate) (EMAGMA)

Several studies have been reported in the literature on the usage of third polymer component to compatibilize polyester and polyolefins blends in order to improve the mechanical properties of the blends. Holsti-Miettinen et al., (1995) used the epoxy functionalized polymer, ethylene/ethyl acrylate/glycidyl methacrylate (GMA), as reactive compatibilizer for PBT/ polypropylene (PP) and liquid crystalline polymer (LCP) /PP blends. Other reactive compatibilizers include Ethylene-Butyl Acrylate-Glicidyl Methylacrylate (E-BA-GMA) terpolymer, which can be used to compatibilize poly (butylene terephthalate) (PBT)-PP, PBT-polyamide (PA), and poly (ethylene terephthalate) (PET)-polyolefin blends. Heat-resistant wire and cable applications are one of the application for these terpolymers. (Markarian, 2004).

A wide range of reactive compatibilizers have been effectively tested, and styrene-butadiene-styrene (SBS) block copolymer is the first successful one was used (Paul & Barlow, 2004). Others compatibilizers that were used in PET/polyolefin blends are ethylene-glycidyl-methacrylate copolymers (GMA) and ethylene/ethyl acrylate glycidyl methacrylate terpolymer (E-EAGMA). Meanwhile, Kaci et al (2005) investigated the effect of the EBAGMA terpolymer on the morphological and mechanical properties in LDPE-PET blends. They reported that the morphological and mechanical properties increased and with addition of the EBAGMA terpolymer compatibilizer.

Poly (Ethylene- co- Methyl Acrylate-co- Glycidyl Methacrylate) (EMAGMA) can be compared with (EBAGMA) since EMAGMA are having almost similar composition with EBAGMA. The chemical structure of EMAGMA and EBAGMA was shown in Figure 2.2 (a) and (b). The usage of EMAGMA as a compatibilizer for the polymer blend system such as polyester/polyolefin blend system are not much done yet in research. So, since, EMAGMA are almost similar with the EBAGMA, it is expected that EMAGMA can act as compatibilizer in the polymer blend system in order to improve the mechanical properties of the blends.



(a)

(b)

Figure 2.2: Chemical structure of (a) Poly (Ethylene- co- Methyl Acrylate-co- Glycidyl Methacrylate) (EMAGMA) (b) Poly (Ethylene-Butyl Acrylate-Glycidyl Methylacrylate) (EBAGMA)

2.6.2 Polyethylene grafted maleic anhydride (PE-g-MA)

One of the most widely used polyolefin polymers is polyethylene (PE) due to it does not have any polar groups in its backbone. Liang et al., (2003) stated that, generally, in order to enhance its miscibility with other polymer components, polyethylene is modified with a polar monomer such as polyethylene-graft-maleic anhydride (PE-g-MAH). Figure 2.3 illustrates the chemical structure of PE-g-MAH.

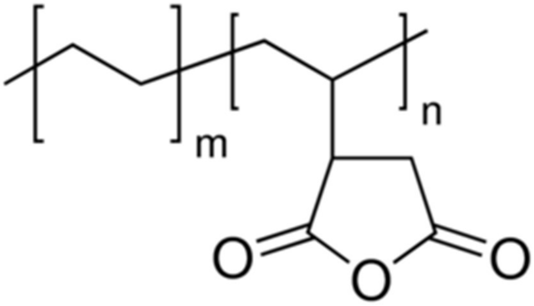


Figure 2.3: Chemical structure of Polyethylene grafted maleic anhydride (PE-g-MA)

Due to low cost of maleic anhydride and high activity of the anhydride group, maleic anhydride (MA) modified polyolefins, including PE, PP, and EPDM, have been one of the most important class of functional polyolefins in industry (Trivedi & Culbertson, 1982). Adhesion, hydrophilicity of the polymer, and compatibility with polar polymers considerably can be improved by MA modified polyolefin. As a results, MA modified polyolefins are used in many commercial applications, such as glass fiber reinforced polyolefins (Garagnai et al., 1982), multilayer sheets of paper for chemical and food packaging (Ashley, 1998) and polymer blends with polyamides and polyesters (Felix et al,. 1991; Paul et al., 1994).

Due to the synthesis of the graft copolymer was easier and cheaper than that of the statistical copolymer, compatibilization with grafted copolymer was considered as an interesting method. Kalfoglou et al. (1995) studied the compatibilizer effectiveness for PET/HDPE blends. They reported that, on the basis of morphological and tensile testing, the best compatibilizing effect was obtained with copolymer containing epoxy functions because they could react with the hydroxyl and carbonyl end groups of PET.

In another study, Lusinchi et al. (2001) studied the in situ compatibilization of HDPE/PET blends. In the molten state, the HDPE-g-MA formed first and then the anhydride groups reacted with the end group of PET. By making a comparison with those blends obtained by adding of graft copolymer to the blends, the one-step processing offered much better results.

Therefore, HDPE/PET blend system can be comparable with PBT/LDPE blend system in this research since both of the systems are polyester/polyolefin blend system. Other than that, the compatibilizer used also can be comparable with PE-g-MA since both of the compatibilizers are maleic anhydride modified polyolefin. Therefore, EMAGMA and PE-g-MAH are used as compatibilizer for PBT/LDPE blend system in this project and being expected to have better result since the chosen compatibilizers are best candidates reactive compatibilizers for polyester-related blends.