A STUDY OF COMPATIBILIZATION AND PROPERTIES OF RECYCLED HIGH DENSITY POLYETHYLENE (HDPE)/POLYETHYLENE TEREPHTHALATE (PET) BLENDS

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การศึกษาความเข้ากันได้และสมบัติของพอลิเมอร์ผสมระหว่างพอลิเอทิลีนชนิดความหนาแน่นสูงและพอลิเอทิลีนเทอเรพทาเลทที่ผ่านการใช้งานแล้ว

นางสาวสุกัญญา เจริญขวัญ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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สุกัญญา เจริญขวัญ : การศึกษาความเข้ากันได้และสมบัติของพอลิเมอร์ผสมระหว่าง
พอลิเอทิลีนชนิดความหนาแน่นสูงและพอลิเอทิลีนเทอเรพทาเลทที่ผ่านการใช้งานแล้ว
(A STUDY OF COMPATIBILIZATION AND PROPERTIES OF RECYCLED HIGH
DENSITY POLYETHYLENE (HDPE)/POLYETHYLENE TEREPHTHALATE (PET)
BLENDS) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.กษมา จารุกำจร, 94 หน้า.

จุดประสงค์ของวิทยานิพนธ์นี้เพื่อศึกษาคุณสมบัติของพอลิเมอร์ผสมระหว่างพอลิเอทิลีนชนิดความหนาแน่นสูงและพอลิเอทิลีนเทอเลฟทาเลทที่ผ่านการใช้งานแล้วและวิเคราะห์ว่าพอลิเมอร์ผสมสามารถถูกนำไปใช้แทนไม้เนื้ออ่อนโดยการพิจารณาจากคุณสมบัติเชิงกล สัดส่วนของการผสม ชนิดและปริมาณของสารช่วยให้เข้ากัน และชนิดของสารตัวเติมถูกใช้เป็นปัจจัยหลักในการศึกษาเชิงเปรียบเทียบ พอลิเมอร์ผสมของพอลิเอทิลีนชนิดความหนาแน่นสูงและพอลิเอทิลีนเทอเลฟทาเลทที่อัตราส่วน 80/20, 60/40, 40/60, และ 20/80 %โดยน้ำหนัก โดยถูกเตรียมในเครื่องอัดรีดชนิดแกนคู่หมุนในทิศทางเดียวกัน ชิ้นทดสอบถูกเตรียมโดยใช้เครื่องฉีด คุณสมบัติเชิงกล กระแสวิทยา ความร้อน สัณฐานวิทยา การดูดซึมน้ำ และความหนาแน่นของพอลิเมอร์ผสมเปลี่ยนแปลงตามอัตราส่วนขององค์ประกอบ

ความเข้ากันได้ของพอลิเมอร์ผสมนี้สามารถถูกปรับปรุงโดยการเติมสารช่วยให้เข้ากันคือโคพอลิเมอร์ของพอลิเอทิลีนและมาเลอิคแอนไฮดรายด์ และโคพอลิเมอร์ของพอลิเอทิลีนชนิดความหนาแน่นสูงและไกลซิดิลเมทธาครีเลท ปริมาณสารช่วยให้เข้ากันคือ 2, 4, 6, และ 8 ส่วนในร้อยส่วนของพอลิเมอร์ผสม พอลิเมอร์ผสมที่ถูกปรับปรุงความเข้ากันได้มีขนาดเฟสกระจายเล็กกว่าพอลิเมอร์ผสมที่ไม่ได้ถูกปรับปรุงความเข้ากันได้ การยึดติดระหว่างเฟสต่อเนื่องและเฟสกระจายเพิ่มขึ้นเมื่อมีการเติมสารช่วยให้เข้ากันส่งผลต่อการปรับปรุงคุณสมบัติเชิงกลของพอลิเมอร์ผสม สารช่วยให้เข้ากันไม่เพียงแต่เพิ่มค่าความหนืดของพอลิเมอร์ผสมแต่ยังมีผลกระทบต่อสภาพเป็นผลึกพอลิเมอร์ผสมด้วย นอกจากนี้พบว่าโคพอลิเมอร์ของพอลิเอทิลีนชนิดความหนาแน่นสูงและไกลซิดิลเมทธาครีเลทมีประสิทธิภาพมากกว่าโคพอลิเมอร์ของพอลิเอทิลีนและมาเลอิคแอนไฮดรายด์เนื่องจากมีความว่องไวปฏิกิริยาของหมู่ไกลซิดิลเมทธาครีเลทกับหมู่ที่ปลายของพอลิเอสเทอร์ที่สูงกว่าปริมาณที่เหมาะสมของโคพอลิเมอร์ของพอลิเอทิลีนชนิดความหนาแน่นสูงและไกลซิดิลเมทธาครีเลทและโคพอลิเมอร์ของพอลิเอทิลีนและมาเลอิคแอนไฮดรายด์ สำหรับพอลิเมอร์ผสมของพอลิเอทิลีนชนิดความหนาแน่นสูงและพอลิเอทิลีนเทอเลฟทาเลทที่อัตราส่วนการผสม 20/80 เป็น 2 และ 6 ส่วนในร้อยส่วนของพอลิเมอร์ผสม ตามลำดับ

เส้นใยแก้วชนิดสั้นและแคลเซียมคาร์บอเนตถูกใช้เป็นสารตัวเติมที่ปริมาณ 10 ส่วนในร้อยส่วนของพอลิเมอร์ผสมเพื่อเสริมแรงในพอลิเมอร์ผสม การเติมเส้นใยแก้วชนิดสั้นลงในพอลิเมอร์

ผสมปรับปรุงคุณสมบัติแรงดึง แรงอัด และแรงกระแทก อย่างไรก็ตาม การเติมแคลเซียมคาร์บอเนตลงในพอลิเมอร์ผสมไม่มีผลกระทบทางบวกต่อคุณสมบัติเชิงกลของพอลิเมอร์ผสม ด้วยเหตุนี้สารช่วยให้เข้ากันถูกผสมกับเส้นใยแก้วชนิดสั้นหรือแคลเซียมคาร์บอเนตเพื่อปรับปรุงคุณสมบัติของพอลิเมอร์คอมโพสิท

พอลิเมอร์คอมโพสิทระหว่างพอลิเอทิลีนชนิดความหนาแน่นสูง พอลิเอทิลีนเทอเลฟทาเลทและเส้นใยแก้วชนิดสั้นไม่สามารถใช้แทนไม้เนื้ออ่อนได้โดยตรงเพราะคุณสมบัติเชิงกลบางอย่างต่ำกว่า จากการทดลองพบว่าโมดูลัสของแรงดึงและแรงอัดของพอลิเมอร์คอมโพสิทต่ำกว่าของไม้เนื้ออ่อน ความหนาแน่นสูงกว่าไม้เนื้ออ่อน ถึงแม้ว่ามีความต้านทานแรงดึงและแรงอัดดีกว่าของไม้เนื้ออ่อนก็ตาม เมื่อไม้พลาสติกถูกนำมาใช้โดยเฉพาะการใช้งานแบบรับน้ำหนัก การแอ่นตัวของพลาสติก คุณสมบัติการคืบควรจะถูกชดเชยโดยการพิจารณาพื้นที่หน้าตัดให้ใหญ่ขึ้นหรือมีจุดรองรับที่มีระยะสั้นมากขึ้น

สาขาวิชาวิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา____________________

ปีการศึกษา 2550 ลายมือชื่ออาจารย์ที่ปรึกษา________________

SUKUNYA CHAREUNKVUN : A STUDY OF COMPATIBILIZATION AND
PROPERTIES OF RECYCLED HIGH DENSITY POLYETHYLENE
(HDPE)/POLYETHYLENE TEREPHTHALATE (PET) BLENDS
THESIS ADVISOR : ASST. PROF. KASAMA JARUKUMJORN, Ph.D. 94 PP.

HDPE/PET BLEND, PE-g-MA, HDPE-g-GMA, COMPATIBILIZER, SHORT GLASS FIBER, CALCIUM CARBONATE

This thesis aimed to study the properties of recycled HDPE and PET blends and analyze if the blends could replace the softwood from mechanical properties aspect. Blend compositions, compatibilizer types and contents, and filler types were used as main parameters in the comparative study. The blends of HDPE/PET at various compositions of 80/20, 60/40, 40/60, and 20/80 wt% were prepared in a co-rotating twin screw extruder. The specimens were molded using injection molding machine. Mechanical, rheological, thermal, morphological properties, water absorption, and density of the blends were varied by the composition ratio.

Compatibility of these blends could be improved by adding the compatibilizers: polyethylene grafted with maleic anhydride (PE-g-MA) and high density polyethylene grafted with glycidyl methacrylate (HDPE-g-GMA). The compatibilizer contents were 2, 4, 6, and 8 phr. The compatibilized blends had a smaller size of dispersed phase than that of the uncompatibilized blends. The adhesion between matrix and dispersed phase was enhanced with addition of the compatibilizers leading to improve the mechanical properties of the blends. The compatibilizers not only increased in the melt viscosity but also affected on the crystallinity of the blends. Moreover, HDPE-g-GMA had been found more effective than PE-g-MA due to its higher reactivity of GMA functionality with polyester terminal groups. The optimum content of HDPE-g-GMA and PE-g-MA for 20/80 HDPE/PET was 2 and 6 phr, respectively.

Short glass fiber and calcium carbonate were used as the fillers at 10 phr content to reinforce the blends. Incorporating the short glass fibers into the blends improved the flexural, compressive, and impact properties. However, adding calcium carbonate into the blends yielded no positive impact on the mechanical properties of the blends. As a result, the compatibilizers were mixed with short glass fiber or calcium carbonate to improve the prosperities of the composites.

HDPE/PET/short glass fiber composites could not directly substitute the soft wood because of some inferior mechanical properties. The experiments showed that their flexural and compressive modulus was lower than that of the soft wood; their densities were however higher than the soft wood, and their flexural and compressive strength were higher than those of soft wood. When plastic lumbers were utilized in as structural elements, the deformation and creep properties should be compensated such as by increasing moment of inertia of the cross sections or by reducing the span of the structural elements.

School of Polymer Engineering　　Student’s Signature____________________

Acadamic Year 2007　　Advisor’s Signature____________________

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Sukunya Chareunkvun

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CHAPTER I

INTRODUCTION

1.1 General introduction

Nowadays, plastics are widely used as packaging, furniture, electronic parts, and housewares. This has caused an increasing concern regarding the environment and problem of plastic waste disposal. Alternative methods for handling plastic waste include burial, incineration, depolymerization, and recycling. Plastic recycling is a convenient way to solve the problem of the waste management (Awaja and Pavel, 2005). There are three methods of the plastic recycling: mechanical recycling, feedstock recycling, and energy recovery. The mechanical recycling is easy and straight forward. However, separation of post-consumer mixed plastics into individual plastics is costly and complete sorting is impossible due to the variety of plastic wastes. The development of blending recycled plastic technologies is driven by practical use of unsortable mixtures, development of upgraded products for higher level application, blending the mixtures of recycled to improve product quality, and intentionally mixing recycled plastics to obtain new green products (Markham and Mangraj, 1997). High density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) are the thermoplastics widely used as packaging (bottles, films, etc.) and contribute about 72% of total plastics used in rigid containers (Ernst and Youngs, 1994). These plastics are chosen to study their blend properties since they are major portion of the post-consumer household wastes. In addition, HDPE and PET are easy to separate from the post-consumer household wastes. However, the blends of HDPE and PET are immiscible. The immiscible blends form a two-phase system with poor physical and mechanical properties due to weak adhesion at the interface. Compatibilization is generally needed to improve the adhesion and enhance the properties of the polymer blends. The compatibility of these heterogeneous blends can be improved by the addition of compatibilizers (Dimitrova, La Mantia, Pilati, Toselli, Valenza and Visco, 2000; Dagli and Kamdar, 1994).

During the 1990s, a number of technologies emerged to utilize recycled plastics in products design to replace dimensional wood lumber. One prime example of this application was recycled plastic lumber (RPL). The manufacture of RPL from post-consumer was promising as it consumed large quantities of waste plastics (Climenhage, 2003). RPL is a wood-like product made from recycled plastic or recycled plastic mixed with other materials. RPL has many astonishing characteristics that wood lacks. It offers the advantages of being resistant to insects, rot, moisture, many chemicals, and low maintenance materials. It does not need chemical treatments to achieve or maintain their properties. In addition, it has cost effective, high quality, and environmentally performance. However, it has low modulus of elasticity and high levels of creep. Reinforcing materials e.g. glass fibers and wood fibers have been incorporated into the plastic lumber to increase the stiffness of the lumber. Foaming agents, UV stabilizers, and pigments are typically incorporated into the plastic to enhance the appearance or performance of the lumber product (Breslin, Senturk, and Berndt, 1998).

1.2 Research objectives

The main objectives of this study are as below:

(i) To study the physical, mechanical, rheological, thermal, and morphological properties of recycled HDPE/PET blends at various compositions including density, heat distortion temperature, water absorption, tensile properties, flexural properties, impact strength, viscosity, melting temperature, crystallization temperature, crystallinity degree, and morphology.

(ii) To study the effect of compatibilizer types and contents on the physical, thermal, rheological, mechanical, and morphological properties of recycled HDPE/PET blends.

(iii) To study the effect of fillers on the physical, thermal, rheological, mechanical, and morphological properties of recycled HDPE/PET blends.

(iv) To study the possibility of making the plastic lumber from the recycled HDPE/PET blends.

1.3 Scope and limitation of the study

In this study, the blends of HDPE and PET were investigated. HDPE obtained from drinking water bottles and PET obtained from drinking water and soft drink bottles. The blends of HDPE/PET at various compositions of 80/20, 60/40, 40/60, and 20/80 wt% were prepared in a co-rotating intermeshing twin screw extruder. Polyethylene grafted with maleic anhydride (PE-g-MA) and high density polyethylene grafted with glycidyl methacrylate (HDPE-g-GMA) were used as compatibilizers in the blends. The compatibilizer contents were 2, 4, 6, and 8 phr. The test specimens were prepared by injection molding. The testing properties were density, water absorption, tensile properties, flexural properties, compressive properties, impact strength, rheological properties, thermal properties, and morphological properties. In addition, shot glass fiber (SGF) and calcium carbonate ($CaCO_3$) were use as fillers in these blends. The filler content was fixed at 10 phr. The density and mechanical properties of HDPE/PET blends were investigated and compared with properties of a soft wood.

CHAPTER II

LITERLATURE REVIEW

The main idea of this study is to obtain post-consumed materials with enhanced mechanical properties and at the same time to give them new uses. However, the development of new multiphase blend materials is dependent primarily on the controlling of interfacial chemistry and microstructures. There are several material parameters that could influence morphology: viscosity ratio, composition, elasticity, shear stress, and interfacial modification. The morphology can be improved by controlling these parameters to obtain an increase the mechanical properties. Immiscible polymer blends have large interfacial tension, poor interfacial adhesion, and poor mechanical properties. To enhance these properties, it is necessary to improve adhesion between two phases in the blend (Avila, and Duarte, 2003). The challenge is to develop processes or techniques that allow to control of both the morphology and interfaces of phase-separated blends. Such processes or techniques are called compatibilization. Polymer blends with intentionally modified morphology and interfaces are called compatibilized blends. HDPE and PET contain a major portion of post-consumer waste and are recycled to reduce the waste especially packaging. Blending of these polymers is an alternative method to reduce the waste. However, HDPE and PET are immiscible (Torres, Robin, and Boutevin, 2001). Several studies on the compatibilization of both of virgin and recycled HDPE/PET blends have been reported.

2.1 The study of compatibilization of virgin HDPE/PET blends

During the past decade, several researchers had studied blends of PET and HDPE. Dagli and Kamdar (1994) investigated the effects of component addition protocol on the reactive compatibilization of HDPE/PET blend in a co-rotating intermeshing twin screw extruder. The blend compositions of 80 wt% HDPE and 20 wt% PET with varying amounts (2.5-10 phr) of the functionalized polymers were used. The ethylene-glycidyl methacrylate copolymer (E-GMA) was found to be very effective in compatibilization this blend by forming a compatibilizer in-situ. The changing of the sequence of component addition could have an effect on compatibilization. It was related with the residence time, component viscosity and distribution of functionalized polymer. The best properties were achieved when the reactive polymer was mixed initially with the nonpolar component of the blend that the E-GMA was blended first with HDPE and then with PET. The satisfactory results were also obtained when all components were blended together in the extruder. The initial closer contact of E-GMA (polar) with HDPE (nonpolar) resulted in better compatibilization. During the melting of the HDPE and E-GMA, the E-GMA molecules appeared to orient themselves in a way that favored the copolymer formation right at the interface. Initial close contact of E-GMA (polar) with PET (polar) resulted in a coarser morphology and inferior mechanical properties. During the melting of the PET and E-GMA, the E-GMA-PET copolymer molecule’s remained in the PET phase and it was not able to emerge at the interface. This was reflected in the vastly different morphologies and mechanical properties of the blends using different sequences and modes of component addition.

Jabarin and Bhakkad (1995) studied ternary blends of PET, HDPE, and maleicanhydride grafted polyolefin resin (Mitsui Admer AT 469C). The blend compositions and processing variables were studied. A self-wiping co-rotating twin screw extruder was used for melt blending operations. The blend compositions were used to prepare ternary blends: PET80/HDPE15/Admer5, PET80/HDPE10/Admer10, and PET80/HDPE5/Admer15. Each of the compositions was extruded at screw speed of 100, 200, 300, and 350 rpm. The results indicated that melt viscosities of these ternary blends were dependent upon the blend composition, but independent of the twin screw speed of processing. SEM results indicated that the HDPE and Admer phases had been dispersed in the PET matrix in the form of discrete droplets. The average sizes of the dispersed phase particles decreased with increasing Admer content and screw speed. The improvements in ternary blend impact resistance were observed when Admer concentration and screw speed were increased. The adhesion between the Admer chains and the PET matrix caused a toughening effect in PET led to a decrease in modulus.

Kalfoglou, Skafidas, and Kallitsis (1995) investigated the effect of compatibilizer types on morphological properties and mechanical properties of PET and HDPE blends. The compatibilizers were ethylene-glycidyl methacrylate copolymer (E-GMA), an ethylene ethylacrylate glycidyl methacrylate terpolymer (E-EA-GMA), a hydrogenated styrene butadiene-styrene copolymer grafted with maleic anhydride (SEBS-g-MA), and MA-modified ethylene-methyl acrylate copolymer (E-MeA-g-MA). The blends were prepared in a co-rotating twin screw extruder. The composition of PET/HDPE/compatibilizer was 70/20/10. They had found that the compatibilizing effictiveness decreased in sequence, E-GMA>E-EA-GMA>SEBS-g-

MA>E-MeA-g-MA. The different reactivities of the compatibilizers depended on the type of functionality in the compatibilizers. In the case of GMA-containing compatibilizers, the dispersed phase of HDPE in component was more efficiently stabilized due to high reactivity. GMA might react with both carboxyl and hydroxyl terminal group of the polyester but MA might only react with the hydroxyl moieties and partly so because of the reversibility of the esterification reaction at the high mixing temperatures. The different blend morphologies can be explained the mechanical properties. The ultimate tensile properties and especially energy to tensile failure depended on adhesion between the different phases in the compatibilized blend. The increased ability to disperse in GMA compatibilized ternaries led to an increase interface across which grafting occured. This led to improve tensile properties compared to blends obtained with MA compatibilizers.

Pietrasanta, Robin, Torres, and Boutevin (1999) studied the reactive compatibilization of HDPE/PET blends. The compatibilizers used were E-GMA and E-EA-GMA with variable contents of reactive functions (1 to 8 wt% of glycidyl methacrylate). The blends of HDPE/PET in weight compositions of 80/20, 60/40, 40/60, and 20/80 with or without compatibilizers were studied. All blend compositions with 5 wt% E-EA-GMA were prepared in a co-rotating intermeshing twin screw extruder followed by injection moulding or directly by injection moulding. One stage of processing was sufficient because the extrusion followed by an injection with regard to the injection alone did not improve the Young’s modulus, maximum strength, strength at break, and elongation at break of the blends significantly except for the impact strength of HDPE/PET (80/20) blended with 5 wt% E-EA-GMA prepared by extrusion. The glycidyl methacrylate functionalized polyolefins as reactive compatibilizers in single step was sufficient. Moreover, the rate of shearing brought by the screw of the injection moulding machine was sufficient to ensure a dispersion of the disperse phase and a reduction of the interfacial tension. This study showed the possibility to compatibilize blends of HDPE and PET by injection moulding. This melt processing was interesting in an industrial because it permitted the transformation of a blend of polymers in one step.

Guerrero, Lozano, Gonzalez, and Arroyo (2000) reported the effect of a compatibilizer on the mechanical properties of HDPE/PET blends. The blend of HDPE/PET in weight compositions of 75/25, 50/50, and 25/75 with and without compatibilizers were prepared in an internal mixer. The compatibilizer was a copolymer of ethylene and methacrylic acid partially neutralized with zinc (Surlyn). The olefinic part of Surlyn was compatible with HDPE, whereas the carboxylic end groups would form strong hydrogen bonds with carbonyl group of PET. There was no evidence of adhesion between two phases in the case of uncompatibilized blends. The viscosity of blends with Surlyn had increased. This indicated that there was less slippage at the interface. The addition of 7.5% of Surlyn in PET/HDPE (75/25 wt%) improved the elongation at break from 2.6 to 41.5% which was double of neat PET value. Izod impact strength of the blend also increased due to a high adhesion between two phases.

Kim, Park, Kim, and Suh (2000) studied the compatibilization of HDPE/PET blends. High-density polyethylene grafted with the blocked isocyanate group (HDPE-g-BHI) was used as a reactive compatibilizer for an immiscible HDPE/PET blend. The blend ratios of the HDPE-g-BHI/PET or HDPE/PET were 90/10, 70/30, 50/50, 30/70, and 10/90 by weight. During the melt blending in an internal mixer, the chemical reaction occurred between the isocyanate group and carboxyl or hydroxyl end groups of PET. SEM micrographs of cryogenically fractured surface in HDPE-g-BHI/PET blends exhibited that HDPE-g-BHI/PET blends had a much finer dispersion of the dispersed phase than that of HDPE/PET due to the decrement of the interfacial tension between the continuous and dispersed phases. An in situ-formed graft copolymer reduced interfacial tension and increased interfacial adhesion between the two phases. The tensile strength and elongation at break of reactive compatibilized blends showed higher values than those of uncompatibilized blends. The result was confirmed by dynamic mechanical analysis. The HDPE-g-BHI/PET blends showed a greater storage modulus than that of the HDPE/PET blends at the same composition. This result could be interpreted as due to the formation of an in-situ graft copolymer. DSC results for HDPE/PET and HDPE-g-BHI/PET at the compositions 30/70 and 10/90 blends showed that at the same composition appeared to be little difference in the endothermic heat by PET melting and the exothermic heat by PET crystallization. These results showed that the crystallinity of the continuous PET phase in the HDPE/PET blends remained unchanged regardless of the reactive compatibilization of the blocked isocyanate group grafted onto HDPE.

Lusinchi, Boutevin, Torres, and Robin (2001) studied in situ compatibilization of HDPE/PET (60/40) blends by interfacial grafting of maleic anhydride (MA) without initiator in the molten state. The grafting reaction of MA onto HDPE was carried out in a batch mixer varying reaction parameters of the temperature, roller speed, and time of reaction. In a first step, the reactive copolymer was prepared in situ by grafting MA onto HDPE. In a second step, succinic anhydride reacted with functional end groups of PET. The in situ grafting of MA onto HDPE led to the formation of a compatibilizer at the interface of HDPE/PET blends. This paper showed that interesting grafting yields of 0.3-2.5 wt% were obtained when the grafting of MA onto HDPE in the molten state happened without any free radical initiator. Moreover, there were no crosslinking reactions because they did not use an initiator. So, this processing had more environmental friendly. The addition of a small content MA directly to HDPE/PET blends improved mechanical properties such as strength at break and elongation at break and morphology. The HDPE/PET blends without MA had a coarse morphology with larger domain size in comparison to compatibilized blends. The larger domain size did not appear of adhesion between the matrix and dispersed phase. The compatibilization of the blends with adding MA in one step of processing was an interesting way particularly for recycled blends because this method did not require prior expensive synthesis and led to better results when compared to those obtained by adding of graft copolymers to the blends.

Torres et al., (2001) studied the compatibilization of HDPE-PET (70/30 wt%) blends by adding grafted or statistical copolymers. HDPE was successfully functionalized using a melt free-radical grafting technique. Grafting was initiated in two ways: adding an initiator in the polymer-monomer mixture or activation by ozonization of polymer. The effects of the compatibilizers were obtained by studying the morphology, thermal, and mechanical properties of HDPE/PET blends. It can be seen that statistical copolymer was more effective in compatibilizing HDPE/PET blends than grafted copolymers. Significant improvement of elongation at break and impact strength of compatibilezed blends was found. Ozonization of HDPE by the introduction of a peroxide led to a better grafting yield and a better grafting efficiency of the blends. The morphology, elongation at break and Charpy impact strength of the compatibilized blends were improved. The grafted copolymers formed mainly of HDPE were miscible in the matrix and not located preferably at the interface, unlike the statistical copolymer, which was compatible and placed at the interface. So, the statistical copolymer offered good interfacial adhesion between two phases. However, compatibilization of blends with grafted copolymers was an interesting method because it was easy and cheap in comparison to statistical copolymer. The DSC results could be directly related to the mechanical properties of the blends. The melting temperatures (T_m) of HDPE and PET in the blends with or without compatibilizer were close to those of pure HDPE and PET. The enthalpy of melting (H_m) and the crystallinity degree ($\%X_c$) of HDPE decreased when PET was added to the blends. This tendency was more pronounced when the blends were compatibilized with 5 wt% statistical copolymer or 5 wt% HDPE ozonized-g-GMA. The enthalpy of melting (H_m) of PET increased strongly when HDPE was added to the blends. This incline was more affected when the blends were compatibilized. These results showed that interactions had been created between HDPE and PET in presence of these two compatibilizers.

2.2 The study of compatibilization of recycled HDPE/PET blends

Akkapeddi and Vanbuskirk (1992) investigated the compatibilization of postconsumer PET-polyolefin blends. The various types of polyolefins were polyethylene (HDPE, LDPE, and LLDPE) and polypropylene (PP). The melt blends were prepared in a single screw extruder and a co-rotating twin screw extruder. The E-GMA copolymer was found to be a good compatibilizer for all polyolefin. The reaction between PET and E-GMA led to higher melt viscosity for this binary blend compared to the melt viscosities of all the other component polymers. The content of

E-GMA and the method of mixing need to be controlled when E-GMA was used as a compatibilizing agent in PET-polyolefin blends. Addition of 10% E-GMA in a PET/HDPE (1.8:1) blend significantly improved the toughness and heat resistance. This blend had a PET matrix with HDPE as the dispersed phase. At higher E-GMA levels, the melt viscosity of PET phase containing the PET/E-GMA graft copolymer was higher than of the HDPE phase. This effect resulted in an apparent phase inversion which led to lower vicat softening temperature.

Iniguez, Michel, Gonzalez-Romero, and Gonzalez-Nunez (2000) studied the morphological stability of postconsumer PET/HDPE blends at different composition (10%-90% by volume of PET in HDPE) with and without a compatibilizer. It was shown that the addition of styrene-ethylene/butylenes-styrene (SEBS) triblock copolymer (containing 70 wt% of a random copolymer of hydrogenated ethylene-1 butene, and 30 wt% of styrene) in PET/HDPE blend not only modified its morphology by inducing the formation of a finer dispersion, but also stabilized the morphology. The compatibilized blends showed a little change of a droplet size when they were reprocessed in an internal mixer, compared with the particles size of the mixtures obtained from the twin screw extruder. So, the influence of the reprocessing for compatibilized blends morphology was negligible. For uncompatibilized blends of 10, 20, and 30% by volume of PET, the modulus and tensile strength increased with PET concentration, while the elongation at break decreased. These tendencies coincided with the results obtained by Kim et al (2000). For the case of compatibilized blends, the modulus and the tensile strength did not change. However, the elongation at break increased significantly. When the PET was the dispersed phase, the particle size showed a relatively little increment with PET concentration. However, when the

HDPE was the dispersed phase, the drop sizes were much higher than PET. This could be explained that the viscosity ratio was low (0.25) when PET was the dispersed phase and particle disintegration was the process that govern the particle size blends. At higher viscosity ratios (4.0) when HDPE was the dispersed phase, the droplet breakup process became much slower and consequently started to dominate droplet size. Under such conditions, the droplet size increased with viscosity ratio and changed only slightly with concentration.

Pluta, Bartczak, Pawlak, Galeski, and Pracella (2001) investigated the phase structure and viscoelastic properties of compatibilized blends of recycled PET and HDPE in weight compositions of 75/25 and 25/75. These blends were prepared in a twin screw extruder. They found that compatibilization of both PET-rich and HDPE-rich blends with E-GMA was more effective in relation to the size of dispersed phase than with SEBS-g-MA. The DSC studies showed that addition of the compatibilizer did not substantially change the crystallization behavior of blends. The presence of polyethylene in the blends markedly influenced crystallization of PET component. On the other hand, crystallization of the PE component in the blends was much less influenced by the presence of other blend components than the crystallization of PET. The crystallinity of the PET component in the PET-rich blends decreased stronger than that in the PE-rich blends. This result illustrated that the presence of HDPE in the blends markedly influenced the crystallization behavior of the PET component. The interaction of the compatibilizer with PET component indicated in DMTA data through temperature shift and the intensity change of the PET relaxation process. This effect was much more visible for the PET-rich blends compatibilized with SEBS-g-

MA than those compatibilized with E-GMA. In the case of R-PE-rich blends a similar trend was observed.

Pawlak, Morawiec, Pazzagli, Pracella, and Galeski (2002) studied blends of postconsumer PET and HDPE in weight compositions of 75/25 and 25/75. Three compatibilizers were E-GMA, SEBS-g-MA, and HDPE-g-MA with variable contents (2, 3, 4, 5, and 10 wt%). The melt blends were prepared in a co-rotating twin screw extruder. The uncompatibilized blends were brittle in tensile tests and very low elongation at break. The modified blends with E-GMA or SEBS-MA were ductile. An increasing in the absorbed impact energy in Izod impact tests and the elongation at break were observed. Morphological observations showed a decrease in mean size of compatibilized blends. The applied compatibilizers depressed the interfacial tension in the melt and reacted with PET, led to smaller sizes of the dispersed phase. The increase in viscosity of compatibilized blends was the evidence of reaction during blending. The best results of mechanical and morphological properties were obtained for the 75%/25%/4 pph PET/HDPE/E-GMA and 25%/75%/10 pph PET/HDPE/SEBS-g-MA blends. The HDPE-g-MA was much less effective for systems with PET as the major component, but it was more effective as a compatibilizer for HDPE-rich blends. For the optimum content of the E-GMA compatibilizer for the 75%/25% PET/HDPE system was found to be about 4 pph. A higher content of E-GMA might result in the crosslinking of HDPE and inferior the properties of the blends.

Pracella, Rolla, Choinna, and Galeski (2002) studied the effect of reactive compatibilization on the morphology of recycled PET/HDPE blends in weight 25/75 and 75/25. The compatibilizers used for HDPE/PET blends were high-density polyethylene grafted with maleic anhydride (HDPE-g-MA), ethylene propylene copolymer grafted with maleic anhydride (EPR-g-MA), ethylene glycidyl methacrylate copolymer (E-GMA), ethylene-acrylic acid copolymer (E-AA), and styrene-ethylene/butylenes-styrene block copolymer grafted with maleic anhydride (SEBS-g-MA) at various concentrations (5, 10, and 15 pph). The binary blends of PET with E-GMA showed the highest torque during melt mixing, which was associated to change of melt viscosity and related to the occurrence of interfacial interactions between the carboxyl/hydroxyl end-groups of PET and epoxy functionality of E-GMA. The uncompatibilized blend showed a brittle fracture, without yielding and very low of elongation at break. A large increasing of elongation at break of ternary blends from 110% to about 370%, together with higher stress at break from 19 to 23 MPa were found with increasing the E-GMA content in the range 2-4 pph. The reduction of dispersed particle size in the presence of the compatibilizer related to decrease of interfacial tension and suppress of coalescence which depended on the amount of compatibilizer in the blend.

Aglietto, Coltelli, Savi, Lochiatto, and Ciardelli (2002) studied the post-consumer polyethylene terephthalate (PET)/ very low density polyethylene (VLDPE) blends through reactive processing. The blend was prepared in an internal mixer. The addition of LLDPE with 0.8% mol of MA in VLDPE/PET (70/20) blends is a good way to obtain systems with good morphological properties. The SEM results showed a good improvement of phase adhesion and a clear decreasing of dispersed phase diameter comparing uncompatibilized and compatibilized blends.

2.3 The effect of short glass fiber and calcium carbonate as filler on the properties of polymer blends

An important application of recycled materials is considered to obtain reinforced composites. The incorporation of fillers into thermoplastics has been widely performed in industry to enhance certain properties. Calcium carbonate, wood flour and glass fiber are commonly used to increase the stiffness of recycled plastic. In addition, the effects of carbon fiber, straw, and other plastics have all been studied (George and Dillman, 2000). Reinforcement of polymeric materials by short fibers has grown rapidly. Glass fibers are the most used reinforcing materials in structural reinforced thermoplastics. They have many desirable characteristics such as high tensile strength, high chemical resistance, and excellent insulating properties**.** In the case of calcium carbonate, it is a common practice in the plastics industry to reduce the production costs of molded products (Albano, Gonzalez, Ichazo, Rosales, Urbina de Navarro, and Parra, 2000). Several studies have been reported on the reinforcement of polymer blends by the use of short glass fiber and calcium carbonate.

Joshi, Maiti, and Misra (1992) investigated the thermal and rheological behaviour of short glass fiber reinforced composites based on poly(butylene terephthalate) (PBT)/HDPE blends. The composites were prepared by using a single screw extruder with a screw speed of 10-15 rpm and barrel temperatures ranging from 250-260^{o}C. The PBT/HDPE/ionomer ratio was fixed at 76/19/5. Ionomer was poly(ethylene-co-sodium methacrylate). Short glass fiber (SGF) contents varied from 10-30 wt%. The DSC results indicated that the melting temperature of both PBT and HDPE components did not change significantly on the addition of SGF. It was indicated that there was no change in the crystallite size of PBT in the presence of

SGF due to the very fast crystallizing nature of PBT. The degree of crystallinity was increased with the presence of SGF due to heterogeneous nucleation. The crystallization temperature of the blends containing SGF had shifed to higher values. This result was excepted for the composition without the ionomer. It could be seen that the presence of the SGF facilitated the crystallization of PBT as well as HDPE in the blends. Rheological studies showed an increase in viscosity with incorporation of fibers. However, the addition of SGF resulted in a decrease of the extrudate swell.

McLoughlin, Elliott, and Townsend (1999) studied the compatibilization of PP/PET blends and their composites. PP-g-MA and PP-g-GMA were used as the compatibilizer. The fiber glass had a nominal length of 3.2 mm and was coated with an aminosilane. The blends and composites were prepared by using a co-rotating twin screw extruder. Adding a small content of PET to 30 wt% fiber glass filled PP containing PP-g-MA increased tensile strength and flexural modulus. The addition of PET to glass filled PP could be also reduced glass usage without significant property reduction. Adding either the PP-g-MA or the PP-g-GMA to glass filled PP without PET increased tensile strength, tensile elongation, and Izod impact strength. Moreover, incorporation of PP-g-MA into PP/PET composites presented the greater property enhancements than those the composites containing PP-g-GMA at the same weight percent. This trend was likely to depend on the graft content.

Albano et al. (2000) studied the mechanical and morphological behavior of blends of polypropylene (PP) with virgin and recycled HDPE (80/20 wt%), functionalized and non-functionalized ethylene propylene copolymer (EPR 5 wt%), and calcium carbonate (30%). Coupling titanate agent of 1 wt% was used to treat calcium carbonate. The blends were prepared in a W&P intermeshing co-rotating twin screw extruder. A slight increase in Young's modulus for PP blends with recycled HDPE and HDPE as compared to pure PP could be observed. The elongation at break was decreased due to the poor interfacial adhesion between these polymers. The f-EPR was not effective on tensile and impact properties. The use of nf-EPR was favorable because costs of functionalization were reduced. When HDPE was replaced by recycled HDPE with untreated $CaCO_3$ in PP/HDPE/nf-EPR, the Young's modulus and impact strength were decreased, except for elongation at break was increased. This behavior suggested that recycled HDPE and EPR acted together as a plasticizer in the blends. It was also found that the use of treated $CaCO_3$ did not contribute to obtain better mechanical properties.

Gonzalez, Albano, Ichazo, and Diaz (2002) studied the effects of coupling agents on mechanical and morphological behavior of the PP/HDPE (80/20 wt%) blend with the two different particle size of $CaCO_3$. The coupling agents used were titanates, (Lica 01, Lica 09, Lica 12) and a 1:1 mixture of Lica 12 and Lica 01, and zirconate ZN 12. Lica 12 was used at 0.3, 0.5, 0.7, and 1.0 wt% with respect to the filler and the other coupling agents at 0.3 and 0.7 wt%. The blends were prepared in a Werner and Pfleiderer intermeshing co-rotating twin screw extruder. This study illustrated that the addition of the coupling agent to $CaCO_3$ improved the mechanical properties of PP/HDPE/$CaCO_3$ composites. The value of mechanical properties depended on the particular characteristics of coupling agent. Each one gave rise to increase in a specific mechanical property. In the case of Lica 01, an increase was proved in Young'modulus at 0.7 wt% and elongation at break at both concentration (0.3 and 0.7 wt%), whereas ZN 12 caused an increase in elongation at break. The 1.1 mixture of Lica 12 and Lica 01 resulted in an increase in impact resistance of the PP/HDPE/$CaCO_3$ composite.

Tjong, Xu, Yiu Li, and Mai (2002) investigated the mechanical behavior and fracture toughness of MA compatibilized short glass fiber/SEBS/PP hybrid composites. In this study, MA was either grafted to PP (PP-g-MA) or SEBS copolymer (SEBS-g-MA). The mPP blend was prepared by compounding 95% PP with 5% PP-g-MA. The matrix of hybrid composites consisted of either SEBS/mPP or SEBS-g-MA/mPP. The polymer pellets and shot glass fiber (SGF) were loaded into a Brabender twin-screw extruder with operating temperature profiles of 180-220-220-210^{o}C. The results showed that pure PP exhibited low impact strength of 1.95 kJ/m^2 because it was notch-sensitive under impact loading. Incorporation of PP-g-MA into PP led to a slight decrease in impact toughness. A maximum impact toughness of 23.16 kJ/m^2 was achieved by adding the SEBS into mPP due to adhesion between two phases. It was inefficient to improve the impact strength of the blend via grafting of both PP and SEBS with MA. The tensile results showed that the incorporation of SEBS or SEBS-g-MA in mPP led to a sharp drop in the yield stress and stiffness. Addition of SGF restored the stiffness of these blends. SEM observations revealed that the SGF surfaces of both SGF/SEBS/mPP and SGF/SEBS-g-MA/mPP hybrids were coated with a thin layer of matrix material. This implied that the MA functional group of mPP improved the adhesion between SGF and PP, and between SGF and SEBS.

Gnatowski and Koszkul (2005) investigated the influence of compatibilizer and filler type on the properties of polymer blends. The materials in this study were PA6, PP, polybond3150 (thermoplastic MA), glass fiber, and titanium dioxide (TiO_2). The twin screw THEYSHN TSK 75-N extruder and single-screw extruder had been used to mix the ingredients. The addition of 2% polybond in PA6/PP/TiO_2 composite increased in the tensile strength. Adding 30% of glass fiber to the PA6/PP blend one could obtained higher tensile strength. For the same percentage composition of PA6/PP blends, the addition of TiO_2 caused the increase in the value of hardness. Impact resistance of the PA6/PP and polybond with the addition of 30% of glass fiber was higher than those of the blend without glass fiber. The highest softening temperature had been found for the blend of PA6/PP with 2% polybond.

Malchev, David, Picken, and Gotsis (2005) studied the mechanical properties of short glass fiber reinforced PE/PA6. The mixing was prepared in a Collin single screw extruder with a screw speed of 60 rpm and the barrel temperature of $240^{o}C$. The composites of PE/PA6/SGF at various compositions of 65/25/10, 75/15/10, 85/5/10, 70/15/15, and 80/15/5 were prepared. The addition of minor quantities of a second thermoplastic polymer (PA6) could be improved the mechanical properties of short glass fiber composites (PE/SGF). The modulus of the binary composite (PE/SGF 95/5) was lower than the modulus of the ternary composite (PE/PA6/SGF 80/15/5). The high values of the tensile modulus of ternary composites were measured well above the melting point of the matrix phase. The morphology investigation revealed the existence of a fiber network (PA6/SGF) within the matrix polymer (PE). The network formation process was governed by the wetting of the fiber surface by PA6. The modulus of the composites that had been treated to be compatible with the component (PA6) was an order of magnitude higher than the one of the composites made with matrix compatible glass fibers. The tensile modulus of the composites increased with increasing the amount of short glass fiber in the whole temperatures above the melting point of the minor polymeric phase (PA6).

2.4 Recycled plastic lumber

Recycled plastic lumber (RPL) is a wood-like product made from recycled plastic or recycled plastic mixed with other materials. In early 1970's, plastic lumber processes were developed in Europe, Japan, and U.S. At that time, the materials targeted for processing into plastic lumber consisted solely of post-industrial plastic scrap, which was the only source of low-priced plastic available. The development in the plastic lumber was very rapid during 1990. Since that time, the sale of RPL had grown to capture a significant share of the deck board and deck railing market (Climenhage, 2003). The manufacturing processes that had been developed specifically for processing mixed plastic might be roughly categorized into four basic types: intrusion processes based on Klobbie's design, continuous extrusion, the "Reverzer" process, and compression molding. Each of these processes was capable of producing products from a variety of macroscopically inhomogeneous mixtures of waste plastics. Because of the heterogenous nature of these mixtures, commingled processes were limited to produce products of large cross section. The small internal imperfections might be of little consequence for the mechanical properties. Properties of the products were measured by testing several of the large samples, thereby averaging the effects due to the inclusions upon the bulk material (Lampo and Nosker, 1997).

RPL made from commingled plastics might be contained material inclusions and impurities. It resulted in an open porous structure. For example, a cross-sectional profile of a piece of plastic lumber consisted of 80% HDPE, 4% LDPE, and 4% PP. The remaining 12% was attributable to polyvinylchloride (PVC), polystyrene (PS), PET. The piece was solid around the perimeter of the cross section while the area around the core contained numerous pores of varying size. These voids were believed to be caused by a combination of factors. Wherever the polyethylene phase crystallized significant shrinkage occurred. This was due to the bulky nature of the profiles and low heat transfer of the polymers. The remaining core of molten material turned cool slowly, crystallized, and shrinked. However, because the outer skin had already solidified, the external dimensions of the piece stayed approximately the same. Consequently, internal pores or voids formed. Average variation of density depended on position of the sample taken along the length of the profile (Ehrig, 1992).

RPL products could be worked with conventional carpentry tools and had a number of advantages over wood products. It was unaffected by water, salt water or chlorine, which also mean it never needed to be painted or stained. It came in many natural looking color and blends nicely into the natural environment (Lampo, and Nosker, 1997). Common uses of RPL were in agricultural (e.g. ranch fences, gates), civil engineering (e.g. walkways, railings), marine engineering (e.g. piers, boat docks), recreational (e.g. park benches, picnic tables), and others (e.g. roofing shingles). RPL products were highly attractive and could be manufactured to meet a wide variety of design and appearance specifications when wood or some other natural fiber source was added. Moreover, the addition of additives improved the processabilily and the performance of plastic lumber in service. Foaming agents were used to reduce the weight of products and impart a uniform cell or pore structure. Coupling agents were used to increase tensile strength, flexural strength, and impact strength. Extrusion aids were used to increase the throughput and reduce temperature and also reduce melt fracture. Antioxidants were used to improve thermal stability. The use of UV stabilizers was effective in retaining gloss and color. Flame retardants were required in a window or door casing (Climenhage, 2003).

2.5 Long-term structural properties of the plastic lumber

In service, failures of thermoplastics were commonly attributed to aging of the material in its particular environment, brought about by a combination of the effects of heat, light, water, and mechanical stresses on the material. Water absorption was widely recognized as one of the main causes of long-term failure of materials exposed to the atmosphere or in contact with aqueous media. There were several recognized modes of humid ageing: by reversible phenomenon of the matrix, differential swelling related to concentration gradients, embrittlement linked to the degradation of the macromolecular skeleton by hydrolysis, osmotic cracking, and hygrothermic shock with change of water state (Merdas, Thominette, Tcharkntchi, and Verdu, 2002). Several studies had shown the important effects of absorbed water and ageing temperature on the physical and mechanical properties of materials (Foulc, Bergeret, Ferry, Ienny, and Crespy, 2005). It had been observed that hygrothermal ageing induced the decrease of the mechanical strength of the glass fiber reinforced PET composites. Gel permeation chromatography analysis showed that the chemical degradation step of the composites occurred immediately and that the main degradation mechanism was random chain scission. Hydrolysis generated oligomers that either diffused slowly out of the material and solubilised in the ageing bath or crystallized in the interspeherulitic zone. So, the production of oligomers modified not only the hydrophilicity of PET but also its crystalline morphology, both factors being likely to interfere with the absorption process. In long ageing times, hydrolysis might affect even the crystalline zone of PET since the lamellar thickness decreased. Besides, interfacial debonding induced the formation of cracks or voids that led to an additional uptake of water and the final osmotic cracking responsible for the material fracture.

Pegoretti and Penati (2004) studied the effects of hygrothermal aging at 70^{o}C in water, and at 80% relative humidity on the molar mass and thermal properties of recycled PET and its short glass fiber composites. Chopped strands E-glass fibers type 952 were used as reinforcing agents in percentages of 15 and 30 by weight. All components were mixed in a single screw extruder working at 160 rpm and at temperatures in the range 280-310^{o}C. It was found that during the initial period of exposure, water uptake increased linearly with the square root of time and apparent diffusivity decreased as fiber content increased and as relative humidity decreased. Recycled PET showed a decrease of molar mass during aging with a rate depending on the relative humidity conditions. This result can be explained by considering the fact that water diffused only in the amorphous regions and consequently the crystalline fraction was insensitive to hydrolysis. So, one expect that the residual polymer after completed degradation of the amorphous phase was composed of chains of length equal to the crystalline lamellae thickness. DSC result showed that the temperature of the melting peak of recycled PET and its composites was not affected by the investigated hygrothermal aging. However, the area under the endothermic peak increased steadily during aging for all samples. This indicated the presence of a crystallization process favored by temperature and by the reduction of molar mass.

CHAPTER III

EXPERIMENTAL

3.1 Materials

The materials used in this study were recycled HDPE (drinking water bottles), recycled PET (drinking water and soft drink bottles), high density polyethylene (H6430BM, Thai Polyethylene Co., Ltd.), glycidyl methacrylate monomor (GMA, Fluka), and dicumyl peroxide (DCP, Acros). Copolymer of ethylene with 6 wt% glycidyl methacrylate, IGETABOND 2C supplied from Sumitomo Chemical, Japan was used for calibration of grafting level. Polyethylene grafted with maleic anhydride (PE-g-MA, Fusabond E MB100D, DuPont) was obtained from Chemical Innovation Co., Ltd.

Calcium carbonate ($CaCO_3$, Wittaya Srom Co., Ltd.) with average diameter of 2.05 μm and glass fiber (GF, Saint Gobain Vetrotex Co., Ltd.) were used as reinforcing fillers in the blends. The glass fiber was obtained in roving form and then cut into an approximate length of 4 cm.

3.2 Experimental

3.2.1 Synthesis of HDPE-g-GMA

High density polyethylene grafted with glycidyl methacrylate (HDPE-g-GMA) was prepared by using internal mixer (Hakke Rheomix 3000p) equipped with roller rotors. The composition of HDPE/DCP/GMA was 100/0.6/10 phr. All components were mixed together for 10 min at 180°C with a rotor speed of 60 rpm.

3.2.2 Characterization of HDPE-g-GMA

The grafted polymers were dissolved in a hot xylene and then precipitated by acetone. The homopolymer of GMA remained in acetone. The samples were dried under vacuum at 70°C for 48 hrs. The grafted GMA content of HDPE-g-GMA was determined by Fourier transform infrared spectrophotometer (FTIR, Perkin Elmer). HDPE-g-GMA were made into thin films (100-200 μm) by compression molding at 150°C. The number of scan was 16 at a resolution 4 cm^{-1}. The range of measurement was between 4000 and 600 cm^{-1}. The epoxy group which is characteristic of GMA at 910 cm^{-1} was used to determine the grafting level. An ethylene unit band (CH_2 rocking) at 720 cm^{-1} was used as the internal standard (Jarukumjorn and Min, 2000).

3.2.3 Preparation of HDPE/PET blends

Recycled HDPE and PET were cleaned by water and ground by a mechanical grinder (Retsch grinder machine). The blends of HDPE/PET at various compositions of 80/20, 60/40, 40/60, and 20/80 wt% were investigated. Polyethylene grafted with maleic anhydride (PE-g-MA) and high density polyethylene grafted with glycidyl methacrylate (HDPE-g-GMA) were used to compatibilize the blends. The compatibilizers were added in the HDPE/PET blends at 2, 4, 6, and 8 phr. Before blending, the reground HDPE and PET were dried in an oven at 105°C and 160°C, respectively for 4 hrs. After that, they were tumble blended and fed into a co-rotating intermeshing twin screw extruder (Brabender DSE 35/17D) at barrel temperature of 255-260-265-270°C. The screw speed was 50 rpm. The extrudates were cooled and stranded in a water bath before pelletization. Granulated blends were dried at 105°C for 4 hrs before shaping. The blend specimens for mechanical testing were prepared by injection molding (Chuan Lih Fa, model CLF-80T) at barrel temperature of 240-260-265-270°C, injection speed of 60%, injection pressure of 33%, and holding pressure of 50%. In addition, the blend specimens for compressive testing were prepared by compression molding (Go Tech) at temperature of 280°C.

3.2.4 Preparation of HDPE/PET/filler composites.

All the composites were prepared by the same procedure as the blends. The filler content was 10 phr. Before mixing, the glass fiber and calcium carbonate were dried in an oven at 200°C for 24 hrs. The filler was tumble blended with the other components and incorporated through a feed port located at initial.

3.3 Material characterization

3.3.1 Physical properties

3.3.1.1 Density

The density of PET, HDPE/PET blends, and their composites were determined using a pyknometer with distilled water as a medium while the density of HDPE was determined using Methyl ethyl ketone as a medium (ASTM D792).

3.3.1.2 Water absorption

Water absorption of HDPE, PET, their blends, and composites were performed according to ASTM D570. The samples were immersed in distilled water at room temperature. Five samples were tested in each blend sample.

Percentage increase in weight during immersion is calculated as follows:

$$\text{Increase in weight, \%} \quad = \quad \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \text{ X } 100 \qquad (1)$$

3.3.2 Thermal properties

3.3.2.1 Melting temperature (T_m), crystallization temperature (T_c), and crystallinity degree (%X_c)

Thermal properties of HDPE, PET, their blends, and composites were determined using Differential Scanning Calorimetry (Perkin Elmer Instruments model UNIX DSC-7). The samples were first heated to 280°C, cooled to 40°C, and then re-heated to 280°C under nitrogen atmosphere. The heating and cooling rates were 10°C/min. Melting temperature, crystallization temperature, and crystallinity degree were obtained according to ASTM D3417.

The crystallinity of the sample was calculated by the following equation:

$$\text{Crystallinity degree} \quad = \quad \left(\Delta H_{\text{sample}} / \Delta H_{100\%\text{crystalline}}\right) \text{ X } 100 \qquad (2)$$

where ΔH_{sample} is the heat of fusion of sample (J/g).

$\Delta H_{100\%\text{crystalline}}$ is the heat of fusion of pure crystalline (J/g).

$\Delta H_{100\%\text{crystalline of PET}}$ is 119.8 J/g and $\Delta H_{100\%\text{crystalline of PE}}$ is 293.0 J/g (Wunderlich and Dole, 1957).

3.3.2.2 Heat distortion temperature (HDT)

Heat distortion temperature of HDPE, PET, their blends, and composites were investigated using HDT testing machine (ATLAS, model HDV 1 Manual DTVL/VICAT) at a heating rate of 2°C/min with the standard load of 455 kPa (ASTM D648). Silicone oil was used as heating transfer media. The injected rectangular cross section specimens with 127 mm in length, 13 mm in depth, and 3.5 mm in width were tested. Three specimens were immersed under the calculated loading weight at the assigned standard load. The HDT value was read from the thermometer when the specimen had been deflected to 0.25 mm or 0.01 in.

3.3.3 Rheological properties.

Melt flow index (MFI) of HDPE, PET, their blends, and composites was obtained using a Kayeness melt flow indexer at 270°C with a load cell of 2.16 kg.

Viscosity at various shear rates of HDPE, PET, their blends, and composites was measured using the Kayeness capillary rheometer at 270°C.

3.3.4 Mechanical properties

3.3.4.1 Tensile properties

Tensile properties of HDPE, PET, their blends, and composites were examined using an Instron universal testing machine (model 5565) with a load cell of 5 kN, a crosshead speed of 5 mm/min, and a gauge length of 80 mm. Tensile tests were performed according to ASTM D638. The dimension of dumbbell shaped specimens at 12.7 mm in width at narrow section, 20 mm in overall width, 80 mm in gauge length, 165 mm in overall length, and 3.5 mm in thickness were prepared by injection molding. Five samples were tested in each blend sample.

3.3.4.2 Flexural properties

Flexural properties of HDPE, PET, their blends, and composites were examined according to ASTM D5943 using an Instron universal testing machine (model 5565) with a load cell of 5 kN and a crosshead speed of 5 mm/min. The three points bending test figure was followed to determine the flexural properties. The specimen length was 70 mm and span length was 56 mm. Five samples were tested in each blend sample.

3.3.4.3 Compressive properties

Compressive properties of recycled HDPE/PET blends and composites were examined using an Instron universal testing machine (model 5565) with a load cell of 50 kN, a crosshead speed of 1.27 mm/min. Compressive test was performed according to ASTM D695. The rectangular specimens from compression molding were cut to a width, thickness, and height of 12.7 by 12.7 by 25.4 mm., respectively. Five tests were performed in each blend sample.

3.3.4.4 Izod impact properties

Impact properties of HDPE, PET, their blends, and composites were studied using an Atlas testing machine (model BPI). Impact tests were performed according to notched Izod impact strength (ASTM D256). The total impact energy of 2.7 J was selected. The test specimens with 12.7 mm in thickness, 64 mm in length, and 3.5 mm in width were prepared by injection molding. Ten specimens were tested. The impact resistance was reported as impact strength (J/m^2) that was the failure energy divided by the cross section area of the sample.

3.3.5 Morphological properties

Morphological properties of HDPE/PET blends and composites were examined using a scanning electron microscope (SEM, JEOL model JSM 6400) at 10 kV. The samples were freeze-fractured in liquid nitrogen and coated with gold before analysis.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Analysis of HDPE-g-GMA

Infrared spectrometry is used to determine the grafting level of HDPE-g-GMA. This analysis is performed with a Fourier transform infrared spectrophotometer (FTIR). Mixtures of IGETABOND 2 C and HDPE with different compositions (2, 4, and 6 wt% GMA) are prepared. The infrared spectra of HDPE and HDPE-g-GMA at 2, 4, and 6 wt% of GMA are shown in Figure 4.1. The IR spectra of HDPE-g-GMA show three peaks located at 990 cm^{-1}, 910 cm^{-1}, and 850 cm^{-1} corresponding to the characteristic absorption band of epoxide function (Torres et al., 2000) and three peaks located at 720 cm^{-1}, 1368 cm^{-1}, and 1460 cm^{-1} corresponding to the characteristic absorption bands of polyethylene (Lusinchi et al., 2001). This result confirms that the grafting of GMA onto HDPE has occurred. The intensity of epoxy peak at 910 cm^{-1} increases with increasing the grafting yield of GMA.

In order to determine the grafting level, FTIR calibration curve is constructed. The intensity ratios of epoxy group (910 cm^{-1}) from GMA and CH_2 rocking (720 cm^{-1}) from PE are measured. FTIR calibration curve of HDPE grafted GMA is shown in Figure 4.2. The linear correlation between the intensity ratios and amount of GMA is found. The grafting level of the HDPE/DCP/GMA 100/0.6/10 is 4.16 wt%. HDPE-g-GMA is used as the compatibilizer.

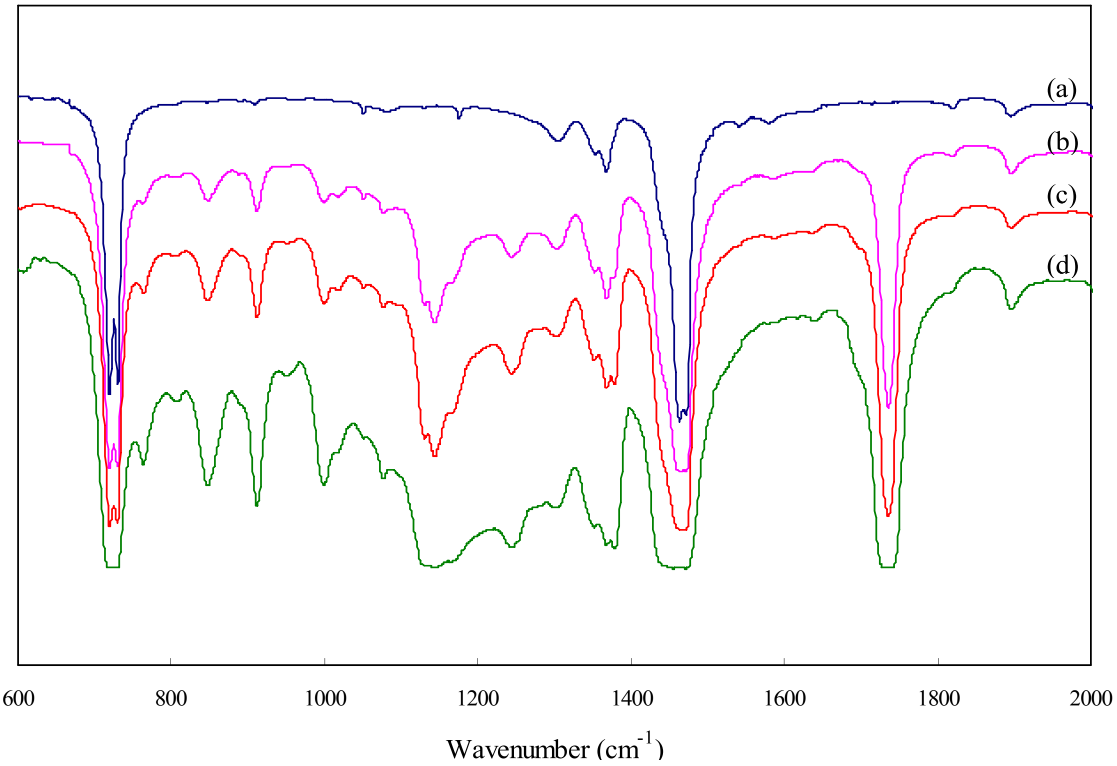


Figure 4.1 The infrared spectra of HDPE and HDPE-g-GMA at varied content of GMA (a) HDPE, (b) HDPE-g-GMA (2 wt%), (c) HDPE-g-GMA (4 wt%), and (d) HDPE-g-GMA (6 wt%)

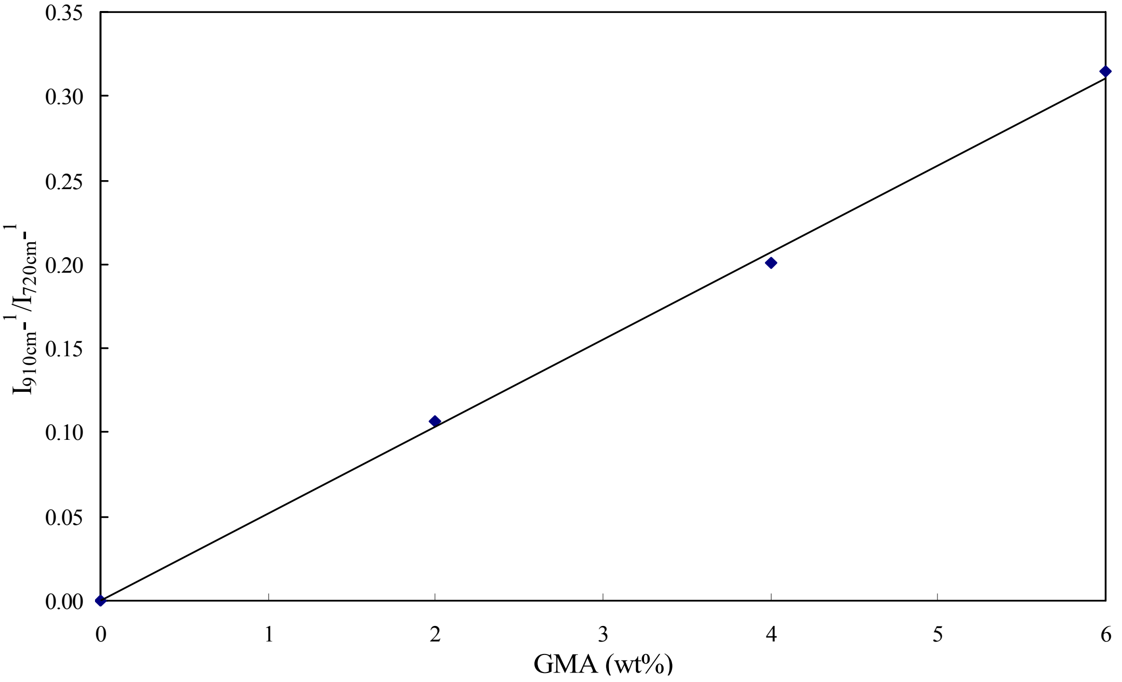


Figure 4.2 Calibration curve for the determination of the grafting yield of GMA onto HDPE by FTIR.

4.2 The effect of blend compositions on properties of HDPE/PET blends

4.2.1 Density

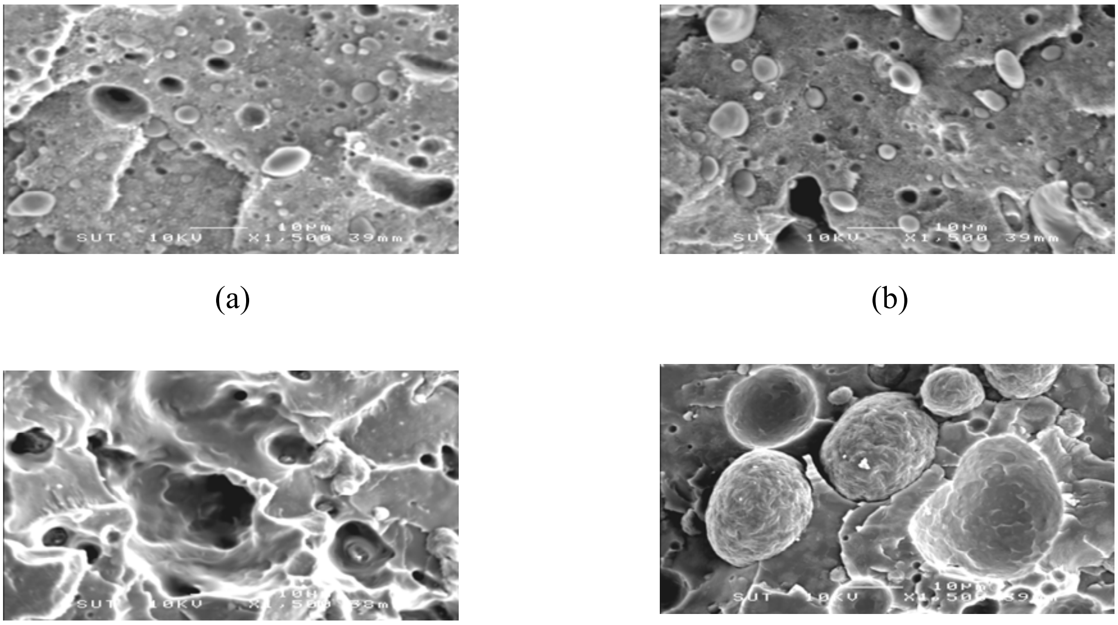
Density of HDPE, PET, and their blends are shown in Table 4.1. Density of HDPE and PET are 0.97 and 1.38 g/cm^3, respectively. Density of HDPE/PET blends increase with increasing PET content in the blends.

Table 4.1 Density of HDPE, PET, and their blends

Composition (wt%)	**Density (g/cm^3)**
HDPE	0.98±0.02
HDPE/PET 80/20	1.10±0.01
HDPE/PET 60/40	1.14±0.02
HDPE/PET 40/60	1.17±0.01
HDPE/PET 20/80	1.19±0.02
PET	1.38±0.01

4.2.2 Morphological properties

SEM micrographs of recycled HDPE/PET blends are shown in Figure 4.3. In case of HDPE-rich blends, the dispersion of the dispersed phase is better than that of PET-rich blends. This may result from that HDPE has higher viscosity than PET during blending. The presence of holes on the matrix formed by the pullout of particles indicates that there is low adhesion between the continuous and the dispersed phases. Iniguez et al. (2000) studied the morphological stability of post consumer HDPE/PET at different compositions. They found that the droplet size increased with viscosity and composition of dispersed phases.



(a) (b)

(c) (d)

Figure 4.3 SEM micrographs of (a) HDPE/PET 80/20, (b) HDPE/PET 60/40, (c) HDPE/PET 40/60, and (d) HDPE/PET 20/80 (x 1500)

4.2.3 Mechanical properties

The effects of PET contents on tensile strength, tensile modulus, tensile strain at break, flexural strength, flexural modulus, and impact strength of HDPE/PET blends are given in Table 4.2. Mechanical properties of the blends depend on blend compositions. Tensile strength, tensile modulus, flexural strength, and flexural modulus of HDPE/PET blends slightly increase with increasing PET contents while tensile strain at break and impact strength of the blends decrease.

Table 4.2 Mechanical properties of HDPE, PET, and their blends

Composition (wt%)	**Tensile**			**Flexural**		**Impact strength (J/m^2)**
	strength (MPa)	**modulus (MPa)**	**strain at break (%)**	**strength (MPa)**	**modulus (MPa)**	
HDPE	18.10±0.12	731.60±29.07	Not broken	24.10±0.52	805.96±30.15	20241.12±25.54
HDPE/PET 80/20	20.37±0.35	872.24±37.25	10.87±1.09	30.02±0.68	945.76±14.39	5763.29±29.91
HDPE/PET 60/40	22.66±1.22	1007.86±23.98	4.04±0.42	35.58±1.14	1211.86±28.40	2928.71±58.64
HDPE/PET 40/60	20.19±0.72	1146.72±18.17	2.44±0.15	31.78±1.74	1427.76±71.62	1685.55±41.22
HDPE/PET 20/80	30.85±0.73	1320.73±53.03	3.46±0.16	54.49±0.47	1872.54±44.90	2578.41±77.12
PET	56.98±1.15	1663.53±26.64	4.42±0.26	89.92±2.38	2789.27±18.60	1435.42±55.47

4.2.4 Rheological properties

Shear viscosities of HDPE, PET, and their blends at 270°C are shown in Figure 4.4. HDPE is the most viscous among the materials. Viscosities of the blends are dependent on the blend compositions. The viscosities of the HDPE/PET blends increase as a decrease of PET contents in the blends. MFI of the blends, as shown in Figure 4.5, decrease with an increase of HDPE contents.

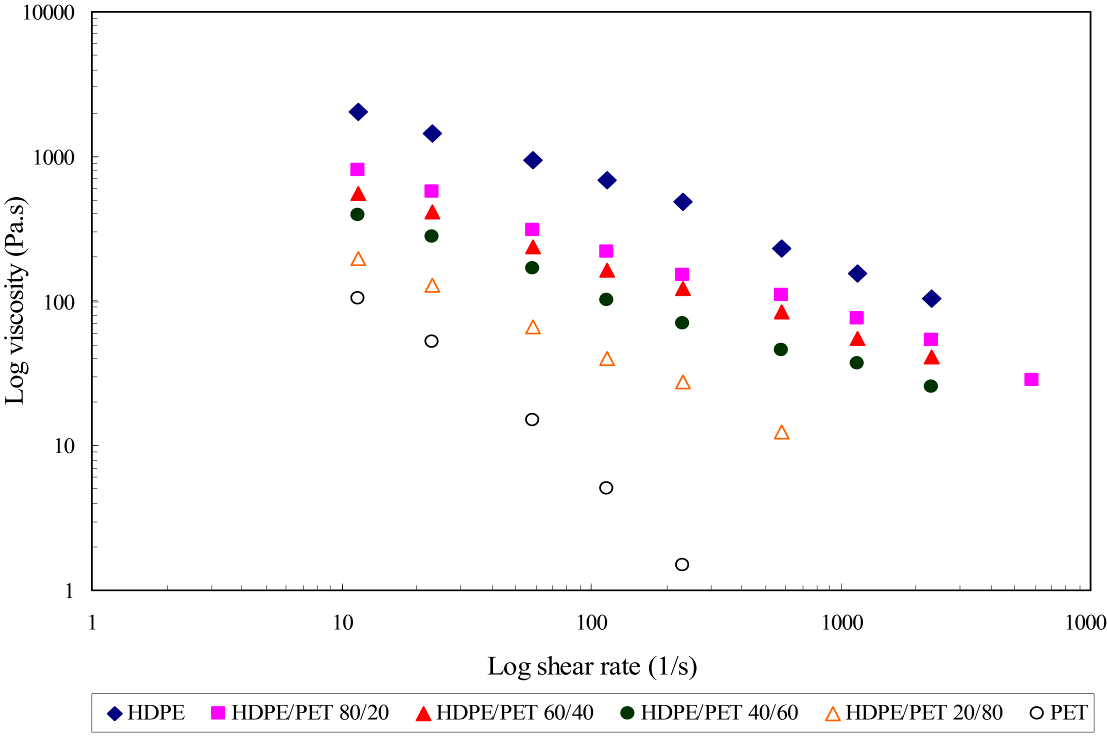


Figure 4.4 Shear viscosities of HDPE, PET, and their blends

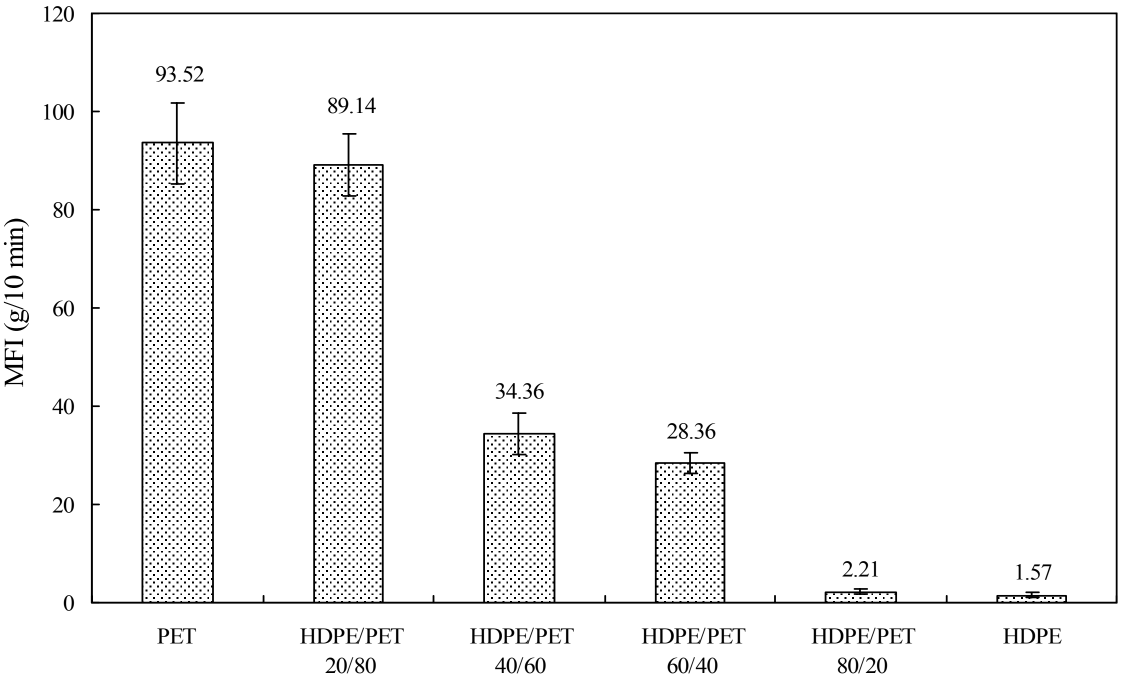


Figure 4.5 MFI of HDPE, PET, and their blends

4.2.5 Thermal properties

DSC curves of HDPE, PET, and their blends at various compositions of 80/20, 60/40, 40/60, and 20/80 wt% from the second heating scan are shown in Figure 4.6. Melting temperatures of HDPE and PET component are detected at 132.35°C and 246.77°C, respectively.

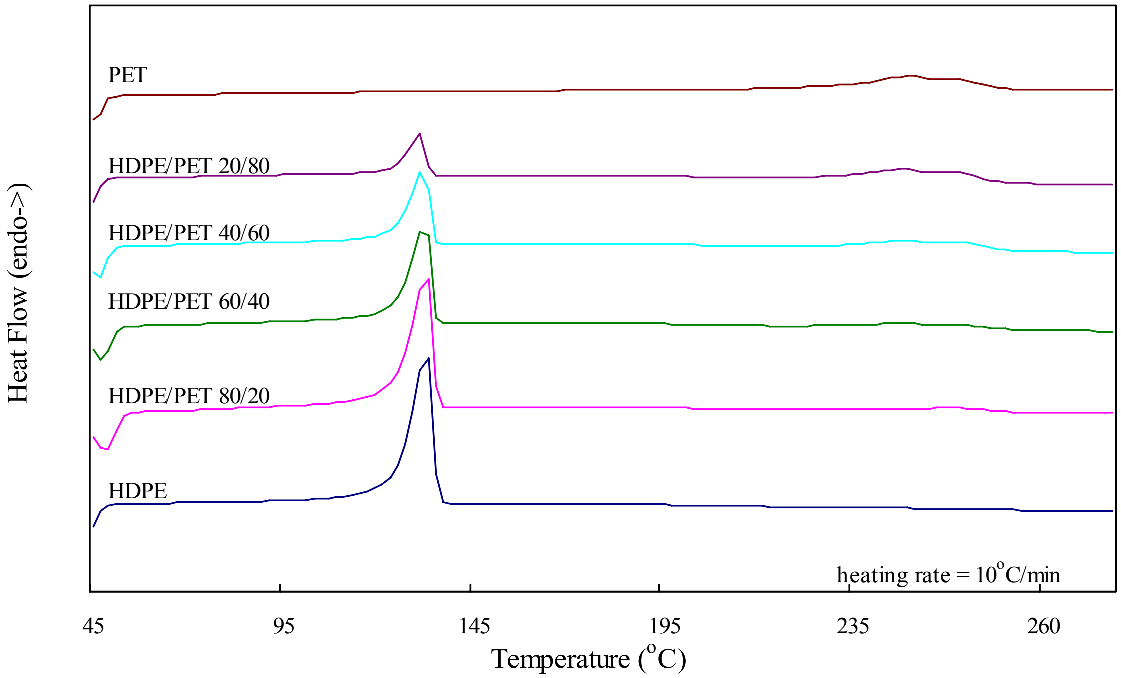


Figure 4.6 DSC curves of HDPE, PET, and their blends

The melting temperature (T_m), crystallization temperature (T_c), enthalpy of melting (ΔH_m) and crystallinity degree ($\%X_c$) of HDPE, PET, and their blends are shown in Table 4.3. The melting temperatures of HDPE and PET component in the blends are closed to those of recycled HDPE and PET. This behavior is normal for immiscible polymer blends in melt state (Wilfong, Hiltner, and Baer, 1986). Similarly, Torres et al. (2000) had studied reactive compatibilization blends of HDPE and PET recyclates. They had found no significant change in the melting temperature of HDPE and PET in the blends. ΔH_m and $\%X_c$ of HDPE component decrease with adding PET to the blends while ΔH_m and $\%X_c$ of PET component decrease with increasing HDPE contents. The above changes demonstrate that the presence of HDPE or PET in the blend markedly influences the crystallization behavior of the PET and HDPE components, respectively. Pluta et al. (2001) also obtained similar results on HDPE/PET blends.

Table 4.3 Calorimetric characterization of HDPE, PET, and their blends

Composition (wt%)	**HDPE component**				**PET component**			
	T_c (^oC)	**T_m (^oC)**	**ΔH_m (J/g)**	**X_c (%)**	**T_c (^oC)**	**T_m (^oC)**	**ΔH_m (J/g)**	**X_c (%)**
HDPE	116.80	132.35	207.84	70.94	-	-	-	-
HDPE/PET 80/20	116.01	132.47	160.06	54.63	-	248.57	4.44	3.71
HDPE/PET 60/40	116.37	131.99	107.31	36.62	198.96	247.99	7.29	6.08
HDPE/PET 40/60	116.49	131.70	67.51	23.04	198.34	248.60	8.38	6.99
HDPE/PET 20/80	116.74	131.10	40.44	13.80	198.84	247.99	18.91	15.78
PET	-	-	-	-	198.41	246.77	23.81	19.87

HDT of HDPE, PET, and their blends are shown in Figure 4.7. HDT of HDPE and PET are 65.3 and 69.3°C, respectively. HDT of HDPE/PET blends slightly increases with increasing PET contents.

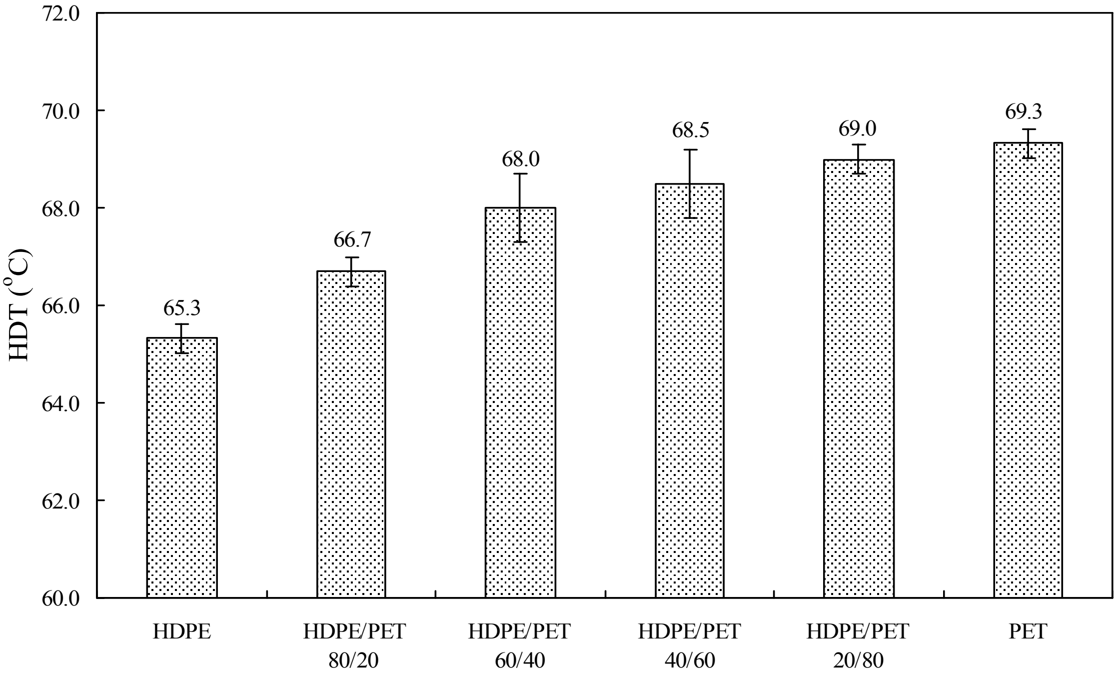


Figure 4.7 HDT of HDPE, PET, and their blends

4.2.6 Water absorption

Relationship between water absorption rate and immersion time of HDPE, PET, and their blends is shown in Figure 4.8. The water absorption rate increases with the immersion time. The water absorption rate of PET is higher than that of HDPE due to the hydrophilic group (ester groups) in PET (Merdas et al., 2002). The water absorption rate of HDPE/PET blends increases with increasing PET contents. After immersion times of 30 days, the water absorption rate of all compositions seem to be constant.

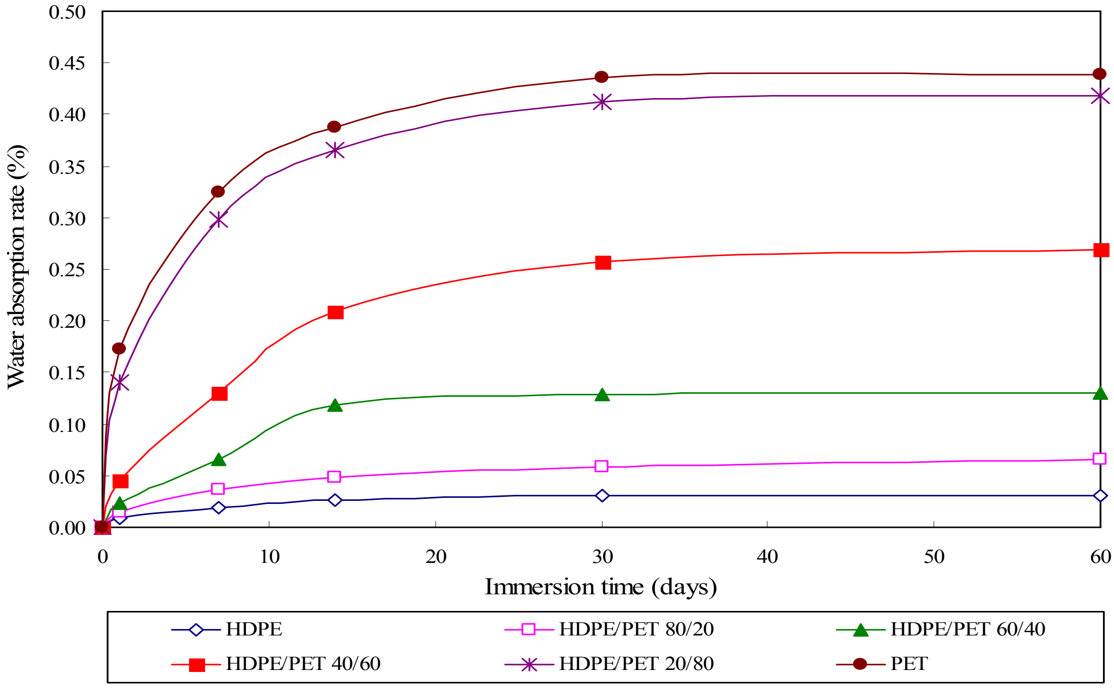


Figure 4.8 Water absorption rate versus immersion time of HDPE, PET, and their blends

The effect of water absorption on the tensile strength of HDPE, PET, and their blends is shown in Figure 4.9. No significant change in the tensile strength of each material after water immersion is found.

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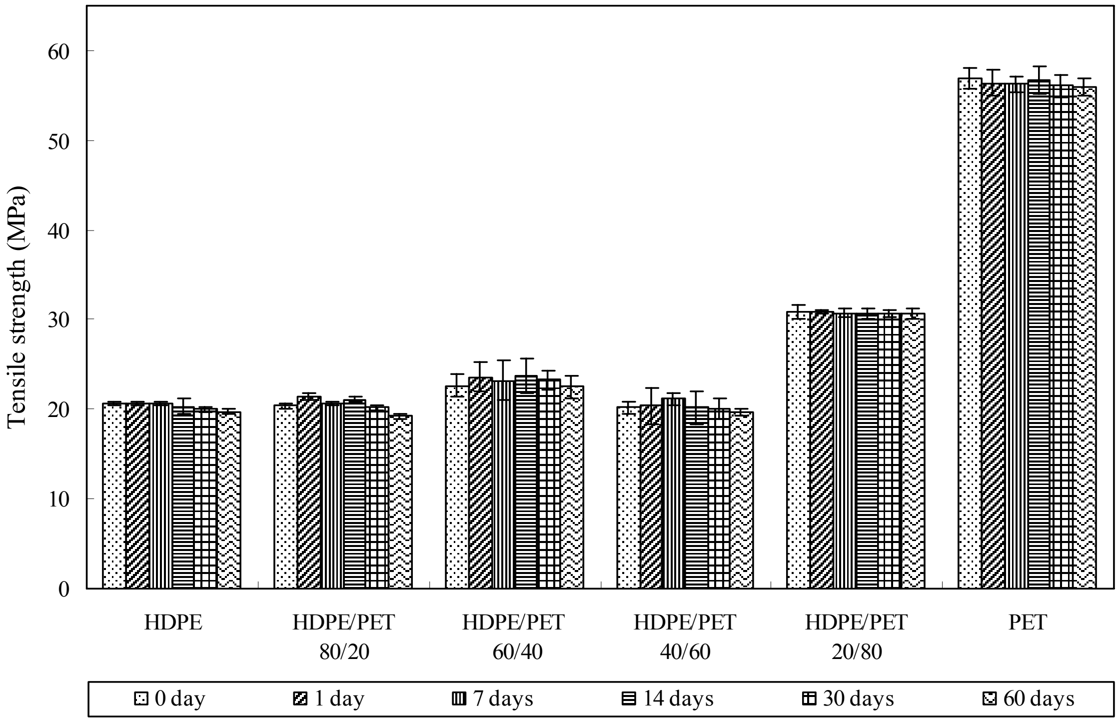


Figure 4.9 Effect of water absorption on tensile strength of HDPE, PET, and their blends

One of the main objectives of this research is to study the possibility of making the plastic lumber from the recycled HDPE/PET blends. Therefore, the blend composition of 20 wt% HDPE and 80 wt% PET is chosen to further study due to their suitable mechanical properties compared with soft wood. In order to enhance the mechanical properties of the blends, the effect of adding compatibilizers and fillers on the properties of the blends is investigated.

4.3 The effect of compatibilizer types and contents on properties of HDPE/PET blends

4.3.1 Density

The blend compositions of 80 wt% PET and 20 wt% HDPE with 2, 4, 6, and 8 phr of PE-g-MA and HDPE-g-GMA are investigated. Density of the uncompatibilized and compatibilized blends is shown in Table 4.4. Density of the HDPE/PET blends is increased with the addition of the compatibilizers. Compatibilizer contents insignificantly affect on the density of the blends.

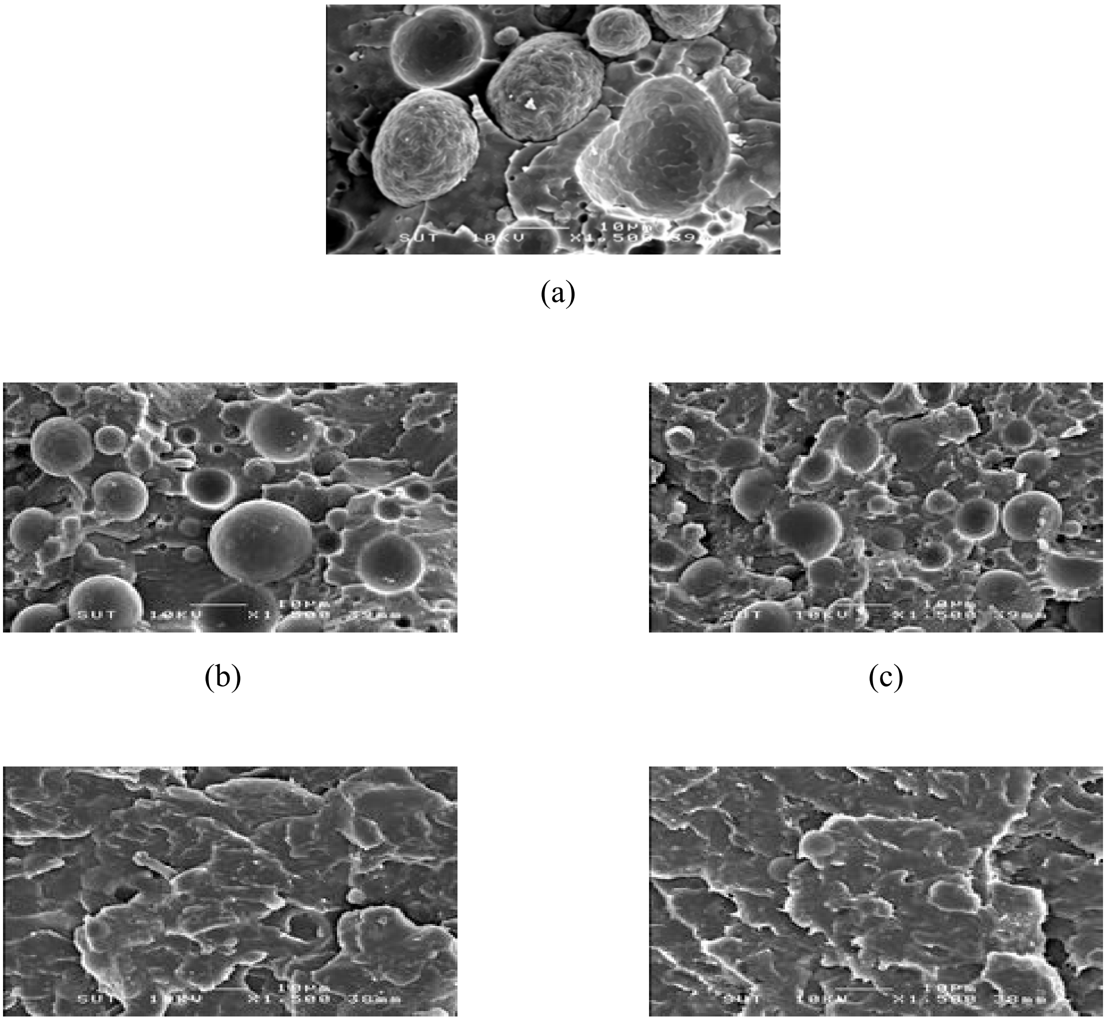
Table 4.4 The effect of compatibilizer types and contents on the density of HDPE/PET blends (20/80 wt%)

Composition (wt%)	Density (g/cm^3)	Composition (wt%)	Density (g/cm^3)
HDPE/PET 20/80	1.19±0.02	HDPE/PET 20/80	1.19±0.02
HDPE/PET/PE-g-MA 20/80/2	1.25±0.01	HDPE/PET/HDPE-g-GMA 20/80/2	1.29±0.00
HDPE/PET/PE-g-MA 20/80/4	1.25±0.01	HDPE/PET/HDPE-g-GMA 20/80/4	1.28±0.01
HDPE/PET/PE-g-MA 20/80/6	1.24±0.01	HDPE/PET/HDPE-g-GMA 20/80/6	1.28±0.01
HDPE/PET/PE-g-MA 20/80/8	1.24±0.01	HDPE/PET/HDPE-g-GMA 20/80/8	1.27±0.01

4.3.2 Morphological properties

Morphologies of the uncompatibilized and compatibilized blends are shown in Figure 4.10. The uncompatibilized HDPE/PET blend shows a coarse morphology with larger domain size in comparison to the compatibilized blends. The larger particle size does not show an adhesion between the matrix and dispersed phase.

This is confirmed the incompatibility of the two components. The compatibilizer controls the morphology of blends by preventing of coalescene and reduction of the interfacial tension. The dispersed phase sizes depend on the compatibilizer content. The improvement in the interfacial adhesion and reduction in the size of the dispersed phase with increasing the compatibilizer content are observed. In case of the HDPE-g-GMA compatibilized blends, a dispersion of the dispersed phase is better than that of the PE-g-MA compatibilized blends. In addition, the particle size of the dispersed phase of the HDPE-g-GMA compatibilized blends is smaller and the interfacial adhesion appears to be stronger than that of PE-g-MA compatibilized blends. This result might due to high reactivity between GMA and PET chain ends (Kalfoglou et al., 1995).



(a)

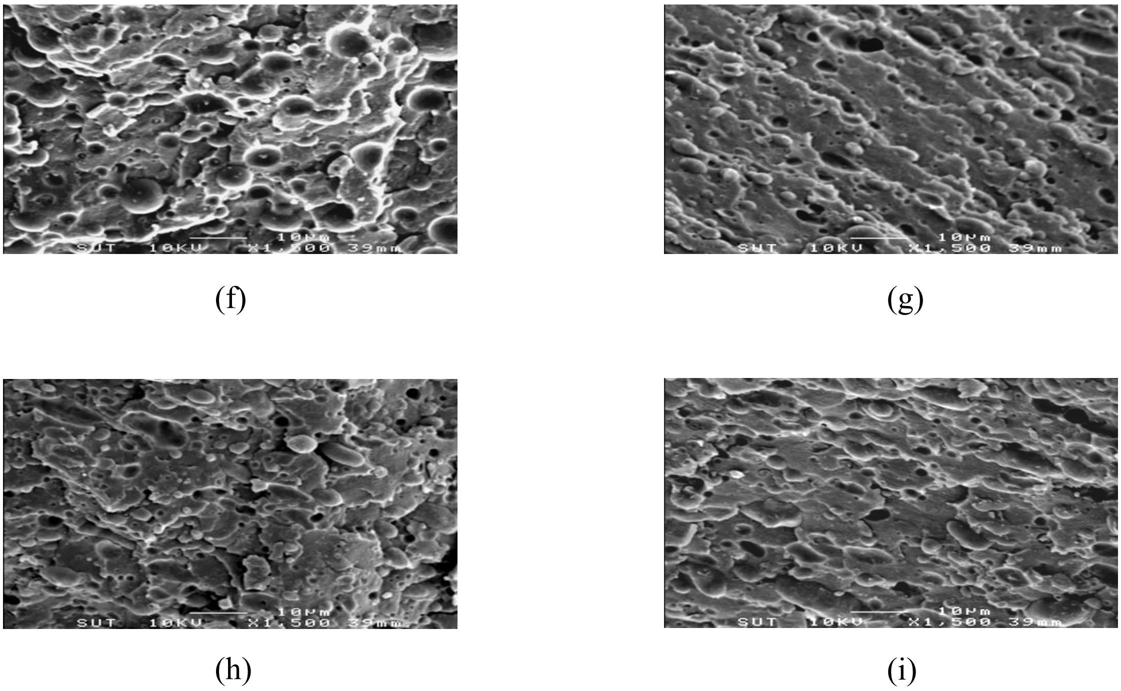
(b)

(c)

(d)

(e)

Figure 4.10 SEM micrographs of (a) HDPE/PET 20/80 (b) HDPE/PET/PE-g-MA 20/80/2, (c) HDPE/PET/PE-g-MA 20/80/4, (d) HDPE/PET/PE-g-MA 20/80/6, (e) HDPE/PET/PE-g-MA 20/80/8, (f) HDPE/PET/HDPE-g-GMA 20/80/2,(g) HDPE/PET/HDPE-g-GMA 20/80/4, (h) HDPE/PET/ HDPE-g-GMA 20/80/6, and (i) HDPE/PET/HDPE-g-GMA 20/80/8 (x 1500)



(f) (g)

(h) (i)

Figure 4.10 SEM micrographs of (a) HDPE/PET 20/80 (b) HDPE/PET/PE-g-MA 20/80/2, (c) HDPE/PET/PE-g-MA 20/80/4, (d) HDPE/PET/PE-g-MA 20/80/6, (e) HDPE/PET/PE-g-MA 20/80/8, (f) HDPE/PET/HDPE-g-GMA 20/80/2,(g) HDPE/PET/HDPE-g-GMA 20/80/4, (h) HDPE/PET/ HDPE-g-GMA 20/80/6, and (i) HDPE/PET/HDPE-g-GMA 20/80/8 (x 1500) (Continued)

Loyens and Groeninckx (2002) reported that the two functional groups of the compatibilizers (MA or GMA) would react in a different manner with the PET functional end groups resulting in the formation of graft copolymers across the interface. The overall reaction schemes generally expected are shown in Figure 4.11. The compatibilization performance between these two functional groups is considered the functional reactivity of the carboxylic and/or hydroxyl groups at the chain ends of the PET. The MA is expected to react with the hydroxyl group of the PET to form the desired compatibilizer while the GMA is expected to react with both carboxyl and hydroxyl terminal group of the PET. Similar studies had been reported by Sun, Hu, and Lambla (1996) and Kalfoglou et al. (1995).

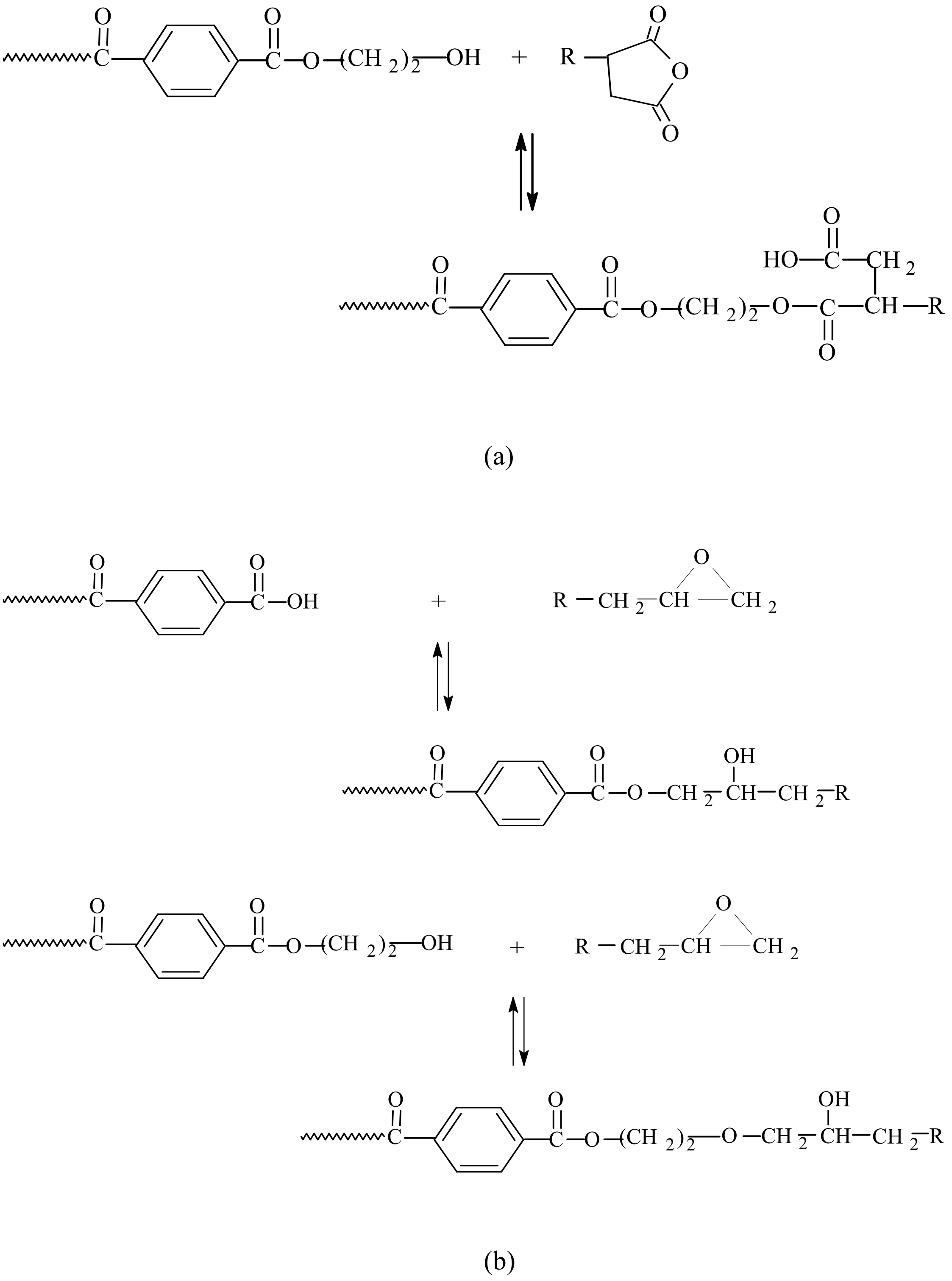


Figure 4.11 Chemical reaction schemes : (a) maleic anhydride and PET functional end groups and (b) epoxide and PET functional end groups (Loyens and Groeninckx, 2002)

Compatibilization reaction of MA or GMA with PET functional end groups can be confirmed by using FTIR technique. The spectra of the uncompatibilized blend, PE-g-MA, and PE-g-MA compatibilized blends are shown in Figure 4.12. IR peak at 1778 cm^{-1} is characteristic of MA group in PE-g-MA as shown in curve (b) of Figure 4.12 (Lusinchi et al., 2001). The absorption at 1778 cm^{-1} disappears in the compatibilized blends. This indicates the chemical reaction between MA and hydroxyl group of PET, as shown in Figure 4.11 (a). IR spectra of PE-g-MA compatibilized blend could not give clear evidence for component reaction because PET carbonyl absorption interfered with the absorption bands of MA appearing in the same range (Kalfoglou et al., 1995).

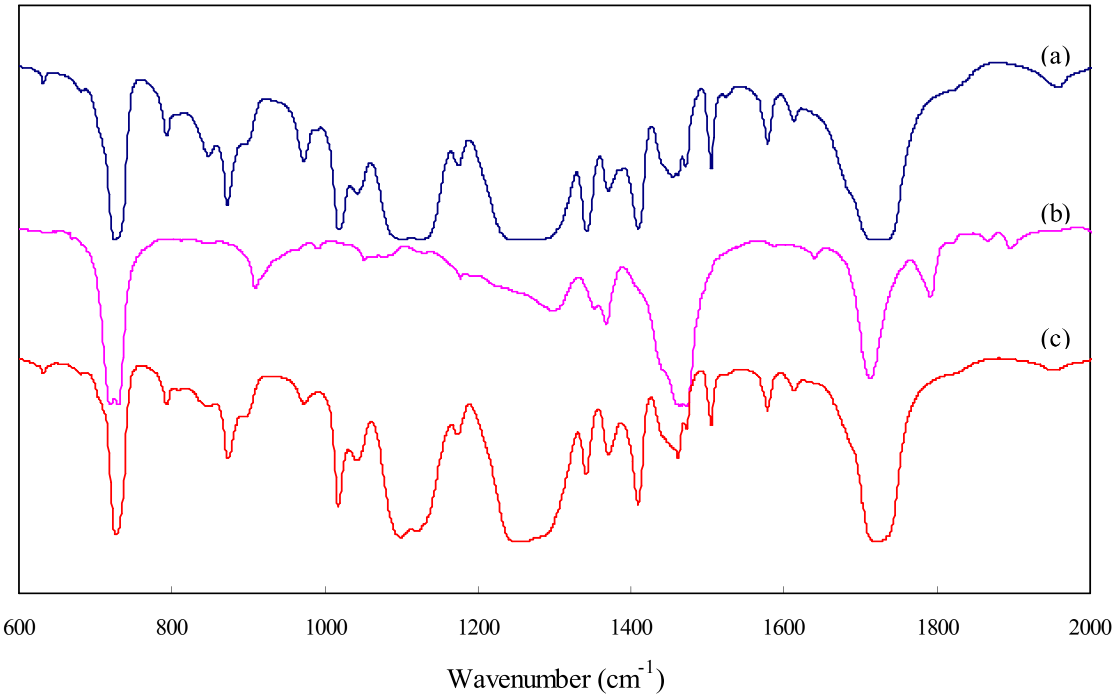


Figure 4.12 The infrared spectra of (a) HDPE/PET 20/80, (b) PE-g-MA, and (c) HDPE/PET/PE-g-MA 20/80/2

The IR spectra of the uncompatibilized blend, HDPE-g-GMA, and HDPE-g-GMA compatibilized blends are shown in Figure 4.13. The disappearance of the epoxy group at 910 cm^{-1} after melt blending is a proof of epoxy ring opening reactions with PET (Tsai and Chang, 1996). The chemical reaction mechanism is shown in Figure 4.11(b). However, chemical structures of the reaction products can not be positively identified from the spectra.

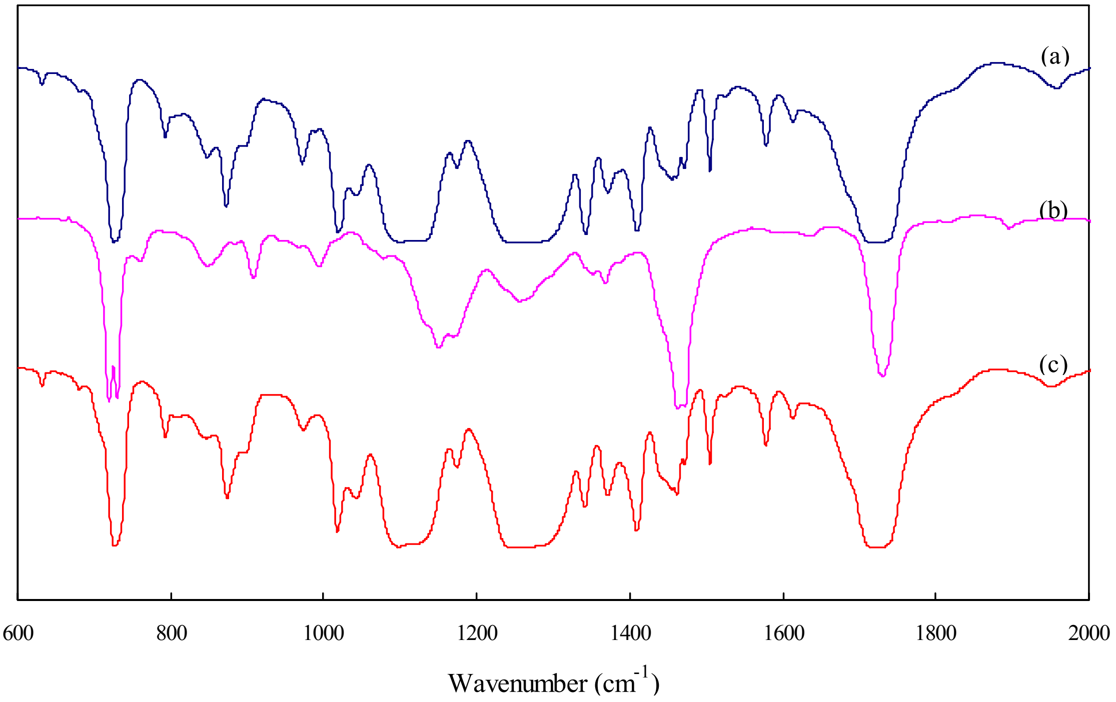


Figure 4.13 The infrared spectra of (a) HDPE/PET 20/80, (b) HDPE-g-GMA, and (c) HDPE/PET/HDPE-g-GMA 20/80/2

4.3.3 Mechanical properties

The mechanical properties of the blends are related to the phase morphology. The uncompatibilized blend has poor mechanical properties due to weak adhesion at the interface. The addition of the compatibilizers causes an improvement in tensile strength, tensile strain at break, flexural strength, compressive strength, and impact strength of the blends as shown in Table 4.5. However, tensile modulus slightly decreases in the same composition range due to elastomeric behaviour of these copolymers (Dimitrova et al., 1999). The mechanical properties of HDPE/PET blends as a function of compatibilizer contents are shown in Figure 4.15. In the case of PE-g-MA compatibilized blends, an increase of tensile strength (from 34 MPa to 41 MPa), tensile strain at break (from 3 to about 10%), flexural strength (from 53 MPa to 60 MPa), and compressive strength (from 81 to 104 MPa) are found with increasing the PE-g-MA content in the range 2-6 phr. At the compatibilizer content of 2-4 phr, HDPE-g-GMA compatibilized blends have the tensile strength, tensile modulus, tensile strain at break, flexural strength, compressive strength, and impact strength higher than that of PE-g-MA compatibilized blends. However, when HDPE-g-GMA content is increased to be 6-8 phr the tensile strength, tensile strain at break, flexural strength, and impact strength are lower than that of PE-g-MA compatibilized blends. The interfacial adhesion increases with adding HDPE-g-GMA resulting in an increase of these mechanical properties until reaching a saturation value. A further increase of HDPE-g-GMA content may result in the crosslinking reaction and worsen properties of the blends (Pawlak et al., 2002).

Loyens and Groeninck (2002) proposed two reactions involved during blending of PET/EPR/EPR-g-GMA. Firstly, the compatibilization reaction will lead to the formation of graft copolymers at the interface between PET and EPR. This results in the dispersion of the minor phase and inhibits coalescence. Secondly, the present crosslinking reactions will interfere with the phase morphology formation. The particles will become more viscous and less deformable. Droplet break up is prevented. These crosslinking reactions, as shown in Figure 4.14, are additional and possibly even competitive to the compatibilization reactions. The first crosslinking reaction involves the secondary hydroxyl groups present on the graft copolymer formed at the interface. The second crosslinking reaction is based on the difunctionality of the PET matrix, as each PET chain contains two functional end groups capable of reaction with the epoxide functionality.

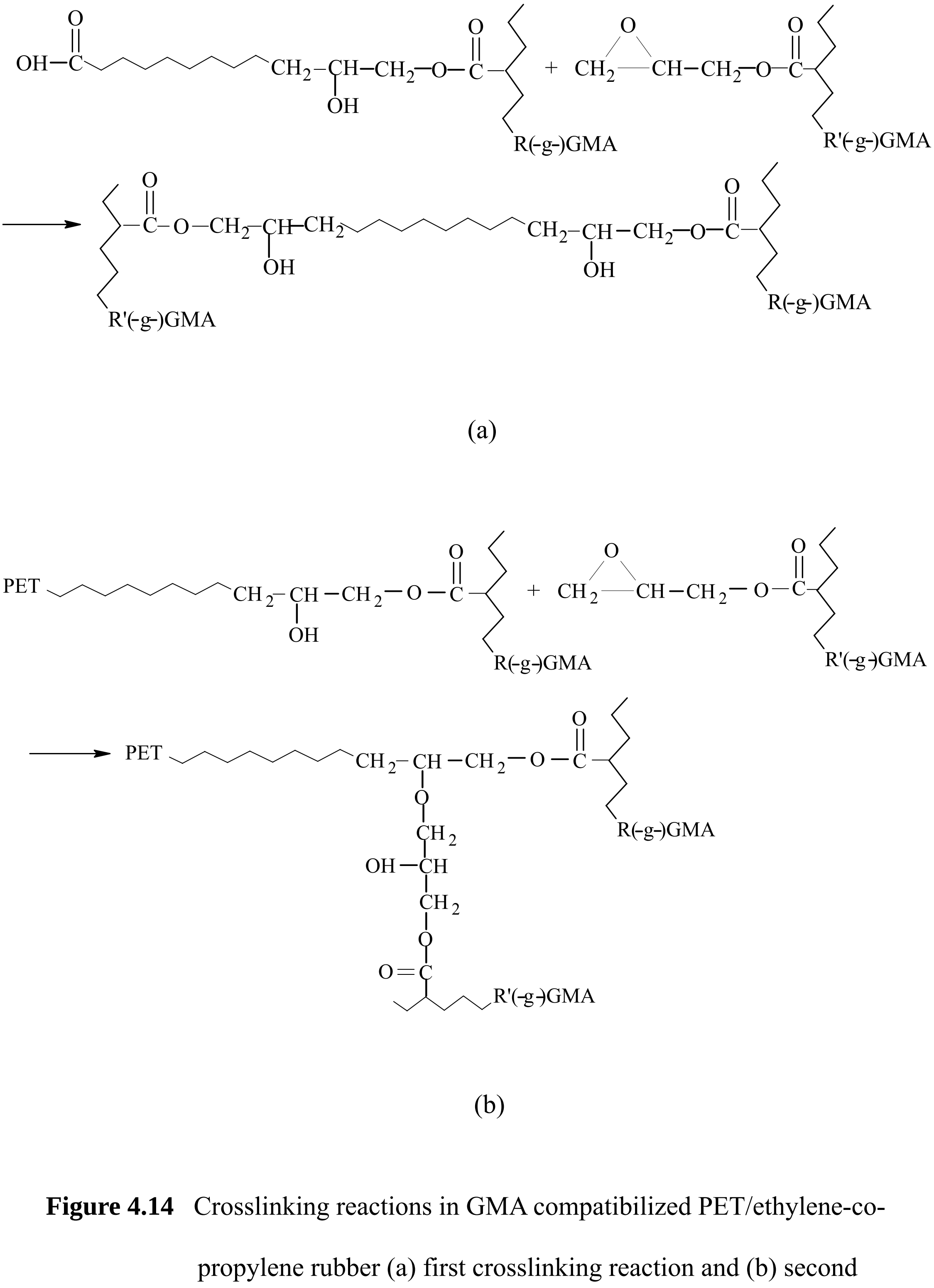
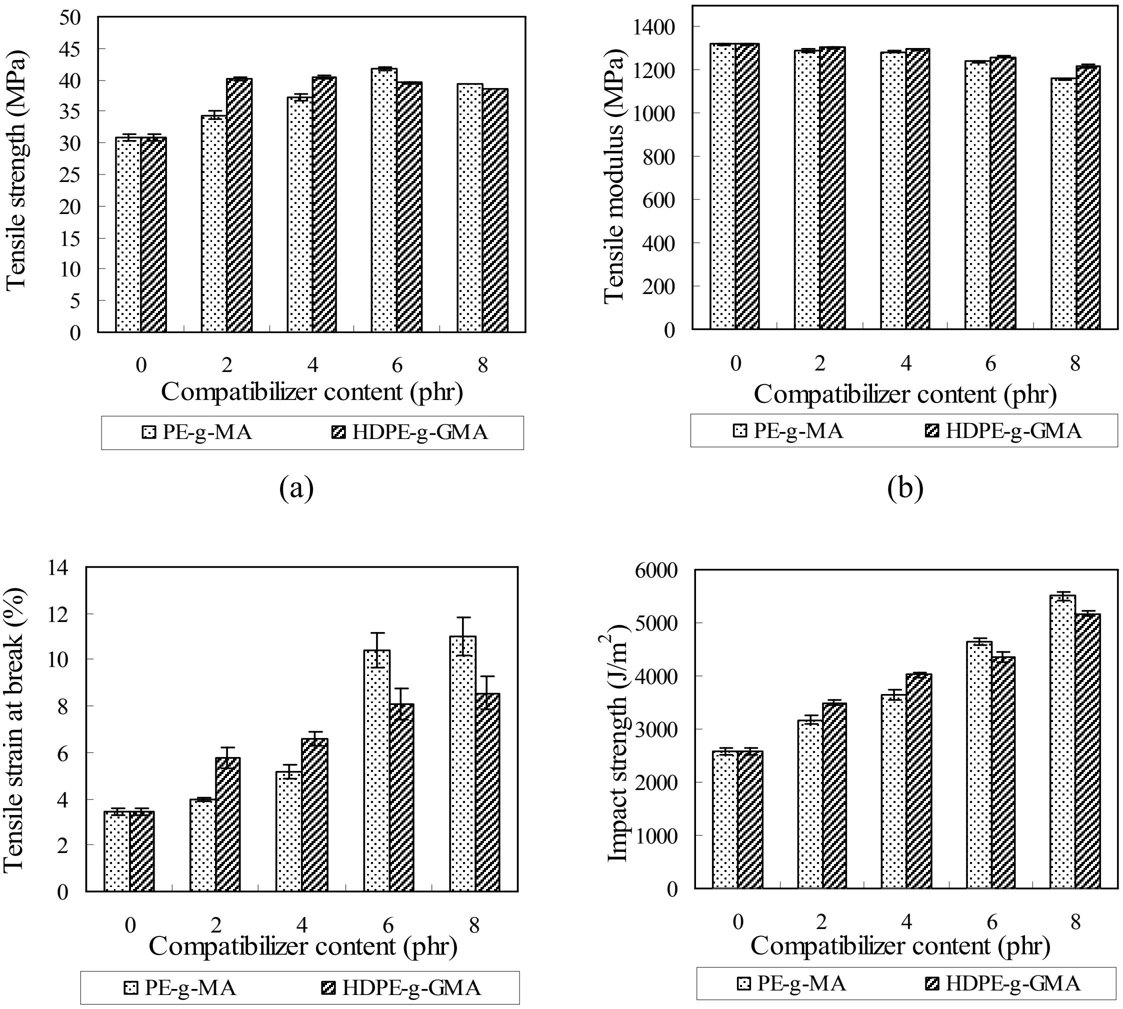


Figure 4.14 Crosslinking reactions in GMA compatibilized PET/ethylene-co-propylene rubber (a) first crosslinking reaction and (b) second crosslinking reaction (Loyens and Groeninckx, 2002)

Table 4.5 The effect of compatibilizer types and contents on the mechanical properties of HDPE/PET blends (20/80 wt%)

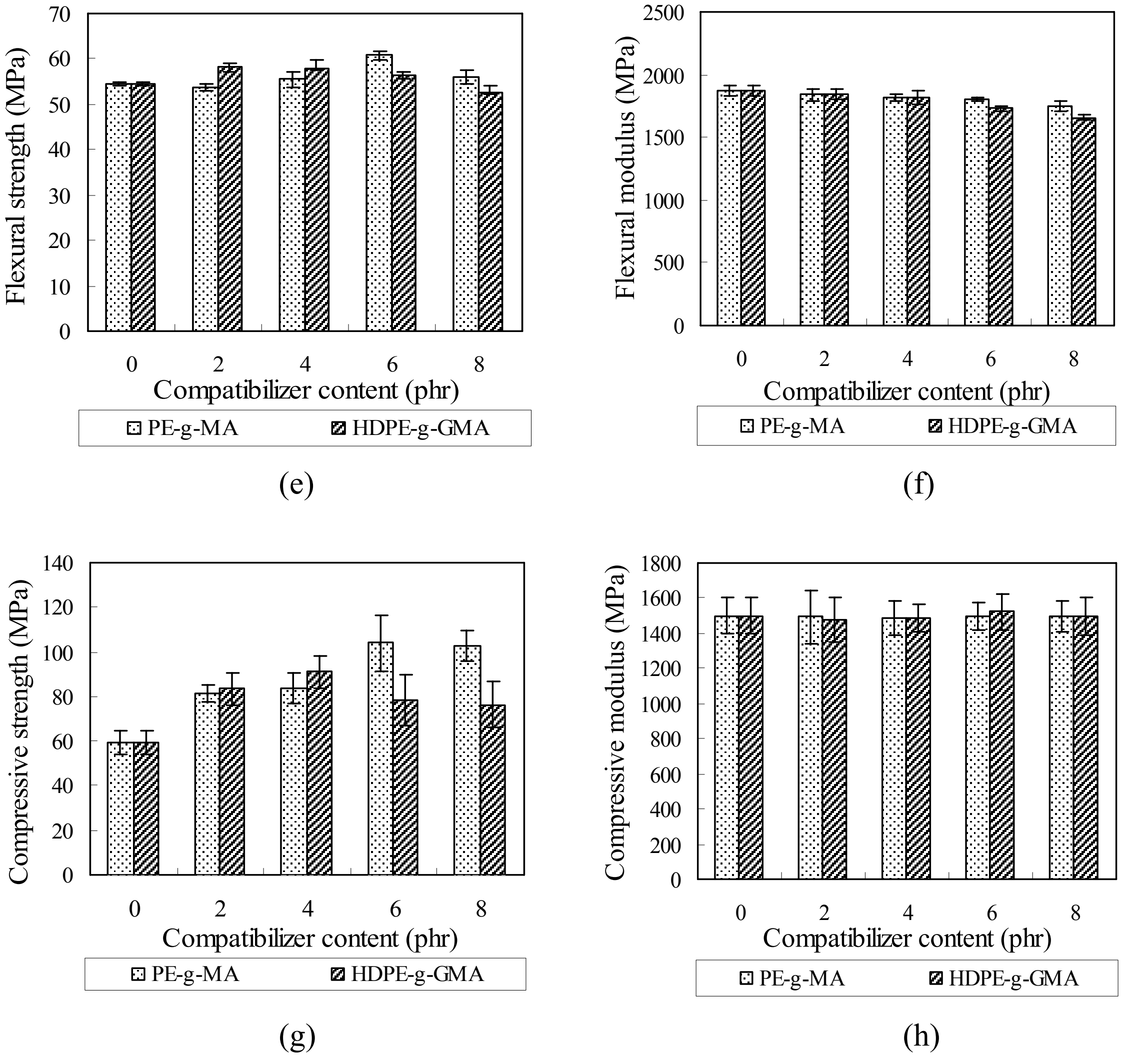
Composition (wt%)	**Tensile**			**Flexural**		**Compressive**		**Impact strength (J/m^2)**
	strength (MPa)	**modulus (MPa)**	**strain at break (%)**	**strength (MPa)**	**modulus (MPa)**	**strength (MPa)**	**modulus (MPa)**	
HDPE/PET 20/80	30.85±0.73	1320.73±53.03	3.46±0.16	54.49±0.47	1872.54±44.90	59.52±5.27	1500.76±106.00	2578.41±77.12
HDPE/PET/PE-g-MA	34.41±0.53	1291.91±12.25	3.94±0.08	53.72±0.74	1839.69±46.03	81.37±3.59	1492.26±149.81	3176.87±84.45
HDPE/PET/HDPE-g-GMA	40.11±0.66	1305.89±50.82	5.77±0.44	58.15±1.11	1845.32±39.43	83.40±5.23	1475.55±127.40	3489.75±52.63
20/80/2								
HDPE/PET/PE-g-MA	37.24±0.62	1285.37±35.11	5.17±0.31	55.45±1.68	1820.29±24.22	78.53±7.02	1489.11±98.45	3635.25±92.76
HDPE/PET/HDPE-g-GMA	40.43±0.20	1296.85±18.80	6.57±0.30	57.99±0.56	1816.06±50.51	91.07±7.45	1487.21±78.94	4022.22±42.65
20/80/4								
HDPE/PET/PE-g-MA	41.80±0.41	1239.35±39.61	10.40±0.77	60.73±0.78	1800.20±13.08	103.88±12.50	1494.56±79.95	4641.24±74.86
HDPE/PET/HDPE-g-GMA	39.52±0.20	1262.44±46.88	8.10±0.67	56.45±0.66	1729.03±19.20	78.51±9.30	1493.58±100.23	4363.63±90.23
20/80/6								
HDPE/PET/PE-g-MA	39.36±0.29	1159.92±79.43	10.98±0.83	55.87±1.48	1750.59±36.93	102.88±6.75	1499.69±88.83	5503.45±93.02
HDPE/PET/HDPE-g-GMA	38.59±0.15	1219.57±59.15	8.54±0.71	52.71±0.50	1659.49±20.26	76.38±7.54	1496.70±103.85	5174.51±42.55
20/80/8								



(a) (b)

(c) (d)

Figure 4.15 The effect of compatibilizer types and contents on the mechanical properties of HDPE/PET (20/80 wt%) (a) tensile strength, (b) tensile modulus, (c) tensile strain at break, (d) impact strength, (e) flexural strength, (f) flexural modulus, (g) compressive strength, and (h) compressive modulus



(e) (f)

(g) (h)

Figure 4.15 The effect of compatibilizer types and contents on the mechanical properties of HDPE/PET (20/80 wt%) (a) tensile strength, (b) tensile modulus, (c) tensile strain at break, (d) impact strength, (e) flexural strength, (f) flexural modulus, (g) compressive strength, and (h) compressive modulus (Continued)

The optimum content of the PE-g-MA compatibilizer for the HDPE/PET (20/80 wt%) is 6 phr. Higher content of the compatibilizer does not offer further significant improvement in the mechanical properties. Similarly, Pracella, et al. (2002)

reported that the average particle size rapidly decreased with increasing the compatibilizer content until to reach an equilibrium value. The equilibrium concentration roughly corresponded to the amount of copolymer necessary to saturate the interface, and in these conditions the particle size reduction is mainly due to suppression of coalescence. In case of HDPE-g-GMA compatibilizer, the optimum content is 2 phr. Blends containing HDPE-g-GMA compatibilizer higher than 2 phr show no significant decrease of the disperse phase size and no significant effect on the tensile and flexural properties.

4.3.4 Rheological properties

Rheological measurements are used to demonstrate the occurrence of compatibilization reaction (Tsai and Chang, 1996). The viscosity of the uncompatibilized and compatibilized blends by adding 2, 4, 6, and 8 phr of the PE-g-MA and HDPE-g-GMA are shown in Figure 4.16. The viscosities versus shear rate of all the compatibilized blends are higher than that of the uncompatibilized blend. The viscosity of the blends increases with increasing quantity of the both compatibilizers. The increase in viscosity of compatibilized blends indicates occurrence of interfacial interactions between the hydroxyl end-groups of PET and the reactive MA functionalized polyolefins and between the carboxyl/hydroxyl end-groups of PET and epoxy groups of GMA as reactive compatibilizers (Kalfoglou et al., 1995). The similar results were reported by Dagli and Kamdar (1994); Pracella et al. (2002); Pawlak et al. (2002). The viscosities of the compatibilized blends with HDPE-g-GMA are higher than those blends with PE-g-MA. This is supported that epoxy groups of GMA give rise to stronger interaction with the PET chain ends. The result is in agreement with Pracella et al. (2002). They found that the interaction between epoxy group of GMA and polyester chains appeared to be stronger than that of MA or AA functionalized polyolefins due to an increase of the melt viscosity for compatibilized blends PET/PE with PE-g-GMA.

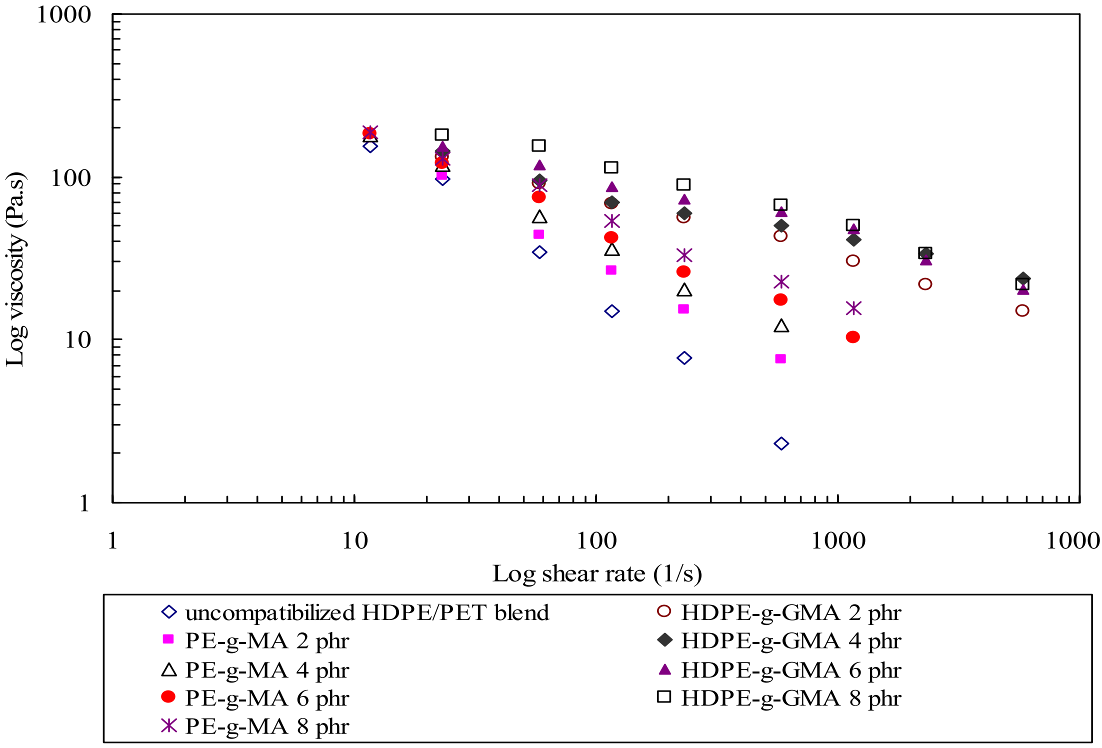


Figure 4.16 The effect of compatibilizer types and contents on the viscosities of HDPE/PET blends (20/80 wt%)

Melt flow index (MFI) of the uncompatibilized and compatibilized blends are shown in Figure 4.17. It clearly demonstrates that the higher compatibilizer contents in the blends result in the lower MFI. This result indicates that the viscosity of the blend increases with increasing quantity of the both compatibilizers. MFI results are well corresponding with viscosity results measured from capillary rheometer.

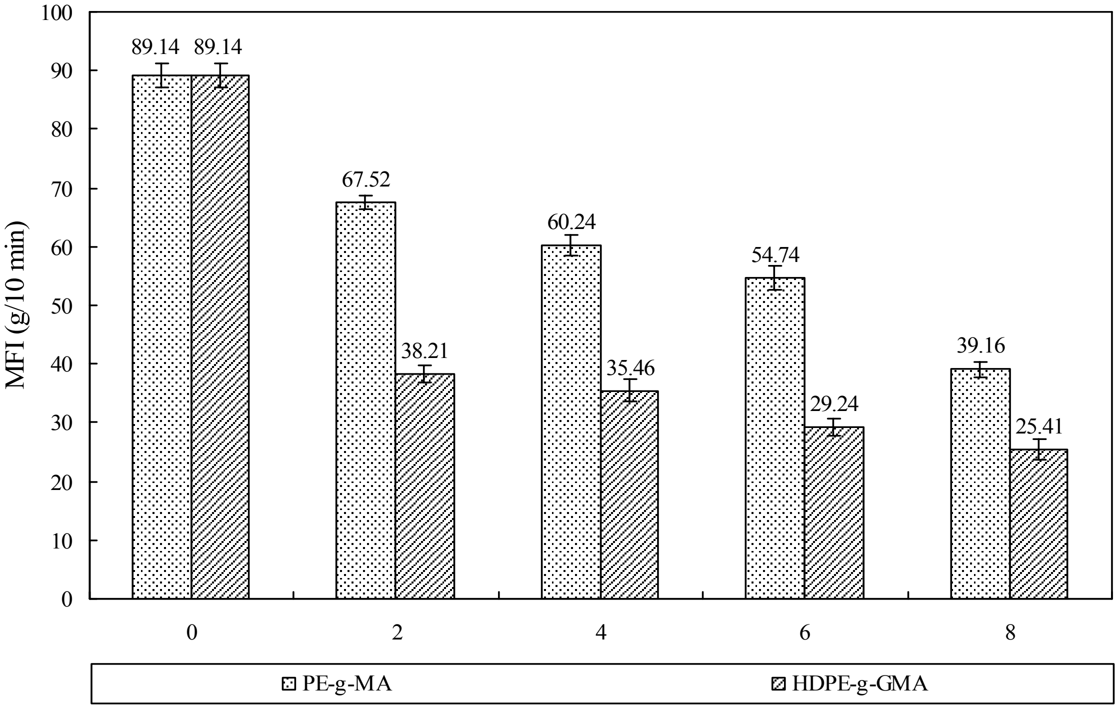


Figure 4.17 The effect of compatibilizer types and contents on melt flow index of HDPE/PET blends (20/80 wt%)

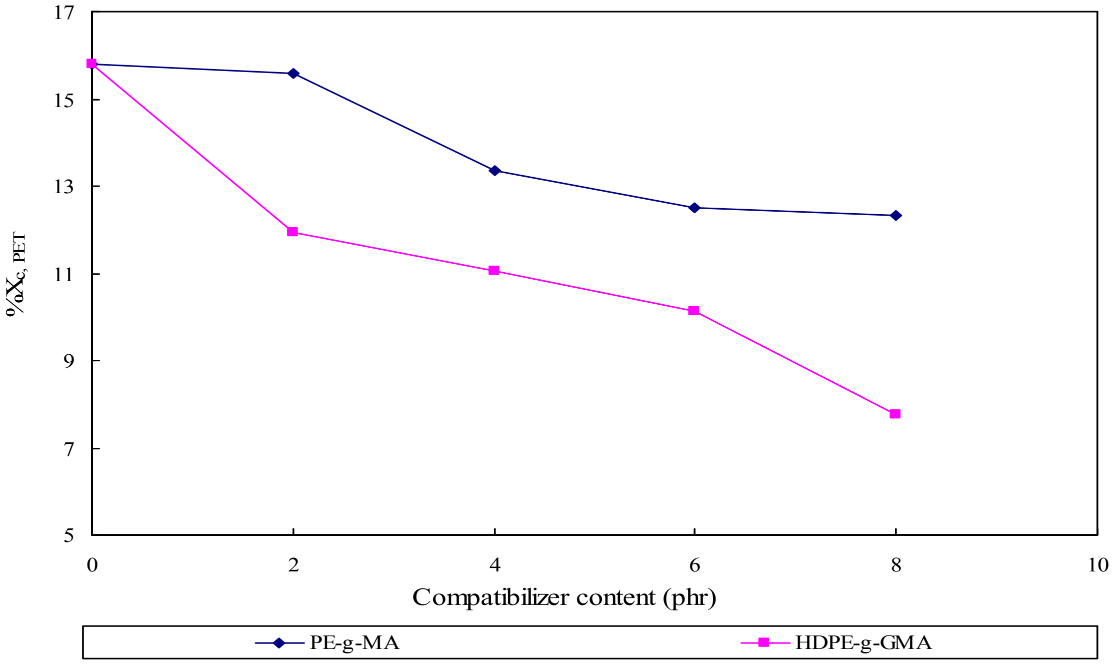
4.3.5 Thermal properties

Thermal properties of HDPE/PET blends by adding 2, 4, 6, and 8 phr of the compatibilizers are listed in Table 4.6. The crystallization temperature (T_c) of HDPE phase remains almost constant for all compositions examined while the T_c of PET component in the compatibilized blends is shifted to temperature lower than that observed for uncompatibilized blend. The similar results were obtained by Jabarin and Bhakkad (1995). They reported that the T_c of HDPE component was remained nearly constant with increasing of maleic anhydride grafted polyolefin while the T_c of PET was observed to decrease as increasing the amount of the compatibilizer. The reduction of the T_c of PET indicates a decrease in the crystallization rate of PET due to the presence of the compatibilizer. The addition of PE-g-MA to the blends does not significantly affect on the T_m of both HDPE and PET components. While T_m of PET in the blends compatibilized with HDPE-g-GMA is shifted to temperature lower than those of the uncompatibilized blend. Pawlak et al. (2002); Pracella et al. (2002) obtained similar results on the compatibilization of HDPE/PET blends. The shift of the T_m of PET with the amount of HDPE-g-GMA was observed. These melting point displacements indicated compatibility between the components with the presence of the compatibilizer that caused an increase of the mechanical properties (Lozano-Ramirez and Guerrero-Salazar, 1999).

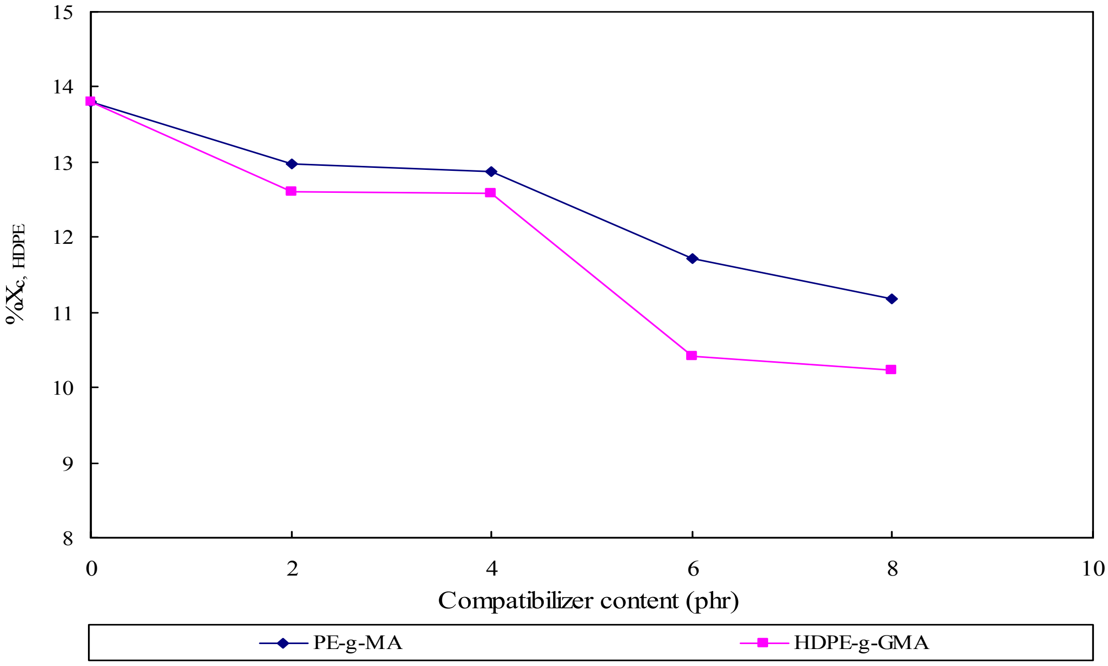
Table 4.6 Calorimetric characterization of uncompatibilized and compatibilized blends with PE-g-MA and HDPE-g-GMA

Composition (wt%)	**HDPE component**				**PET component**			
	T_c (°C)	**T_m (°C)**	**ΔH_m (J/g)**	**X_c (%)**	**T_c (°C)**	**T_m (°C)**	**ΔH_m (J/g)**	**X_c (%)**
HDPE/PET 20/80	116.74	131.10	40.44	13.80	198.84	247.99	18.91	15.78
HDPE/PET/PE-g-MA	116.88	131.02	38.89	12.97	195.91	247.48	18.65	15.57
HDPE/PET/HDPE-g-GMA 20/80/2	117.74	131.24	36.91	12.60	196.97	241.40	14.30	11.94
HDPE/PET/PE-g-MA	116.59	130.78	37.72	12.87	194.72	247.30	16.55	13.36
HDPE/PET/HDPE-g-GMA 20/80/4	117.82	130.80	36.87	12.58	194.87	240.32	13.25	11.06
HDPE/PET/PE-g-MA	116.52	130.43	36.42	12.43	195.28	247.39	15.41	12.86
HDPE/PET/HDPE-g-GMA 20/80/6	117.95	131.04	30.54	10.42	194.70	239.75	12.13	10.13
HDPE/PET/PE-g-MA	116.13	130.46	32.73	11.17	195.7	247.50	14.77	12.32
HDPE/PET/HDPE-g-GMA 20/80/8	117.82	130.51	29.96	10.24	194.72	239.86	9.28	7.75

The effects of the compatibilizer types and contents on the crystallinity degree (%X_c) of PET and HDPE component in the HDPE/PET blends are shown in Figure 4.18. The %X_c of both matrix and dispersed phase depend on the types and contents of the compatibilizer. The %X_c of PET and HDPE component decrease with an increase of the PE-g-MA and HDPE-g-GMA contents. Papadopoulou and Kalfoglou (2000) reported that the crystallinity of PET and PP component were reduced with increasing the SEBS-g-MA contents. Crystallinity reduction might reflect a decrease of the rate of crystallization in the presence of the compatibilizer due to a decrease of the rate of diffusion processes associated with crystallization. These results can be explained by considering both the effect of the miscibility of the functionalized polyolefins with the HDPE phase and that of chemical reactions of functional groups with PET at the interface in the melt (Pracella et al., 2002). The both effects cause a finer and more homogeneous morphology and a reduction in the particle size of the disperse phase. Consequently, the crystallization of PET was inhibited and caused a decrease in the T_m and crystallinity of the PET (Marquez, Gambus, Romero-Rato, and Apartado, 1999).



(a)



(b)

Figure 4.18 The effect of compatibilizer types and contents on the crystallinity degree (%X_c) of (a) PET component and (b) HDPE component in the HDPE/PET blends (20/80 wt%)

HDT of HDPE/PET compatibilized with PE-g-MA and HDPE-g-GMA are shown in Figure 4.19. No remarkable difference on HDT of uncompatibilized and compatibilized blends with PE-g-MA and HDPE-g-GMA is found.

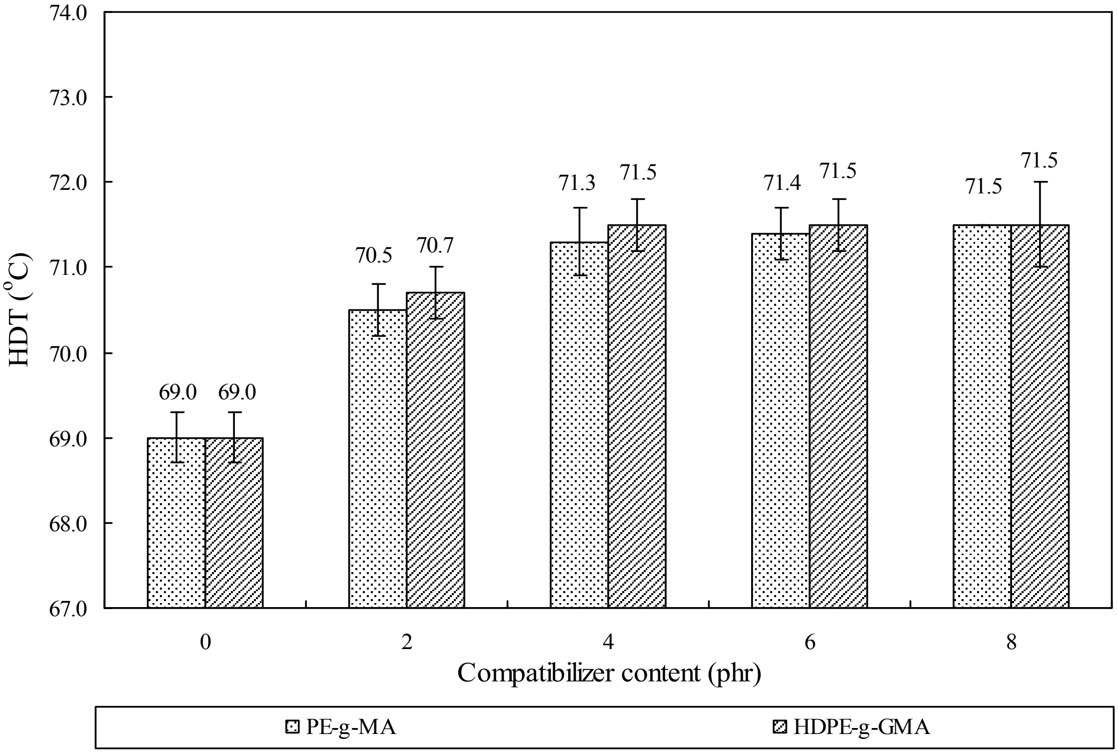


Figure 4.19 The effect of compatibilizer types and contents on HDT of HDPE/PET blends (20/80 wt%)

4.3.6 Water absorption

Water absorption rate versus immersion time of uncompatibilized and compatibilized blends are shown in Figure 4.20. The water absorption rate of the compatibilized blends is lower than that of the uncompatibilized blend. The water absorption measurement indicates that the compatibilized blends are more effective than the uncompatibilized blend in improving the water resistance. Water absorption rate seems to be constant after immersion for 30 days. Bae, Park, Kim, and Suh (2001) reported that the water resistance was improved by the compatibilization between the PET and PP phases. The reduction of water absorption rate was attributed to the finer dispersed phase size which was increased the total surface area for the PP dispersed phase. Arbelaiz et al. (2005) found that the reduction of water absorption rate was attributed to an improvement in an interfacial adhesion resulting in avoidance an easy penetration of water molecules into the compatibilized blends and a decrease water accumulation in the interfacial voids.

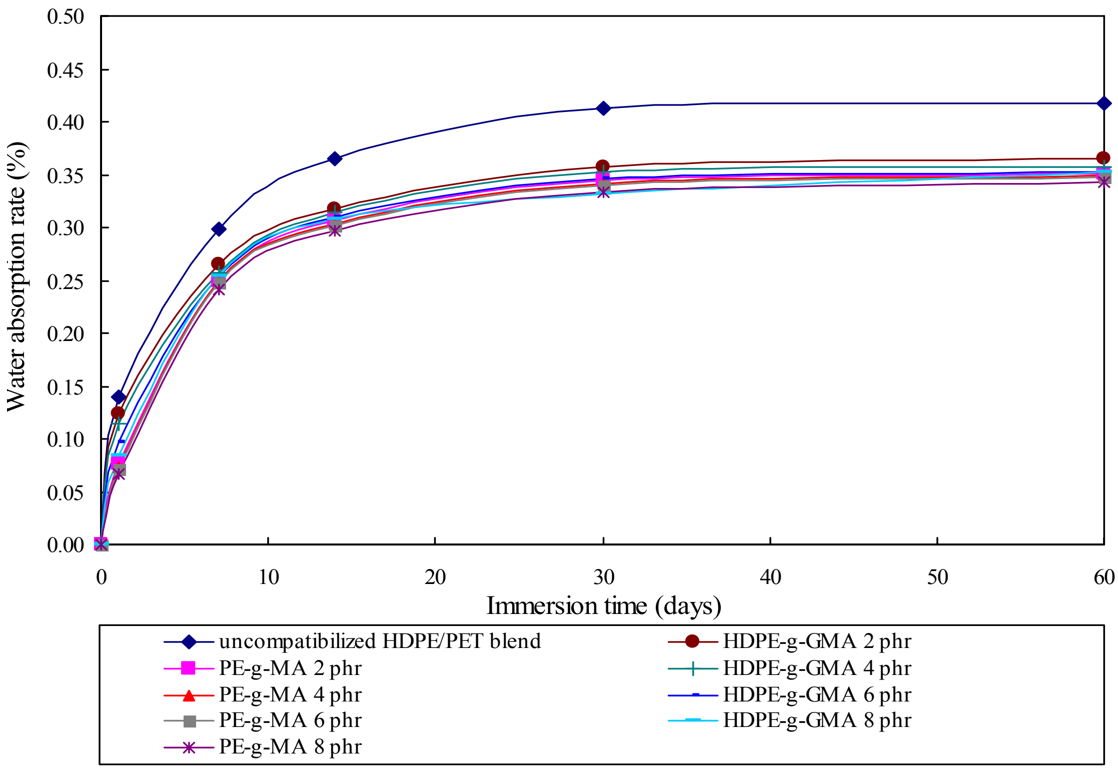


Figure 4.20 Water absorption rate versus immersion time of the uncompatibilized and compatibilized blends

The effect of the water absorption on the tensile strength of the uncompatibilized and compatibilized blends is shown in Figure 4.21. The addition of the compatibilizers insignificantly affect on tensile strength of the blends after immersion. In contrast, Bergeret et al. (2001) found that when PET and PBT were accessible to water, they tended to swell of the amorphous part due to water absorption, thereby developing shear stresses at the interface. Consequently, a decrease of the tensile strength was found.

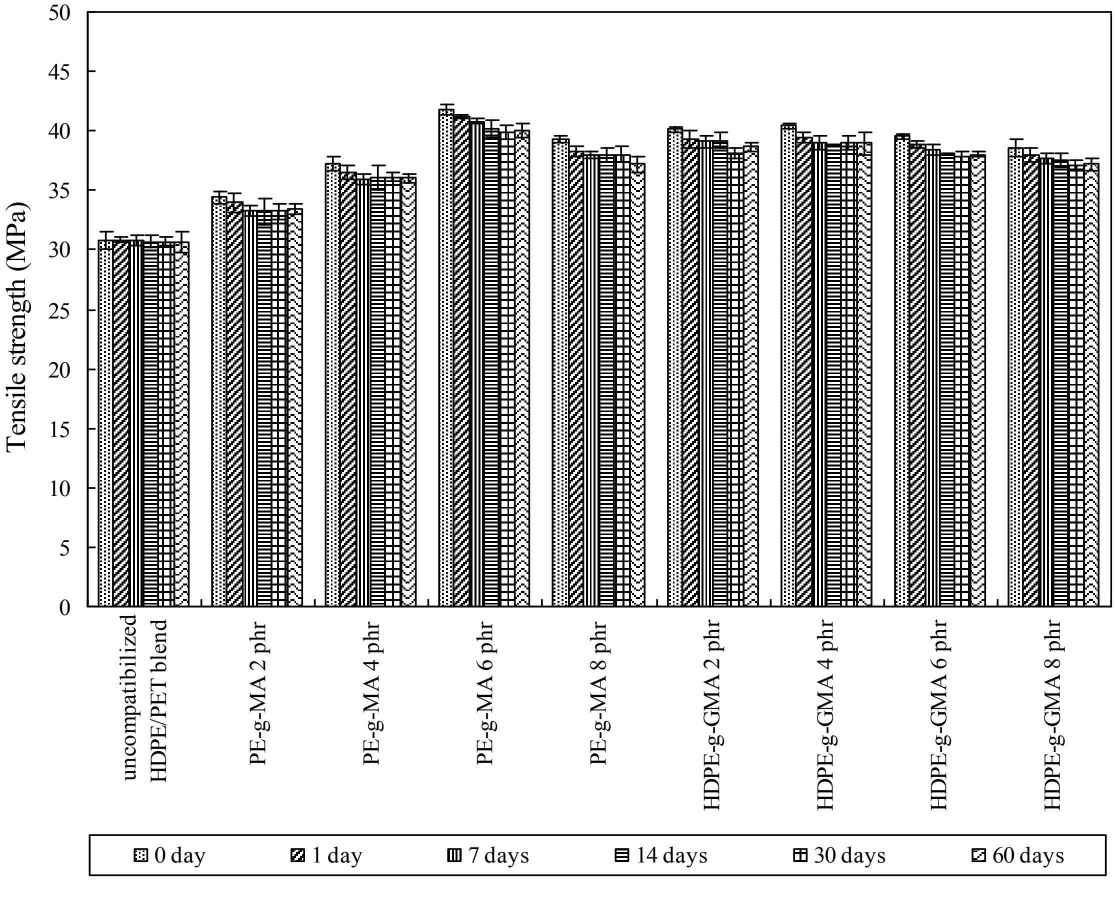


Figure 4.21 The effect of the water absorption on the tensile strength of the uncompatibilized and compatibilized blends

4.4 The effect of filler reinforcement on properties of HDPE/PET blends

Polymer blending and reinforcement had been studied for many years (Malchev et al., 2005). The incorporation of fillers into thermoplastics has been used to enhance certain properties. Glass fibers are the most commonly used fibers in short fiber reinforced polymer composites. They are selected in majority of applications because of their low cost, reasonably high modulus, and high tensile strength. The addition of the fiber to thermoplastics significantly improves both the stiffness and strength. Calcium carbonate ($CaCO_3$) is abundantly available in nature. They are used to reduce cost as well as mold shrinkage (Talreja and Manson, 2001). In this study, short glass fiber (SGF) and $CaCO_3$ at content of 10 phr are used to reinforce the HDPE/PET blends. The content of PE-g-MA and HDPE-g-GMA to compatibilize the composites are 6 and 2 phr, respectively.

4.4.1 Density

Density of the blends and composites is shown in Table 4.7. Addition of SGF and $CaCO_3$ results in insignificant effect on the density of the blends.

Table 4.7 Density of the blends and composites

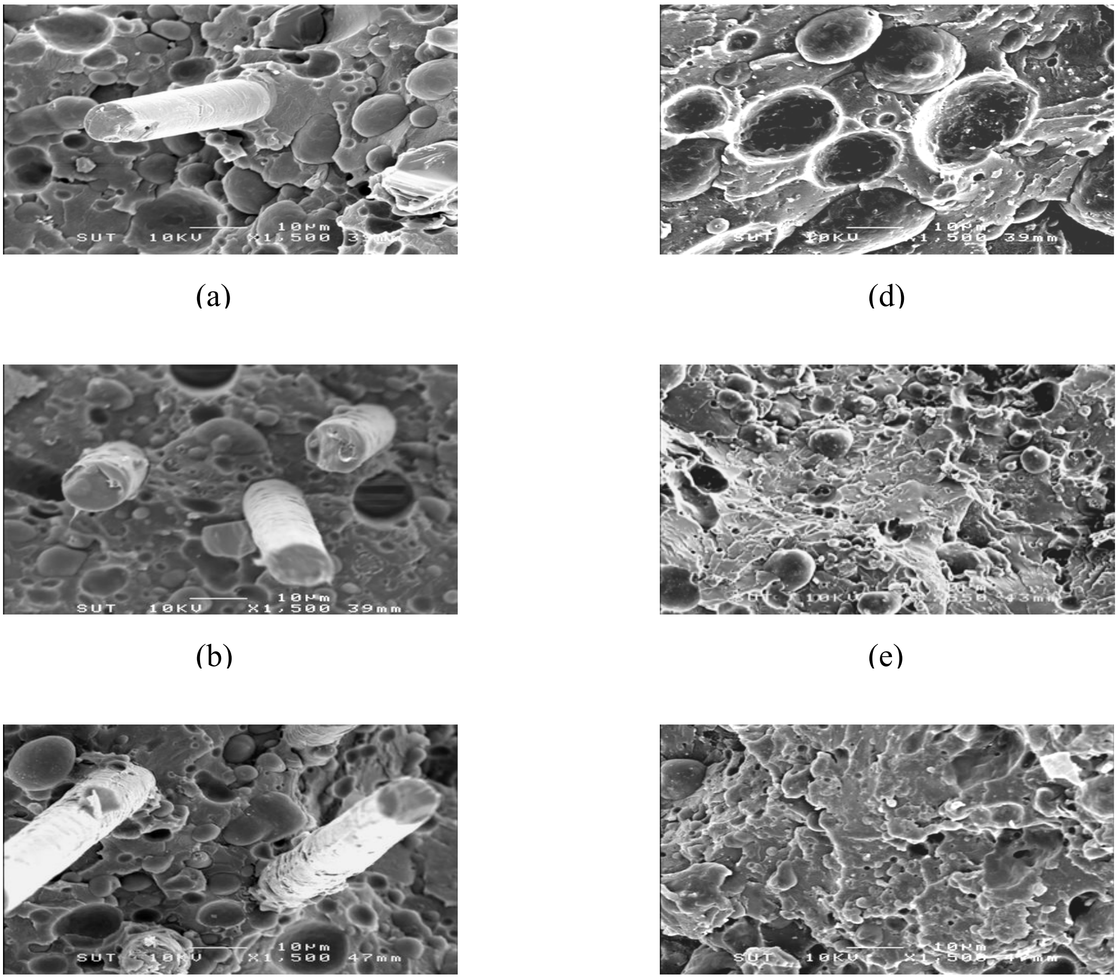
Composition (wt%)	Density (g/cm^3)
HDPE/PET 20/80	1.19±0.02
HDPE/PET/SGF 20/80/10	1.17±0.10
HDPE/PET/$CaCO_3$ 20/80/10	1.15±0.05
HDPE/PET/PE-g-MA/SGF 20/80/6/10	1.20±0.03
HDPE/PET/PE-g-MA/ $CaCO_3$ 20/80/6/10	1.18±0.09
HDPE/PET/HDPE-g-GMA/SGF 20/80/2/10	1.21±0.02
HDPE/PET/HDPE-g-GMA/ $CaCO_3$ 20/80/2/10	1.19±0.04

4.4.2 Morphological properties

SEM micrographs of SGF and $CaCO_3$ reinforced HDPE/PET blends are shown in Figure 4.22. Fracture surfaces of HDPE/PET/SGF composite, as shown in Figure 4.22 (a)-(c), reveal that the compatibilizers enhance the surface adhesion between SGF and polymer since SGF surfaces are more coated with the matrix. It results in an increase in the mechanical properties of the composites. Tselios et al. (1999) studied the glass fiber reinforcement of in situ compatibilized PP/PE blends. They found that the MA groups of PP-g-MA could react with the hydroxyl groups of glass fibers surface. This result might lead to an increase of adhesion between the polymer matrix and the glass fibers. Therefore, the reinforcement of compatibilized blends had higher elongation at break and impact strength compared with the corresponding uncompatibilized blends.

For HDPE/PET/$CaCO_3$ composites, addition of the compatibilizers enhances the filler dispersion and adhesion through the phases. Sahnoune, Lopez-

Cuesta, and Crespy (1999) studied the effect of SEBS-g-MA on the mechanical properties of $CaCO_3$ filled HDPE and reported that the alkaline nature of the $CaCO_3$ and acidic nature of the MA led to strong acid-base interaction and to the formation of ionic bonds between the elastomer and the filler surface.



(a) (d)

(b) (e)

(c) (f)

Figure 4.22 SEM micrographs of (a) HDPE/PET/ SGF 20/80/10, (b) HDPE/PET/ PE-g-MA/SGF 20/80/6/10, (c) HDPE/PET/HDPE-g-GMA/SGF 20/80/2/10, (d) HDPE/PET/ $CaCO_3$ 20/80/10, (e) HDPE/PET/PE-g-MA/$CaCO_3$ 20/80/6/10, and (f) HDPE/PET/HDPE-g-GMA/$CaCO_3$ 20/80/2/10 (x1500)

4.4.3 Mechanical properties

Mechanical properties of the HDPE/PET blends reinforced with SGF and $CaCO_3$ are shown in Table 4.8. In the case of HDPE/PET blends without compatibilizers, addition of SGF increases the tensile, flexural, compressive properties and impact strength. Tensile strength, tensile strain at break, compressive strength, compressive modulus, and impact strength can be improved by adding PE-g-MA to the HDPE/PET/SGF composites. Incorporation of HDPE-g-GMA in HDPE/PET/SGF composite causes an improvement in tensile strength, tensile strain at break, compressive strength, compressive modulus, and impact strength whereas no significant effect on the flexural strength and flexural modulus is observed. These results are corresponding to SEM observation. The transmission of the applied load through the matrix to the fibers depends on the state of the bonding between the matrix and the fibers. These keep the fibers tightly bound to the matrix, thus facilitating the transfer and distribution of the applied load among fibers (Tselios, Bikiaris, Savidis, and Panayiotou (1999).

When $CaCO_3$ is added to HDPE/PET blends, a decrease in tensile strain at break, flexural strength, and impact strength is found. However, flexural modulus and compressive modulus are improved. Tensile strength, tensile strain at break, flexural strength, compressive strength, and impact strength are enhanced by the addition of the compatibilizers. Albano et al. (2000) found that the addition of $CaCO_3$ to the blend of PP and recycled HDPE (80/20 wt%) resulted in a slight increase in tensile modulus and a decrease of tensile strength. This was attributed to the inclusion of particles and their dispersion in the polymer matrix resulting in an increase of stress concentration.

Table 4.8 Mechanical properties of the blends and composites

Composition (wt%)	Tensile			Flexural		Compressive		Impact strength (J/m^2)
	strength (MPa)	modulus (MPa)	strain at break (%)	strength (MPa)	modulus (MPa)	strength (MPa)	modulus (MPa)	
HDPE/PET 20/80	30.85±0.73	1320.73±53.03	3.46±0.16	54.49±0.47	1872.54±44.90	59.52±5.27	1500.76±106.00	2578.41±77.12
HDPE/PET/SGF 20/80/10	39.19±1.96	1666.85±54.87	3.64±0.27	68.06±0.97	2887.53±78.56	75.23±9.87	1755.98±87.45	4527.21±72.51
HDPE/PET/$CaCO_3$ 20/80/10	30.82±0.73	1393.91±45.66	2.76±0.46	40.06±1.22	2093.91±49.57	60.84±6.15	1682.54±94.12	1782.20±64.22
HDPE/PET/PE-g-MA/SGF 20/80/6/10	42.11±0.61	1748.52±55.96	5.97±0.25	59.57±1.97	2652.19±31.19	94.21±12.19	1977.24±113.31	5173.54±82.11
HDPE/PET/PE-g-MA/$CaCO_3$ 20/80/6/10	31.55±1.53	1287.41±19.09	3.76±0.27	46.06±0.67	2012.54±27.50	80.20±4.35	1741.52±118.56	2285.40±78.43
HDPE/PET/HDPE-g-GMA/SGF 20/80/2/10	48.13±0.51	1692.24±33.18	4.95±0.15	67.32±1.52	2811.28±53.82	101.09±1.47	1859.25±89.56	6987.45±95.46
HDPE/PET/HDPE-g-GMA/$CaCO_3$ 20/80/2/10	35.75±0.72	1377.13±29.37	4.43±0.43	50.04±1.52	1973.13±9.56	84.56±1.55	1640.85±74.52	2523.51±82.29

4.4.4 Rheological properties

The viscosity of the blends and composites are plotted in Figure 4.23. The viscosities versus shear rate of the composites are higher than those of the blends since the fillers perturb the normal flow of the polymer and hinder the mobility of chain segments in the melt flow. Adding both compatibilizers increases the viscosities of the composites. In addition, the compatibilized blends reinforced with SGF exhibit higher viscosity than that of the blends reinforced with $CaCO_3$. MFI of the blends and composites are shown in Figure 4.24. Addition of the fillers causes a decrease in MFI. Giraldi et al. (2005) studied glass fiber-PET composites and found that the MFI of PET decreased with incorporation of the glass fiber.

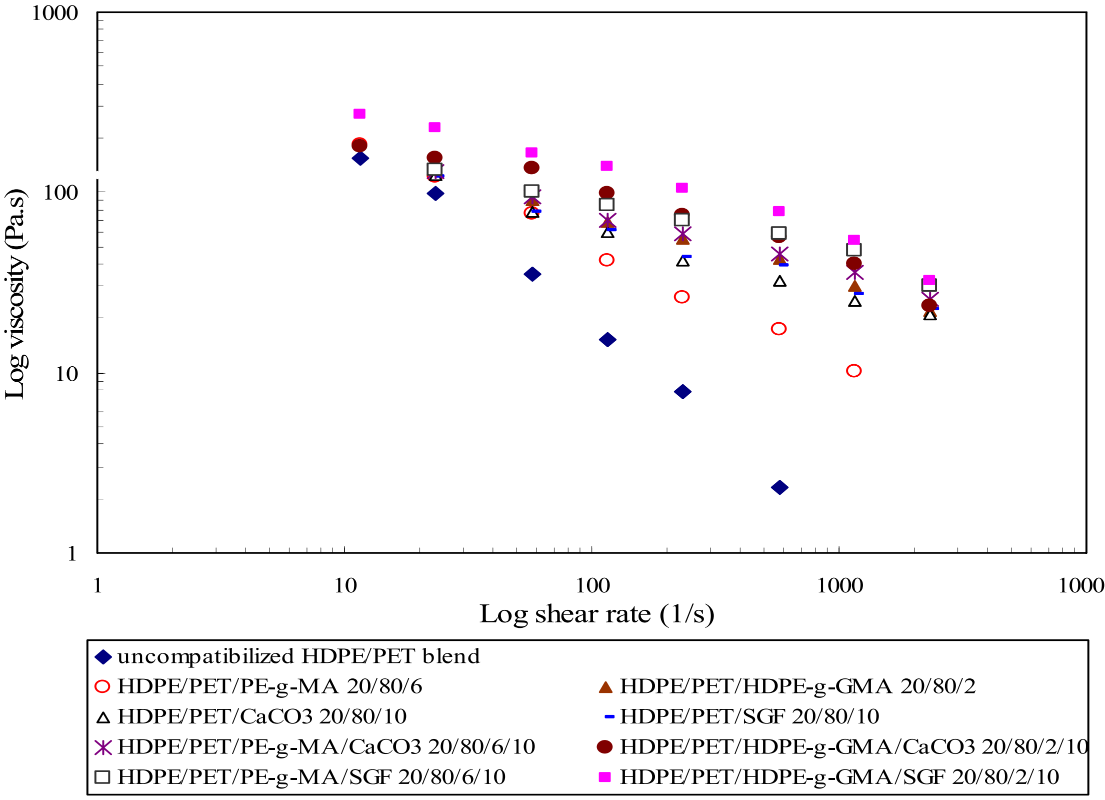


Figure 4.23 Shear viscosities of the blends and composites

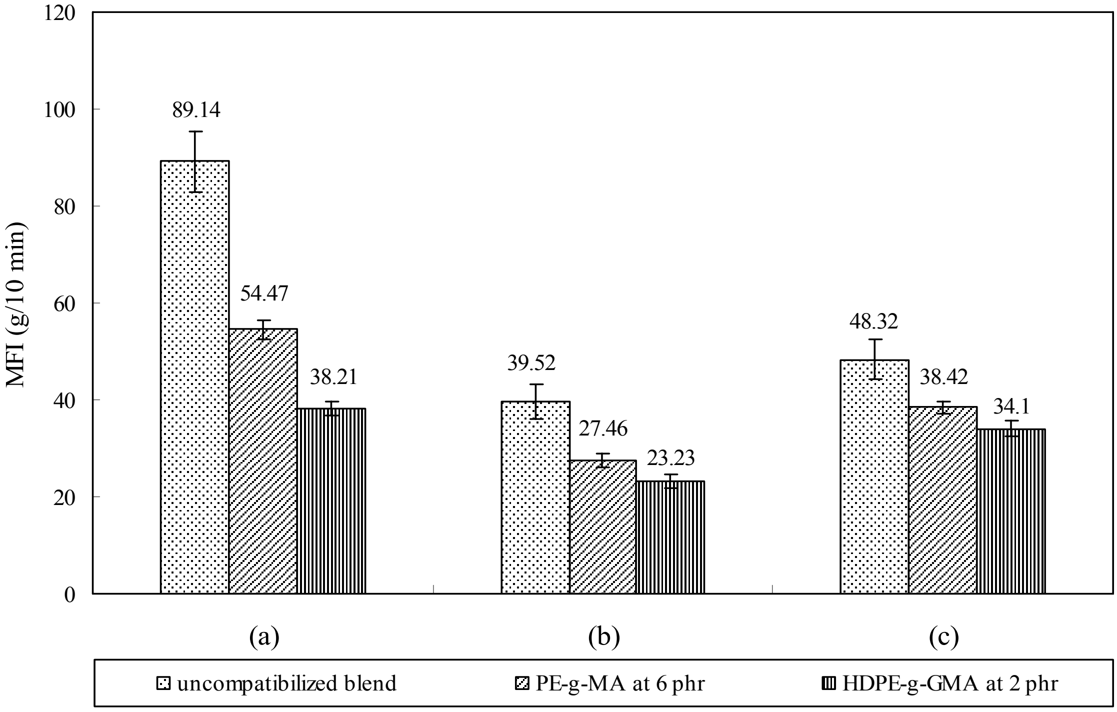


Figure 4.24 MFI of the blends and composites (a) compatibilized HDPE/PET blends, (b) compatibilized HDPE/PET blends reinforced with 10 phr of SGF, and (c) compatibilized HDPE/PET blends reinforced with 10 phr of $CaCO_3$

4.4.5 Thermal properties

The effects of SGF and $CaCO_3$ on the melting and crystallization behavior of HDPE/PET blends are listed in Table 4.9. T_m of both HDPE and PET component does not substantially change on the addition of SGF. The result is in agreement with Joshi et al. (1994). They found that SGF did not significantly affect on T_m of both HDPE and PBT components in HDPE/PBT/SGF composites. This result indicated that there was no change in the crystallite size of PBT in the presence of SGF due to the very fast crystallizing nature of PBT. The presence of the SGF does not affect on T_c of HDPE componet while T_c of PET component has shifted to higher values. This means that the presence of the SGF facilitates the crystallization of PET. The %X_c of HDPE and PET component in the blends reinforced with SGF is higher than that of the blends without SGF. Tselios et al. (1999) found that the SGF acted as nucleating agents and increased the crystallinity of the PP/PE blends. The addition of the compatibilizers in the blends reinforced with SGF insignificantly affect on T_m and T_c of the HDPE and PET component while %X_c of PET component is decreased.

T_m and T_c of HDPE component of the blend reinforced with $CaCO_3$ do not significantly change while the T_m and T_c of PET component have shifted to higher temperature. $CaCO_3$ results in an increase in the %X_c in both HDPE and PET component. These results may be implied that $CaCO_3$ acts like a nucleating agent and increases the rate of crystallization in the PET component (Pingping and Dezhu, 2000). Gonzalez, Albano, Ichazo, and Diaz (2002) found that the $CaCO_3$ acted as a nucleating agent during the crystallization of PP/HDPE. This resulted in an increase of %X_c of the both polymer components. The treatment of $CaCO_3$ with the coupling agents of the titanate type (Lica12) produced a decrease in the heat of fusion of the PP/HDPE blend because the nucleating efficiency of $CaCO_3$ was reduced. In addition, the use of the coupling agents did not influence on the T_c. T_m and T_c of the HDPE and PET component in the blends reinforced with $CaCO_3$ do not affect on adding of the compatibilizers. Adding of the compatibilizers results in a decrease of %X_c of PET component.

Table 4.9 Calorimetric characterization of the blends and composites

Composition (wt%)	**HDPE component**				**PET component**			
	T_c (°C)	**T_m (°C)**	**ΔH_m (J/g)**	**X_c (%)**	**T_c (°C)**	**T_m (°C)**	**ΔH_m (J/g)**	**X_c (%)**
HDPE/PET 20/80	116.74	131.10	40.44	13.80	198.84	247.99	18.91	15.78
HDPE/PET/ SGF 20/80/10	116.75	130.24	44.12	15.05	206.29	248.59	22.78	19.20
HDPE/PET/ $CaCO_3$ 20/80/10	116.24	130.41	42.59	14.54	207.22	248.89	21.30	17.75
HDPE/PET/PE-g-MA/SGF 20/80/6/10	117.03	130.74	41.86	14.29	205.47	248.29	16.95	14.15
HDPE/PET/PE-g-MA/$CaCO_3$ 20/80/6/10	116.20	129.72	39.18	13.37	204.70	249.12	18.25	15.23
HDPE/PET/HDPE-g-GMA/SGF 20/80/2/10	116.16	129.32	42.56	14.53	205.29	248.40	18.94	15.81
HDPE/PET/HDPE-g-GMA/CaCO3 20/80/2/10	116.60	130.33	40.28	13.75	205.94	248.97	17.73	14.80

HDT of the blends and composites are shown in Figure 4.25. As expected, the presence of SGF significantly improves the HDT of the blends. However, $CaCO_3$ does not significantly affect on the HDT.

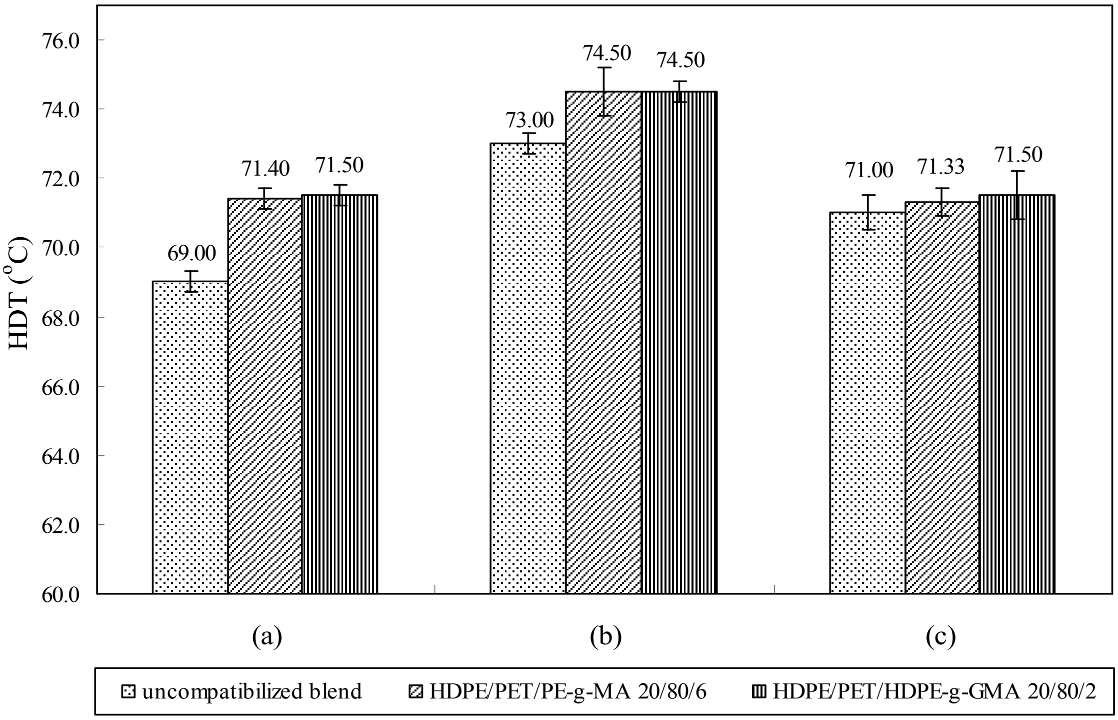


Figure 4.25 HDT of the blends and composites (a) compatibilized HDPE/PET blends, (b) compatibilized HDPE/PET blends reinforced with 10 phr of SGF, and (c) compatibilized HDPE/PET blends reinforced with 10 phr of $CaCO_3$

4.4.6 Water absorption

Water absorption rate versus immersion time of the blends and composites are shown in Figure 4.26. The water absorption rate increases with adding the filler. Water absorption of all composites after immersion times of 30 days seem to be constant. Pires, Foulc, Abadie, Ferry, and Crespy (2001) studied effects of accelerated environment on the mechanical properties of glass fiber reinforced thermoplastic composites based on polyamide 66, poly (ethylene terephthalate), and poly (butylene terephthalate). They found that the water absorption rate of the composites increased with immersion time and aging temperature. The swelling of the amorphous part due to water absorption should induce microcavity formation at the amorphous and crystalline interface. This resulted in a decrease in impact strength of the composites.

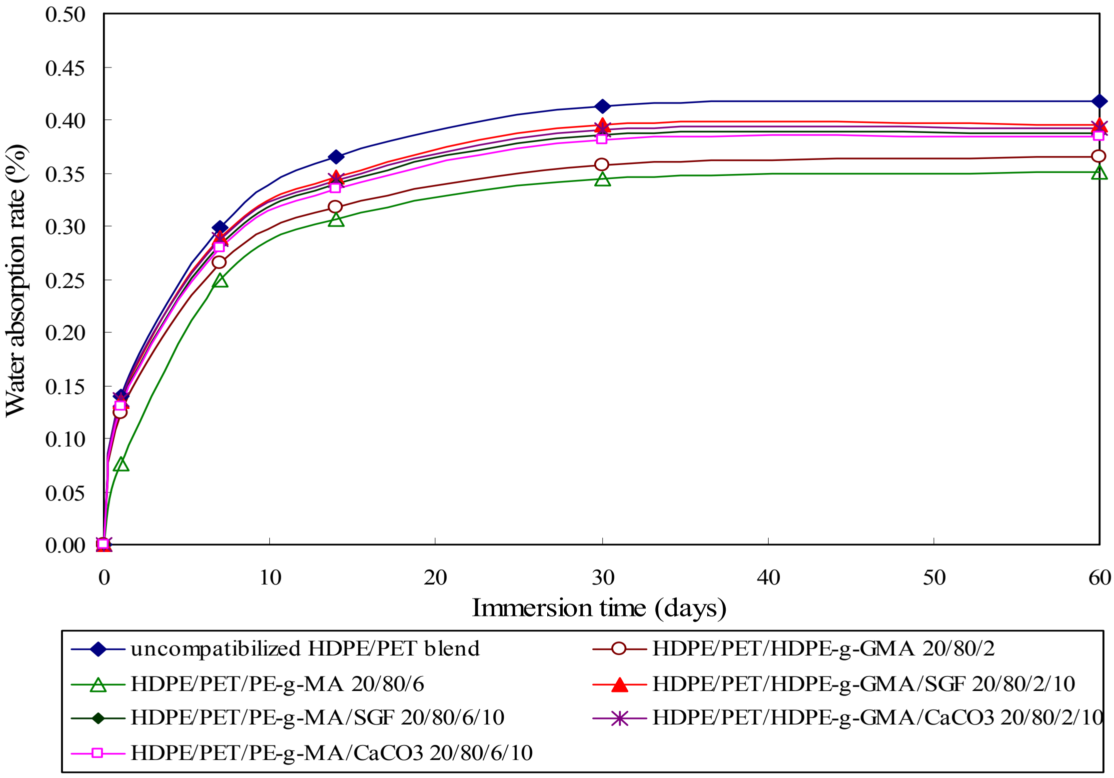


Figure 4.26 Water absorption rate versus immersion time of the blends and composites

The effect of the water absorption on the tensile strength of the composites is shown in Figure 4.27. No significant change in the tensile strength of the composites after water immersion is found because the water does not affect on the molecular structure of the composites.

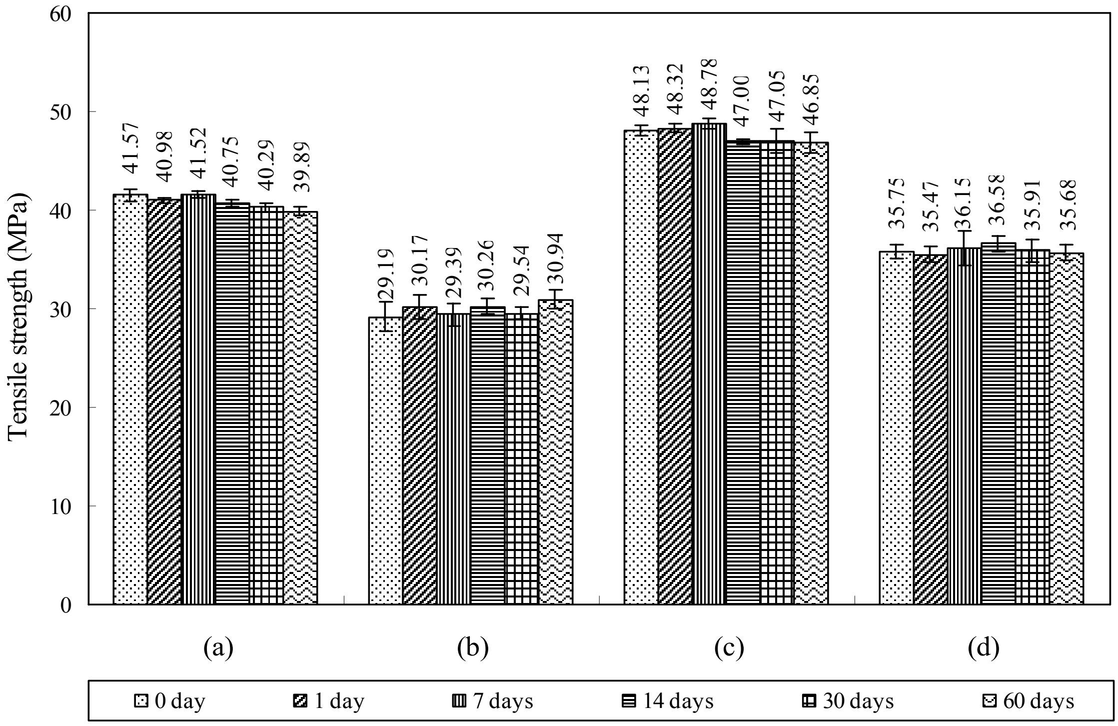


Figure 4.27 Influence of the water absorption on the tensile strength of the composites (a) HDPE/PET/PE-g-MA/SGF (20/80/6/10), (b) HDPE/PET/PE-g-MA/$CaCO_3$ (20/80/6/10), (c) HDPE/PET/HDPE-g-GMA/SGF (20/80/2/10), and (d) HDPE/PET/HDPE-g-GMA/$CaCO_3$ (20/80/2/10)

4.5 Density and mechanical properties comparison for HDPE/PET blend versus soft wood

Density and mechanical properties of the blends reinforced with SGF are shown in Table 4.8. Densities of HDPE/PET blends and their composites are higher than Tectona grandis (soft wood). SGF enhances the mechanical properties of HDPE/PET blends. However, the tensile, flexural, and compressive modulus are lower than that of the soft wood. Lampo and Nosker (1997) reported that the addition of SGF could improve the strength of plastic lumber. Incorporation of the compatibilizers brings about an increase in tensile and compressive properties of the HDPE/PET/SGF composites. Flexural and compressive strength of this composite are better than that of the soft wood while flexural and compressive modulus are worse. Like wood, This composite could be nailed, screw, and sawed.

Generally, plastic lumber was not appropriated for direct substitution for wood of similar dimensions. When plastic lumber were applied, plastic deflection and creep properties were compensated by specifying larger cross sections or more closely spaced support elements (Lampo, and Nosker, 1997).

Table 4.10 Density and mechanical properties of soft wood, HDPE/PET blends, and composites

Materials	**Density (g/cm^3)**	**Tensile**		**Flexural**		**Compressive**	
		strength (MPa)	**modulus (MPa)**	**strength (MPa)**	**modulus (MPa)**	**strength (MPa)**	**modulus (MPa)**
Soft wood (Tectona grandis)[a]	0.62	-	-	62.88	8002.31	32.07	9231.21
HDPE/PET (20/80)	1.19±0.02	30.85±0.73	1320.73±53.03	54.49±0.47	1872.54±44.90	59.52±5.27	1500.76±106.00
HDPE/PET/SGF (20/80/10)	1.17±0.10	39.19±1.96	1666.85±54.84	68.06±0.97	2887.53±78.56	75.23±9.87	1755.98±87.45
HDPE/PET/PE-g-MA/SGF (20/80/6/10)	1.16±0.03	42.11±0.61	1748.52±55.96	59.57±0.25	2652.19±31.19	94.21±12.19	1977.24±113.31
HDPE/PET/HDPE-g-GMA/SGF (20/80/2/10)	1.15±0.02	48.13±0.51	1692.24±33.18	67.32±1.52	2811.28±53.82	101.09±1.47	1859.25±89.56

a: The engineering institute of Thailand under H.M. the King's patronage, 1974

CHAPTER V

CONCLUSIONS

The properties of recycled HDPE/PET blends including mechanical, rheological, thermal, morphological properties, water absorption, and density were under the study. Also, the compatibilizers were used in the experiment to evaluate their impact on the analyzed properties. Polyethylene grafted with maleic anhydride (PE-g-MA) and high density polyethylene grafted with glycidyl methacrylate (HDPE-g-GMA) improved compatibility of HDPE/PET blends. They reduced the particle size of dispersed phase by enhanced interfacial adhesion between matrix and dispersed phase.

By varying the blend composition at 80/20, 60/40, 40/60, and 20/80 wt%, the results were tensile strength, tensile modulus, flexural strength, flexural modulus, heat distortion temperature (HDT), density, and water absorption increased with increasing PET contents while tensile strain at break, impact strength, and viscosity decreased. Dispersed phase size of HDPE-rich blends was smaller than that of PET-rich blends. Moreover, blend compositions affected on crystallinity behavior of the blends.

The results indicated that the compatibilizers improved the mechanical, rheological, thermal, morphological properties, water absorption, and density of the blends. (1) tensile, flexural, compressive, and impact strength, and tensile strain at break improved whereas tensile, flexural, and compressive modulus insignificantly changed, (2) HDT of the compatibilized blends were not influenced, (3) an increase in melt viscosity and depression of crystallinity degree PET and HDPE components in the blends was found due to the presence of chemical reactions between compatibilizers and PET, (4) water absorption resistance was improved; HDPE-g-GMA was more effective than PE-g-MA due to its higher reactivity of GMA functionality with PET terminal groups. The optimum content of HDPE-g-GMA and PE-g-MA for 80/20 HDPE/PET blends was 2 and 6 phr, respectively.

Effect of short glass fiber and calcium carbonate as filler to reinforce the 20/80 HDPE/PET blends was investigated. The incorporation of short glass fibers into the blends enhanced the tensile, flexural, compressive, and impact properties as well as HDT. Reversely, calcium carbonate did not enhance the mechanical properties and provided no significant increase in HDT of the blends. Viscosity and water absorption rate were increased by adding fillers. As a nucleating agent, adding the filler to the composites improve crystallinity degree of PET and HDPE components.

The compatibilizers can improve the filler dispersion and adhesion between fillers and polymer matrices; thus, enhancing the properties of the composites. HDPE-g-GMA increased tensile strength, compressive, and impact strength of the short glass fiber composites without having any significant effect on tensile modulus, tensile strain at break, flexural and compressive modulus, and HDT. Adding the HDPE-g-GMA to calcium carbonate composites improved tensile, flexural, compressive, and impact strength. The compressive properties and impact strength of short glass fiber composites increased with adding PE-g-MA.

HDPE/PET/HDPE-g-GMA/SGF (20/80/2/10 wt%) provides the best mechanical properties. Flexural and compressive strength of this composite were worse than that of the soft wood while flexural and compressive modulus were better. In addition, the densities of this composite were also higher than the soft wood.

The mechanical properties of plastic lumbers are varied by time-temperature. Under the sustained loaded conditions, theirs mechanical properties are subject to permanent deformation. In load bearing application, plastic lumbers shall not be used to replace woods directly due to their plastic deflection and creep properties. Specifying larger cross sections or more spaced support elements can compensate the inferior properties of the plastic lumbers.

Recommendation For Future Work

The main interesting topics for the further studied related to this research study should be followed:

(i) To find the optimum filler content for the HDPE/PET blends

(ii) To investigate the effect of other types of the filler on the properties of the blends

(iii) To make the plastic lumber from the HDPE/PET blends

(iv) To make the laminated veneer lumber from the HDPE/PET blends

Research Publication

Parts of this work were published and presented in the following journal and conferences;

Jarukumjorn, K. and Chareunkvun, S. (2007). Compatibilization of recycled high density polyethylene (HDPE)/polyethylene terephthalate (PET) blends. **Suranaree J. Sci. Technol.** 14: 1-8.

Jarukumjorn, K., Chareunkvun, S., Sucharit, W., and Yaisang, S. (2005). Effect of compatibilizer on mechanical, morphological, and rheological properties of recycled high density polyethylene (HDPE)/polyethylene terephthalate (PET) blends. **In the 31st Congress on Science and Technology of Thailand** (pp. 220). Nakhon Ratchasima, Thailand.

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BIOGRAPHY

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