STUDY ON COMPATIBILIZATION OF RECYCLED POLYPROPYLENE/ POLYETHYLENE TEREPHTHALATE BLEND FROM COASTAL PLASTIC WASTE USING MALEIC ANHYDRIDE

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ABSTRACT

Increase in human activities due to economic growth caused waste generation rate is continuously rising up every year. Due to lack of responsibility and inefficient waste management, plastic waste has become a major source of environmental pollution and in this attempt, marine pollution is one of the serious problem that occur for the past ten years in which plastics are the main waste that always be found. The recycling of heterogeneous plastic waste gives secondary materials with poor properties because of a scarce compatibility among the polymers present in the waste. Compatibilization of heterogeneous blends is thus a primary aim of the research on recycling. Blends of polyolefin are particularly difficult to design due to the different chemical nature of the two classes of polymers. In this work the goal is achieved by using a commercial maleic anhydride to compatibilist polypropylene (PP) and polyethylene terephthalate (PET) blend from recycled plastic waste. All sample of PP/PET blends were prepared in an twin screw extruder with thermal profile used for all the extrusions was 195-200-205-205-200-195°C and the screws speed was 60 rpm. Blends of recycled PP/PET show a morphology with the large voids, due to a limited adhesion between the two phases, and a brittle behaviour with poor mechanical properties. By using small amounts of compatibilizer, the blend adhere very well in which degree of dispersion and surface adhesion increased and the two phases become almost indistinguishable. in this attempt, addition of 9% by mass of maleic anhydride shows the best morphological properties. TGA study shows that there is no big change in thermal degradation means that compatibilizer does not reduce thermal resistance of the blend. Some mechanical properties are also considerably improved. Tensile strength for addition of 9% by mass of maleic anhydride gives the highest tensile strength in which it surpass tensile strength of homogenous PP and much more closer to virgin PP. Morphology study explaining that why addition of 9% of MA gives the highest tensile strength in comparison to the other samples. It can be concluded that interfacial activity does not require large amount of compatibilizer and it only needed to present in optimum amount in which a few percents would be sufficient to improve the morphology and mechanical properties of the polymeric blends.

ABSTRAK

Pencemaran marin telah menjadi salah satu masalah serius sejak sepuluh tahun lepas di mana plastik merupakan sisa yang banyak ditemui. Mengitar semula sisa plastik berbagai jenis menghasilkan material yang mempunyai ciri- ciri yang lemah kerana ketidakserasian antara polimer- polimer tersebut. Penyesuaian adunan pelbagai jenis polimer menjadi matlamat utama kepada penyelidikan berasaskan kitar semula. Adunan poliolefin sukar untuk direka kerana perbezaan tabiat asas dua polimer dari kelas yang berbeza. Matlamat itu dicapai dalam kertas kerja ini dengan menggunakan maleic anhydride (MA) untuk menserasikan adunan polipropilena (PP) dan polietelena terephthalate (PET) yang merupakan sampah marin yang dikitar semula. Kesemua sampel campuran PP/PET ini disediakan di dalam sebuah twin screw extruder dengan profil termal yang digunakan untuk semua proses extrusi adalah 195-200-205-205-200-195°C dan kelajuan putaran skru tersebut adalah 60 rpm. Adunan PP/PET yang dikitar menunjukkan morfologi dengan lompang yang besar, disebabkan oleh rekatan yang terhad di antara dua fasa, dan tingkah laku rapuh dengan sifat-sifat mekanikal yang lemah. Dengan menggunakan jumlah kecil penserasi, campuran teradun dengan baik di mana tahap penyebaran dan lekatan permukaan meningkat dan kedua-dua fasa menjadi hampir tidak dapat dibezakan. Dalam hal ini, penambahan sebanyak 9% maleic anhydride menunjukkan sifat-sifat morfologi yang terbaik. Kajian TGA menunjukkan bahawa tidak ada perubahan besar dalam degradasi terma bermakna penserasi yang digunakan tidak mengurangkan rintangan terma adunan. Sesetengah sifat mekanikal juga bertambah baik. Kekuatan tegangan untuk penambahan 9% maleic anhydride memberikan tensil yang tertinggi di mana ia melebihi kekuatan tegangan PP homogen dan lebih menghampiri kepada PP. Kajian morfologi menjelaskan mengapa penambahan 9% MA memberikan tensil yang tertinggi berbanding dengan sampel lain. Dapat disimpulkan bahawa aktiviti permukaan tidak memerlukan jumlah besar penserasi dan ia hanya perlu untuk membentangkan dalam jumlah yang optimum di mana beberapa peratus adalah mencukupi untuk memperbaiki morfologi dan sifat mekanikal adunan polimer.

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LIST OF ABBREVIATIONS

UMP	University Malaysia Pahang
MA	Maleic Anhydride
TGA	Thermogravimetic Analysis
PVC	Polyvinyl Chloride
PS	Polystyrene
PET	Polyethylene Terephthalate
PP	Polypropylene
SEM	Scanning Electron Microscopy

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Nowadays, world has come to globalization era thanks to economic development and expansion of population. Increase in human activities caused waste generation rate is continuously rising up every year in which the uncontrollable consumption owing to the increasing population and the attitude towards high living standard (Alan Weisman, 2007). In Asia and the other development country, waste consumption has rapidly increased due to the economic development. In Malaysia for example, over 23,000 tonnes of solid waste is produced each day in Malaysia and this amount is expected to rise to 30,000 tonnes by the year 2020. The amount of waste generated continues to increase due to the increasing population and development. Among of these waste including food, paper and plastic waste in which most of these wastes are plastics which represents 24% from overall wastes (Jamaluddin Md. Jahi and Kadaruddin Aiyub, 1997). Due to lack of responsibility and inefficient waste management, plastic waste has become a major source of environmental pollution as plastic wastes can be found easily everywhere, destroying and polluting environment. Regarding this matter, marine pollution is one of the serious problem that occur for the past ten years in which plastics are the main waste that always be found. Study shows that marine pollution is caused by land-based activities such as factory wastes that being disposed directly into the ocean, rubbish that dropped into the street washes then end up in the ocean and also the tourism activities that involving beaches and islands (Jamaluddin Md. Jahi and Kadaruddin Aiyub, 1997). In this pollution, polypropylene and polyethylene terephthalate both are type of coastal plastic waste that always be found alongside other type of plastic wastes such as polyethylene, polystyrene and polyvinylchloride.

Conventional method for waste disposal nowadays is not practical because plastic is non-biodegradable and need to utilize large space to dispose all of these wastes. In order to encounter this problem, recycle or reused is the best answer in which all this coastal waste will be recycle and reused alongside the origin plastic to produce several of products (Jamaluddin Md. Jahi and Kadaruddin Aiyub, 1997). In polymer industry, continuous research is done in order to reduce production cost for many types of applications by using recycled plastics without reducing desired quality. Previous research shows that coastal plastic wastes, and in this attempt, PP and PET has potential to be recycled because it has better mechanical performance after recycled compare to other plastic wastes at disposal area due to exposure to the sunlight and sea water made it has change in its properties. In this attempt, feasibility to blend the recycled polypropylene with the recycled polyethylene terephthalate to prepare polymeric materials was investigated. Compatibility of these blends may be improved by adding a third compatibilizing component or by adding suitable functionalized polymers capable of enhanced specific interactions and chemical reactions in reactive systems. Regarding to this matter, the use of maleic anhydride as compatibilizer also will be investigated. This is important because compatibilization through a third component, acting as a bridge between the two incompatible phases, becomes necessary to stabilize the blend and to improve its mechanical performance.

1.2 PROBLEM STATEMENT

Polypropylene (PP) and polyethylene terephthalate both are type of polyolefin just like polyethylene (PE), polystyrene (PS), and polyvinyl chloride (PVC) that always be found in coastal wastes. Due to coastal condition such as continuous exposure to the sunlight and presence of sea water, mechanical properties and chemical characterization of these wastes tend to change and make it has differences compare to ordinary wastes. Previous research shows that that PP and PET from coastal wastes that being recycled has the best mechanical properties and chemical characterization compare to the other type of coastal plastic. At the same time, uses of 100% recycled plastics in polymer industry is impossible because of poor performance and does not meet requirement to produce desired product. One of the options that available is the blending of PP from recycled waste with the recycled polyethylene terephthalate. This is because polymer blends offer the possibility to prepare polymeric materials with properties tailored to specific needs.

However, blending may resulting in poor bonding due to instability, immiscible and high interfacial tension. In order to obtain materials stable with good properties, the blends have to be compatibilized. In this case, compatibilization through a third component such as maleic anhydride, acting as a bridge between the two incompatible polyolefin, becomes necessary to stabilize the blend and to improve its mechanical performance. In this work, the properties of polyethylene terephthalate (PET) and polypropylene (PP) blends and PET with functionalized MA blends were investigated including effects of the compatibilization on the structure, rheological, and mechanical properties.

1.3 OBJECTIVE

The ultimate aim for this research is to develop another solution for coastal waste management by discovering potential of recycled polyethylene terephthalate (PET) and recycled polypropylene (PP) blends from coastal waste with improvement on its blends compatibility and mechanical properties using maleic anhydride.

1.4 SCOPE OF WORK

Studies of recycling coastal waste is quiet wide with lots of previous researches that have been done before had discovered many improvements. However, to achieve the objectives that have been stated, the scopes for this research has been specified are:

i. Improving the compatibility of the recycled PET/PP blends from coastal waste using maleic anhydride as the compatibilizer.

ii. Examine the best ratio of blend using different amount of compatibilizer.

iii. Analyse the compatibility of PP/PET blend with and without compatiblizer using morphological study.

iv. Analyse the mechanical performance of compatibilized blend and the original blend using mechanical testing.

v. Compare performance of recycled compatibilized PET/PP blends with the recycled PP and original PP.

1.5 SIGNIFICANT OF STUDY

Through the research, it can contribute another solution for coastal waste management by recycling these waste and reuse for polymeric material preparation. Through the research also, the properties of recycled of PET/PP blends from coastal waste obtained and effect of compatibilizer on the blend properties also would be determined in which it is very useful for further study to improve the polymeric blends in order to develop new applications for recyclable blends containing PET and PP resins with good chemical characteristic, mechanical strength and lower cost that utilize coastal plastics waste as recommended for commercial product.

CHAPTER 2

LITERATURE REVIEW

2.1 Marine Pollution

According to United Nations Environmental Programme (1999), marine pollution defined as “The introduction by man, directly, or indirectly, of substances or energy to the marine environment resulting in deleterious effects such as: hazards to human health, hindrance to marine activities, impairment of the quality of seawater for various uses and reduction of amenities. Marine pollution occurs when harmful, or potentially harmful effects, can result from the entry into the ocean of chemicals, particles, industrial, agricultural and residential waste or the spread of invasive organisms. Most sources of marine pollution are land based. The pollution often comes from nonpoint sources such as agricultural runoff and wind blown debris and dust.

2.2 Coastal plastic waste

Marine debris is mainly discarded human rubbish which floats on, or is suspended in the ocean. Eighty percent of marine debris is plastic which is a component that has been rapidly accumulating since the end of World War II (Alan Weisman, 2007). The mass of plastic in the oceans may be as high as one hundred million metric tons. Discarded plastic bags, six pack rings and other forms of plastic waste which finish up in the ocean are the main contribution to marine pollution and at the same time present dangers to wildlife and fisheries. These wastes may result in harmful effects towards human health, difficulties to marine activities, and also deterioration of the quality of seawater for various uses.

2.21 Characteristic of coastal plastic waste

(Andrady, 1998) stated the characteristics differ due to the nature of the surrounding in which the rate of degradation of plastics waste is influenced by several factors. Firstly, high humidity is known to accelerate the rates of degradation of several classes of plastics (Davis and Sims, 1983). This may be due to the "plasticizing" action of small quantities of sorbed water leading to increased accessibility of the matrix to atmospheric oxygen or by the leaching out of stabilizing additives from the formulation.

Unlike the stack of plastic waste at disposal area, coastal wastes were all the time exposed to sunlight which make it undergo a process which results in the plastic material reaching significantly higher temperatures than the surrounding air or mentioned as “heat build-up” (Summers et al., 1983). The higher temperatures generally result in an acceleration of light-induced degradation and may even be high enough to induce significant thermo oxidative degradation which called as photo degradation.

Besides, waste that exposed to the sea invariably tends to undergo fouling phenomena. (Fischer et al., 1984) explained that in the initial stages of fouling, a biofilm forms on the surface of plastic. Gradual enrichment of the biofilm leads to a rich algal growth within it. Consequently, the biofilm becomes opaque, and the light available to the plastic for photo degradation is restricted. Thus, the rate of photo degradation at sea might be determined in part by the rate of fouling.

2.3 Recycling heterogeneous plastic waste

The recycling of heterogeneous plastic waste gives, in general, a secondary materials with poor properties because of a scarce compatibility among the polymers present in the waste (Oromiehie and Meldrum, 1999). Plastic products have traditionally been synthesised from non-renewable resources such as petroleum or natural gas; recently, biopolymers or polymers from natural renewable resources have emerged as an alternative to synthetic plastics. However, plastic waste should also be considered as a resource for the production of new plastic items, with a similar status to fossil and natural based polymers. To reach this status as a reliable resource for plastic products, the development of a suitable technology for the recycling and upgrading of the properties of the waste materials is needed, to make them suitable for the new applications (Utracki, 1998). Some approaches for effective waste plastics upgrading are discussed here.

Mechanical recycling is usually performed by physical means and involves separation, washing, grinding, re-melting and processing polymeric wastes. Some studies have proposed alternatives such as dissolution/reprecipi-tation procedures for the mechanical recycling of some mixed streams, but this review focuses only on thermoplastic polymers and their common re-melting mechanical recycling approach. Mechanical recycling has been identi-fied as the most suitable recovery routefor relatively clean and heterogeneous plastic waste streams.

2.4 Polymeric blend

Since the beginning of the plastics industry it has been recognized that blending yields materials with property profiles superior to the features of the individual components. The blending of polymers provides a means of producing new materials, which combine the useful properties of all of the constituents (Utracki, 1998). The ability to combine existing polymers into new compositions with commercial utilities offers the advantage of reduced research and development expense compared to the development of new monomers and polymers to yield a similar property profile. An additional advantage is the much lower capital expense involved with scale-up and commercialization. Another specific advantage of polymer blends versus new monomer/polymer compositions is that blends often offer property profile combinations not easily obtained with new polymeric structures. Blending technology is more useful in the field of plastics recycling. It is estimated that about one third of all commercially produced polymer materials are blends of two or more polymers. Polymer blend could be defined as a mixture of at least two macro molecular substances, polymers or copolymers, in which the ingredient content is higher than 2 wt% (Utracki, 1998). Preparation of polymer blends can be done by melt mixing,latex blending, solution blending, partial block or graft polymerization. Melt mixing is the most wide spread method of polymer blend preparation in practice especially for plastics-plastics blends.

2.41 Polypropylene/ Polyethylene terephthalate blends

Among thermoplastic polymer alloys the combination of polypropylene (PP) with polyethylene terephthalate (PET) offers some advantages over the pure components. (C.P. Papadopoulou et al., 1999) carried some experiments to examine the characteristic of mechanical, thermal and morphology of PP/PET blends. They explained that PET may enhance the stiffness of PP at higher temperatures while the polyolefin could facilitate crystallization of PET by heterogeneous nucleation further raising blend stiffness. In addition, the lower permeability of PET towards water vapor and oxygen could be usefully utilized in packaging materials if the morphology of the alloy is optimized.

(Oromiehie and Meldrum, 1999) study characterization of recyled polyethylene terephthalate and functionalized polypropylene blends by different methods. They found that an enhancement in morphology, thermal and mechanical properties were due to interaction and adhesion between the functionalized groups with PET end groups . FTIR Spectroscopy confirmed interaction of PET end groups with functionalized PP by shifts in absorption bands of OH and C=O groups to lower frequencies due to functionalization. Solubility test provided further evidence for improved affinity between the functionalized PP and PET compared with untreated compounds.

The intention to study characterization of PP/PET blend from coastal plastic waste is carried out by (Azimah and S. Zaidi, 2011). In this study, they used recycled polypropylene and recycled polyethylene terephthalate of coastal plastic waste that have been collected from beaches around Pahang State. They examined the mechanical characteristic blend of PP/PET in different composition as listed in **Table 2.1**. They found that blend of 93% of PP with 7% of PET gives the highest tensile strength. It verifies that PET can affect the mechanical properties of heterogeneous plastic recycling if and only if it is present at optimum amount.

Table 2.1: Composition of Heterogeneous Coastal Plastic Waste

Source: Azimah, S. Zaidi, 2011

Specimen	**Volume Composition**		**Maximum Stress (MPa)**	**Maximum Strain (%)**	**Elastic Modulus (MPa)**
	Recycle PET (%)	**Recycle PP (%)**			
1	0	100	34.1136	6.18439	1151.56
2	3	97	29.7062	4.23074	1019.36
3	5	95	29.5891	3.70792	1335.86
4	7	93	30.5398	5.33258	1310.85
5	10	90	29.7047	3.35500	1320.41

2.5 Compatibility of heterogeneous blend

The incompatibility of the PP and PET in heterogeneous recycling as well as their difference in melting points produces the material of poor mechanical properties. High temperature of about 240 °C which is required to process PET cause PP to degrade due to its melting point which is lower than PET (La Mantia, 1993). Such incompatibility of PP and PET and their melting points gap are the factors for heterogeneous plastic recycle easily rupture.

Basically, the incompatible blends are characterized by a two-phase morphology, narrow interphase, poor physical and chemical interactions across the phase boundaries and poor mechanical properties (George et al., 1995). Their overall performance depends on the properties of the individual components, the morphology and the interfacial properties between the phases (Liu and Huang, 2001). Therefore, it is crucial to improve the compatibility of these blends in order to add value for commercial purpose. Compatibilization of heterogenous blends lead to better compatibility and properties.

2.51 Compatibilizer

Many commercial compatibilizers and impact modifiers are available for upgrading mixed waste polymers during mechanical recycling. (F Vilaplana and S Karlsson, 2008) review these compatibilizing additives base their function on physical or chemical effects; non-reactive compatibilizers improve the interfacial adhesion due to good miscibility with both polymers of the blend, whereas reactive compatibilizers have chemical activity and create effective links among the components of the blend through reactive extrusion. Non-reactive compatibilizers are usually graft or block copolymers, in which the blocks are chemically similar or even identical to the blend components to be compatibilized; the interfacial adhesion is therefore improved by the physical miscibility of the copolymer segments in the different blend phases The effect of reducing the interfacial tension and promoting adhesion among the blend components results ina finer phase dispersion morphology and improved mechanical properties. Some non-reactive compatibilisers are ethylene-propylene elastomers (EPR) including ethylene-propylene copolymer (EPM) and ethylene propylene-diene copolymer (EPDM), ethylene-vinyl acetate(EVA), methyl methacrylate-butadiene-styrene copolymer (MBS), and styrene-isoprene-styrene (SIS).

Reactive compatibilizers usually include some functional groups that can react with the components of the blend,such as anhydrides, (meth)acrylates, or acrylic acids. The most common reactive segments used for the synthesis of reactive compatibilisers are maleic anhydride (MA), glycidyl methacrylate (GMA), and acrylic acid (AA); thesefunctional groups may be grafted to non-reactive compatibilizers or even to the real polymeric components of theblend to create reactive compatibilisers such as PP-g-MA, PE- g MA, SEBS- g-MA, EPR-g-MA, PP- g-AA, styrene maleicanhydride (SMA), and ethyleneglycidyl methacrylate (EGMA). **Figure 2.1** shows the chemical structure of the most common functional groups used for reactive compatibilization and reactive extrusion of polymeric wastes.

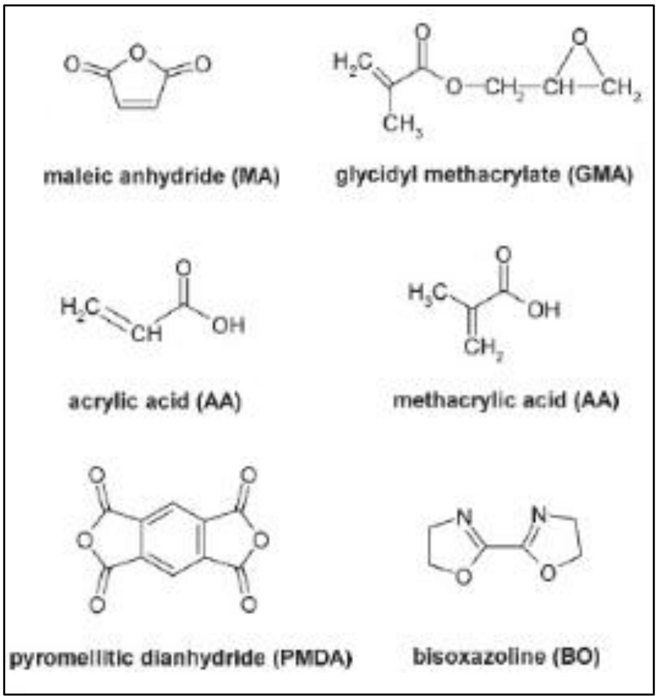

Figure 2.1 Chemical structure of the most common functional groups used for reactive compatibilization

Source: F Vilaplana and S Karlsson, (2008)

2.52 Maleic Anhydride

Maleic anhydride is one the most important class of compatiblizer in commercial applications, due to the unique combination of low cost, high activity, and good processiblity. They are the general choice of material in improving compatibility, adhesion, and paintability of polyolefins.

(B.Ballauri et al., 1998) study compatibilization of recycled polyethylene terephthalate/Polypropylene blends using a functionalized poly(ethylene-butylene) mid-blocks grafted with maleic anhydride, MA-g-SEBS. Two blends were reprocessed, namely PET/PP 1 with equal amounts of the two polymers and PET/PP 2 where the content of PET is two times that of PP. The concentration of MA-g-SEBS ranged from 0 to 12%. By adding a rubber functionalized with maleic anhydride, the morphology and the properties of the blends are strongly modified and the resulting materials show good mechanical properties. In particular, small amounts of this compatibilizer induce a brittle-to-ductile transition with an impressive improvement of some properties, such as, elongation at break and impact strength.

For mechanical mixing for recycled PP/PET blends, maleic anhydride is the most simplest and common compatibilizer to being used to stabilize heterogenous polyolefin blends in which it works as coupling agents, additives, that when added to a blend of immiscible materials during extrusion, modifies their interfacial properties and stabilizes the melt blend.